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CHAPTERS BASED ON CLASS 11th SYLLABUS

1. Some Basic Concepts of Chemistry 1 - 6
2. Structure of Atom 7 - 14
3. Classification of Elements and Periodicity in Properties 15 - 18
4. Chemical Bonding and Molecular Structure 19 - 24
5. States of Matter 25 - 32
6. Thermodynamics 33 - 40
7. Equilibrium 41 - 50
8. The s-Block Elements 51 - 54
10. Hydrocarbons 69 - 76

CHAPTERS BASED ON CLASS 12th SYLLABUS

11. The Solid State & Surface Chemistry 77 - 82
12. Solutions 83 - 88
13. Electrochemistry 89 - 98
15. General Principles and Processes of Isolation of Elements 109 - 112
16. The p-Block Elements 113 - 126
17. The d- and f-Block Elements & Co-ordination Compounds 127 - 140
18. Haloalkanes and Haloarenes 141 - 144
19. Alcohols, Phenols and Ethers 145 - 152
20. Aldehydes, Ketones and Carboxylic Acids 153 - 168
21. Compounds Containing Nitrogen 169 - 180
22. Carbohydrates, Amino Acids, Polymers & Miscellaneous Match the Following 181 - 188
23. Analytical Chemistry 189 - 192
<table>
<thead>
<tr>
<th>Chapter</th>
<th>Pages</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Some Basic Concepts of Chemistry</td>
<td>1 - 16</td>
</tr>
<tr>
<td>2. Structure of Atom</td>
<td>17 - 25</td>
</tr>
<tr>
<td>3. Classification of Elements and Periodicity in Properties</td>
<td>26 - 29</td>
</tr>
<tr>
<td>4. Chemical Bonding and Molecular Structure</td>
<td>30 - 43</td>
</tr>
<tr>
<td>5. States of Matter</td>
<td>44 - 54</td>
</tr>
<tr>
<td>6. Thermodynamics</td>
<td>55 - 64</td>
</tr>
<tr>
<td>7. Equilibrium</td>
<td>65 - 84</td>
</tr>
<tr>
<td>8. The s-Block Elements</td>
<td>85 - 88</td>
</tr>
<tr>
<td>10. Hydrocarbons</td>
<td>105 - 117</td>
</tr>
<tr>
<td>11. The Solid State &amp; Surface Chemistry</td>
<td>118 - 123</td>
</tr>
<tr>
<td>12. Solutions</td>
<td>124 - 133</td>
</tr>
<tr>
<td>13. Electrochemistry</td>
<td>134 - 148</td>
</tr>
<tr>
<td>14. Chemical Kinetics &amp; Nuclear Chemistry</td>
<td>149 - 161</td>
</tr>
<tr>
<td>15. General Principles and Processes of Isolation of Elements</td>
<td>162 - 164</td>
</tr>
<tr>
<td>16. The p-Block Elements</td>
<td>165 - 180</td>
</tr>
<tr>
<td>17. The d- and f-Block Elements &amp; Co-ordination Compounds</td>
<td>181 - 197</td>
</tr>
<tr>
<td>18. Haloalkanes and Haloarenes</td>
<td>198 - 203</td>
</tr>
<tr>
<td>19. Alcohols, Phenols and Ethers</td>
<td>204 - 215</td>
</tr>
<tr>
<td>20. Aldehydes, Ketones and Carboxylic Acids</td>
<td>216 - 239</td>
</tr>
<tr>
<td>21. Compounds Containing Nitrogen</td>
<td>240 - 253</td>
</tr>
<tr>
<td>22. Carbohydrates, Amino Acids, Polymers &amp; Miscellaneous Match the Following</td>
<td>254 - 260</td>
</tr>
<tr>
<td>23. Analytical Chemistry</td>
<td>261 - 268</td>
</tr>
</tbody>
</table>

* The chapters have been divided as per the Class 11th & 12th syllabus followed by the NCERT books. Some of the chapters which are split in the class 11th & 12th syllabus in NCERT have been combined. There might be certain topics/chapters which are not covered in NCERT but are a part of JEE Advanced/IIT-JEE syllabus.
1. An ideal gas is expanded from \((p_1, V_1, T_1)\) to \((p_2, V_2, T_2)\) under different conditions. The correct statement(s) among the following is(are)
   (A) The work done on the gas is maximum when it is compressed irreversibly from \((p_2, V_2)\) to \((p_1, V_1)\) against constant pressure \(p_1\).
   (B) If the expansion is carried out freely, it is simultaneously both isothermal as well as adiabatic.
   (C) The work done by the gas is less when it is expanded reversibly from \(V_1\) to \(V_2\) under adiabatic conditions as compared to that when expanded reversely from \(V_1\) to \(V_2\) under isothermal conditions.
   (D) The change in internal energy of the gas is \((i)\) zero, if it is expanded reversibly with \(T_1 = T_2\), and \((ii)\) positive, if it is expanded reversibly under adiabatic conditions with \(T_1 \neq T_2\).

2. For a solution formed by mixing liquids \(L\) and \(M\), the vapour pressure of \(L\) plotted against the mole fraction of \(M\) in solution is shown in the following figure. Here \(x_L\) and \(x_M\) represent mole fractions of \(L\) and \(M\), respectively, in the solution. The correct statement(s) applicable to this system is(are)

   ![Vapour Pressure Plot](image)

   (A) The point \(Z\) represents vapour pressure of pure liquid \(M\) and Raoult’s law is obeyed from \(x_L = 0\) to \(x_L = 1\).
   (B) The point \(Z\) represents vapour pressure of pure liquid \(L\) and Raoult’s law is obeyed when \(x_L \to 1\).
   (C) The point \(Z\) represents vapour pressure of pure liquid \(M\) and Raoult’s law is obeyed when \(x_L \to 0\).
   (D) Attractive intermolecular interactions between \(L-L\) in pure liquid \(L\) and \(M-M\) in pure liquid \(M\) are stronger than those between \(L-M\) when mixed in solution.

3. The correct statement(s) about the oxoacids, \(\text{HClO}_4\) and \(\text{HClO}\), is(are)
   (A) The central atom in both \(\text{HClO}_4\) and \(\text{HClO}\) is \(\text{sp}^3\) hybridized.
   (B) \(\text{HClO}_4\) is more acidic than \(\text{HClO}\) because of the resonance stabilization of its anion.
   (C) \(\text{HClO}_4\) is formed in the reaction between \(\text{Cl}_2\) and \(\text{H}_2\text{O}\).
   (D) The conjugate base of \(\text{HClO}_4\) is weaker base than \(\text{H}_2\text{O}\).

4. The colour of the \(X_2\) molecules of group 17 elements changes gradually from yellow to violet down the group. This is due to
   (A) The physical state of \(X_2\) at room temperature changes from gas to solid down the group.
   (B) Decrease in ionization energy down the group.
   (C) Decrease in \(\pi^* - \sigma^*\) gap down the group.
   (D) Decrease in HOMO-LUMO gap down the group.

5. Addition of excess aqueous ammonia to a pink coloured aqueous solution of \(\text{MCl}_2\), \(\text{H}_2\text{O}(\text{X})\) and \(\text{NH}_4\text{Cl}\) gives an octahedral complex \(Y\) in the presence of air. In aqueous solution, complex \(Y\) behaves as 1:3 electrolyte. The reaction of \(X\) with excess \(\text{HCl}\) at room temperature results in the formation of a blue coloured complex \(Z\). The calculated spin only magnetic moment of \(X\) and \(Z\) is 3.87 B.M., whereas it is zero for complex \(Y\). Among the following options, which statement(s) is(are) correct?
   (A) Addition of silver nitrate to \(Y\) gives only two equivalents of silver chloride.
   (B) The hybridization of the central metal ion in \(Y\) is \(\text{sp}^3\).
   (C) \(Z\) is a tetrahedral complex.
   (D) When \(X\) and \(Z\) are in equilibrium at \(0^\circ\text{C}\), the colour of the solution is pink.

6. The IUPAC name(s) of the following compound is(are)
   \(\text{H}_2\text{C} = \text{C}(\text{Cl})\text{Cl} \quad \text{H}_2\text{C} \quad \text{Cl} \quad \text{H}_2\text{C} \quad \text{Cl} \quad \text{H}_2\text{C} \\
   (A) 1-chloro-4-methylbenzene
   (B) 4-chlorotoluene
   (C) 4-methylchlorobenzene
   (D) 1-methyl-4-chlorobenzene

7. The correct statement(s) for the following addition reactions is(are)
   (i) \(\text{H}_2\text{C} = \text{C}\text{H} \quad \text{Br}_2\text{CHCl}_3 \rightarrow \text{M and N} \quad \text{H}_2\text{C} \quad \text{H} \quad \text{CH}_3 \quad \text{Br}_2\text{CHCl}_3 \rightarrow \text{O and P} \quad \text{H}_2\text{C} \quad \text{H} \quad \text{CH}_3 \)
   (A) The central atom in both \(\text{HClO}_4\) and \(\text{HClO}\) is \(\text{sp}^3\) hybridized.
   (B) \(\text{HClO}_4\) is more acidic than \(\text{HClO}\) because of the resonance stabilization of its anion.
   (C) \(\text{HClO}_4\) is formed in the reaction between \(\text{Cl}_2\) and \(\text{H}_2\text{O}\).
   (D) The conjugate base of \(\text{HClO}_4\) is weaker base than \(\text{H}_2\text{O}\).
SECTION - II

This section contains 5 questions. The answer to each question is a SINGLE DIGIT INTEGER ranging from 0 to 9, both inclusive.

8. A crystalline solid of a pure substance has a face-centred cubic structure with a cell edge of 400 pm. If the density of the substance in the crystal is 8 g cm⁻³, then the number of atoms present in 256 g of the crystal is . The value of N is .

9. The conductance of a 0.0015 M aqueous solution of a weak monobasic acid was determined by using a conductivity cell consisting of platinized Pt electrodes. The distance between the electrodes is 120 cm with an area of cross section of 1 cm². The conductance of this solution was found to be . The pH of the solution is 4. The value of limiting molar conductivity of this weak monobasic acid in aqueous solution is \( Z \times 10^2 \) S cm⁻¹ mol⁻¹. The value of Z is .

10. The sum of the number of lone pairs of electrons on each central atom in the following species is \([\text{TeBr}_6]^{2-}, [\text{BrF}_5]^+, \text{SF}_6\) and \([\text{XeF}_4]^−\) (Atomic numbers: N = 7, F = 9, S = 16, Br = 35, Te = 52, Xe = 54)

11. Among H₂, He₂⁺, Li₂, Be₂⁺, B₂, C₂, N₂, O₂⁻, and F₂, the number of diamagnetic species is . (Atomic numbers: H = 1, He = 2, Li = 3, Be = 4, B = 5, C = 6, N = 7, O = 8, F = 9)

12. Among the following, the number of aromatic compound(s) is .

SECTION - III

This section contains 6 questions of MATCHING TYPE, contains two tables each having 3 columns and 4 rows. Based on each table, there are three questions. Each question has four options (A), (B), (C) and (D) ONLY ONE of these four option is correct.

(Qs. 13-15): By appropriately matching the information given in the three columns of the following table.

The wave function, \( \psi_{n,l,m_l} \) is a mathematical function whose value depends upon spherical polar coordinates \( r, \theta, \phi \) of the electron and characterized by the quantum numbers \( n, l, m_l \). Here \( r \) is distance from nucleus, \( \theta \) is colatitude and \( \phi \) is azimuth. In the mathematical functions given in the table, \( Z \) is atomic number and \( a_0 \) is Bohr radius.

<table>
<thead>
<tr>
<th>Column 1</th>
<th>Column 2</th>
<th>Column 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i) 1s orbital</td>
<td>( \psi_{n,l,m_l} \propto \left( \frac{Z}{a_0} \right)^{\frac{3}{2}} e^{-\left( \frac{Zr}{a_0} \right)} )</td>
<td>(P) Probability density at nucleus ( \propto \frac{1}{a_0^3} )</td>
</tr>
<tr>
<td>(ii) 2s orbital</td>
<td>One radial node</td>
<td>(Q) Probability density is maximum at nucleus</td>
</tr>
<tr>
<td>(iii) 2pₓ orbital</td>
<td>( \psi_{n,l,m_l} \propto \left( \frac{Z}{a_0} \right)^{\frac{5}{2}} e^{-\left( \frac{Zr}{2a_0} \right)} \cos \theta )</td>
<td>(R) Energy needed to excite electron from ( n = 2 ) state to ( n = 4 ) state is ( \frac{27}{32} ) times the energy needed to excite electron from ( n = 2 ) state to ( n = 6 ) state</td>
</tr>
<tr>
<td>(iv) 3dₓ² orbital</td>
<td>xy-plane is a nodal plane</td>
<td>(S) Energy needed to excite electron from ( n = 2 ) state to ( n = 4 ) state is ( \frac{27}{32} ) times the energy needed to excite electron from ( n = 2 ) state to ( n = 6 ) state</td>
</tr>
</tbody>
</table>
CHEMISTRY

13. For the given orbital in Column 1, the only CORRECT combination for any hydrogen-like species is
   (A) (I)(ii)(S)
   (B) (IV)(iv)(R)
   (C) (II)(ii)(P)
   (D) (III)(iii)(P)

14. For hydrogen atom, the only CORRECT combination is
   (A) (I)(i)(S)
   (B) (II)(i)(Q)
   (C) (I)(i)(P)
   (D) (I)(iv)(R)

15. For He⁺ ion, the only INCORRECT combination is
   (A) (I)(i)(R)
   (B) (II)(ii)(Q)
   (C) (I)(iii)(R)
   (D) (I)(i)(S)

16. For the synthesis of benzoic acid, the only CORRECT combination is
   (A) (II)(i)(S)
   (B) (IV)(iv)(P)
   (C) (I)(iv)(Q)
   (D) (II)(iv)(R)

17. The only CORRECT combination that gives two different carboxylic acids is
   (A) (II)(iv)(R)
   (B) (IV)(iii)(Q)
   (C) (II)(iii)(P)
   (D) (I)(i)(S)

18. The only CORRECT combination in which the reaction proceeds through radical mechanism is
   (A) (III)(ii)(P)
   (B) (IV)(i)(Q)
   (C) (II)(iii)(R)
   (D) (I)(ii)(R)

SECTION - I

This section contains 7 questions. Each question has 4 options (A), (B), (C) and (D). ONLY ONE of these four options is correct.

1. Pure water freezes at 273 K and 1 bar. The addition of 34.5 g of ethanol to 500 g of water changes the freezing point of the solution. Use the freezing point depression constant of water as 2 K kg mol⁻¹. The figures shown below represent plots of vapour pressure (V.P.) versus temperature (T). [molecular weight of ethanol is 46 g mol⁻¹] Among the following, the option representing change in the freezing point is

   (A) ![Plot A]
   (C) ![Plot C]

   (B) ![Plot B]

2. For the following cell, Zn(s) | ZnSO₄(aq) || CuSO₄(aq) | Cu(s)
   when the concentration of Zn²⁺ is 10 times the concentration of Cu²⁺, the expression for ΔG (in J mol⁻¹) is [F is Faraday constant; R is gas constant; T is temperature; E°(cell) = 1.1 V]
   (A) 1.1F
   (B) 2.303RT – 2.2F
   (C) 2.303RT + 1.1F
   (D) –2.2F
3. The standard state Gibbs free energies of formation of C(graphite) and C(diamond) at T = 298 K are 
\[ \Delta_f G^\circ [\text{C(graphite)}] = 0 \text{ kJ mol}^{-1} \]
\[ \Delta_f G^\circ [\text{C(diamond)}] = 2.9 \text{ kJ mol}^{-1} \]

The standard state means that the pressure should be 1 bar, and substance should be pure at a given temperature. The conversion of graphite [C(graphite)] to diamond [C(diamond)] reduces its volume by \(2 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}\). If C(graphite) is converted to C(diamond) isothermally at T = 298 K, the pressure at which C(graphite) is in equilibrium with C(diamond), is

[Useful information: 1 J = 1 kg m^2 s^-2; 1 Pa = 1 kg m^-1 s^-2; 1 bar = 10^5 Pa]

(A) 14501 bar  
(B) 58001 bar  
(C) 1450 bar  
(D) 29001 bar

4. Which of the following combination will produce H2 gas?

(A) Fe Metal and conc. HNO3  
(B) Cu metal and conc. HNO3  
(C) Zn metal and NaOH(aq)  
(D) Au metal and NaCN(aq) in the presence of air

5. The order of the oxidation state of the phosphorus atom in

\[ \text{H}_3\text{PO}_2, \text{H}_3\text{PO}_4, \text{H}_3\text{PO}_3 \text{ and H}_3\text{P}_2\text{O}_5 \]

is

(A) \(\text{H}_3\text{PO}_2 > \text{H}_3\text{PO}_4 > \text{H}_3\text{PO}_3 > \text{H}_3\text{P}_2\text{O}_5 \)

(B) \(\text{H}_3\text{PO}_4 > \text{H}_3\text{PO}_2 > \text{H}_3\text{PO}_3 > \text{H}_3\text{P}_2\text{O}_5 \)

(C) \(\text{H}_3\text{PO}_3 > \text{H}_3\text{P}_2\text{O}_5 > \text{H}_3\text{PO}_4 > \text{H}_3\text{PO}_2 \)

(D) \(\text{H}_3\text{PO}_2 > \text{H}_3\text{PO}_3 > \text{H}_3\text{P}_2\text{O}_5 > \text{H}_3\text{PO}_4 \)

6. The major product of the following reaction is

\[
\text{A} \xrightarrow{\text{i) NaNO}_2, \text{HCl, 0°C}} \text{B} \\
\text{ii) aq NaOH} \]

(A)  
(B)  
(C)  
(D)

7. The order of basicity among the following compounds is

\[
\begin{align*}
\text{I} & \quad \text{II} & \quad \text{III} & \quad \text{IV} \\
\text{A} & \quad \text{B} & \quad \text{C} & \quad \text{D}
\end{align*}
\]

(A) II > I > IV > III  
(B) IV > II > III > I  
(C) IV > I > II > III  
(D) I > IV > III > II

SECTION - II

This section contains 7 questions. Each question has 4 options (A), (B), (C) and (D). ONE or MORE THAN ONE of these four options is (are) correct.

8. The correct statement(s) about surface properties is(are)

(A) Adsorption is accompanied by decrease in enthalpy and decrease in entropy of the system  
(B) The critical temperatures of ethane and nitrogen are 563 K and 126 K, respectively. The adsorption of ethane will be more than that of nitrogen on same amount of activated charcoal at a given temperature  
(C) Cloud is an emulsion type of colloid in which liquid is dispersed phase and gas is dispersion medium  
(D) Brownian motion of colloidal particles does not depend on the size of the particles but depends on viscosity of the solution

9. For a reaction taking place in a container in equilibrium with its surroundings, the effect of temperature on its equilibrium constant K in terms of change in entropy is described by

(A) With increase in temperature, the value of K for exothermic reaction decreases because the entropy change of the system is positive  
(B) With increase in temperature, the value of K for endothermic reaction increases because unfavourable change in entropy of the surroundings decreases  
(C) With increase in temperature, the value of K for endothermic reaction increases because the entropy change of the system is negative  
(D) With increase in temperature, the value of K for exothermic reaction decreases because favourable change in entropy of the surroundings decreases

10. In a bimolecular reaction, the steric factor P was experimentally determined to be 4.5. The correct option(s) among the following is(are)

(A) The activation energy of the reaction is unaffected by the value of the steric factor  
(B) Experimentally determined value of frequency factor is higher than that predicted by Arrhenius equation  
(C) Since P = 4.5, the reaction will not proceed unless an effective catalyst is used  
(D) The value of frequency factor predicted by Arrhenius equation is higher than that determined experimentally

11. For the following compounds, the correct statement(s) with respect to nucleophilic substitution reaction is(are)

\[
\begin{align*}
\text{I} & \quad \text{II} \\
& \quad \text{(I)} & \quad \text{(II)}
\end{align*}
\]
CHEMISTRY

CH₃
\[ \text{(III)} \]
\[ \text{Br} \] 
\[ \text{CH₃} \] 

CH₃
\[ \text{CH₃} \] 

(IV)

A) I and III follow S₆₋₁ mechanism
B) I and II follow S₆₋₂ mechanism
C) Compound IV undergoes inversion of configuration
D) The order of reactivity for I, III and IV is: IV > I > III

12. Among the following, the correct statement(s) is(are)
(A) Al(CH₃)₃ has the three-centre two-electron bonds in its dimeric structure
(B) BH₃ has the three-centre two-electron bonds in its dimeric structure
(C) AlCl₃ has the three-centre two-electron bonds in its dimeric structure
(D) The Lewis acidity of BCl₃ is greater than that of AlCl₃

13. The option(s) with only amphoteric oxides is(are)
(A) Cr₂O₃, BeO, SnO, Sn₂O₃
(B) Cr₂O₃, CrO, SnO, PbO
(C) NO, B₂O₃, PbO, SnO₂
(D) ZnO, Al₂O₃, PbO, PbO₂

14. Compounds P and R upon ozonolysis produce Q and S, respectively. The molecular formula of Q and S is C₈H₈O. Q undergoes Cannizzaro reaction but not haloform reaction, whereas S undergoes haloform reaction but not Cannizzaro reaction.

(i) \[ P \xrightarrow{i)\text{O}_3/\text{CH}_2\text{Cl}_2 \, ii)\text{Zn/H}_2\text{O} \, (\text{C}_8\text{H}_8\text{O}) \]

(ii) \[ R \xrightarrow{i)\text{O}_3/\text{CH}_2\text{Cl}_2 \, ii)\text{Zn/H}_2\text{O} \, (\text{C}_8\text{H}_8\text{O}) \]

The option(s) with suitable combination of P and R, respectively, is(are)

(A) \[ \text{H}_3\text{C} \quad \text{and} \quad \text{H}_3\text{C} \]

(B) \[ \text{H}_3\text{C} \quad \text{and} \quad \text{H}_3\text{C} \]

(C) \[ \text{H}_3\text{C} \quad \text{and} \quad \text{H}_3\text{C} \]

(D) \[ \text{H}_3\text{C} \quad \text{and} \quad \text{H}_3\text{C} \]

15. W and X are, respectively
(A) O₃ and P₃O₆
(B) O₂ and P₃O₁₀
(C) O₂ and P₃O₁₀
(D) O₃ and P₄O₁₀

16. Y and Z are, respectively
(A) N₂O₃ and H₂PO₄
(B) N₂O₅ and H₂PO₄
(C) N₂O₄ and H₂PO₃
(D) N₂O₄ and H₃PO₃

17. The product S is

(A)

(B)

(C)

(D)

18. The reactions, Q to R and R to S, are
(A) Dehydration and Friedel–Crafts acylation
(B) Aromatic sulfonation and Friedel–Crafts acylation
(C) Friedel–Crafts alkylation, dehydration and Friedel–Crafts acylation
(D) Friedel–Crafts alkylation and Friedel–Crafts acylation

SECTION I

This section contains 2 paragraphs, each describing theory, experiments, data etc. Four questions related to the two paragraphs with two questions on each paragraph. Each question has only one correct answer among the four given options (A), (B), (C) and (D).

PARAGRAPH I

Upon heating KClO₄ in the presence of a catalytic amount of MnO₂, a gas W is formed. Excess amount of W reacts with white phosphorus to give X. The reaction of X with pure HNO₃ gives Y and Z.

15. W and X are, respectively
(A) O₃ and P₃O₆
(B) O₂ and P₃O₁₀
(C) O₂ and P₃O₁₀
(D) O₃ and P₄O₁₀

16. Y and Z are, respectively
(A) N₂O₃ and H₂PO₄
(B) N₂O₅ and H₂PO₄
(C) N₂O₄ and H₂PO₃
(D) N₂O₄ and H₃PO₃

PARAGRAPH II

The reaction of compound P with CH₃MgBr (excess) in (C₂H₅)₂O followed by addition of H₂O gives Q. The compound Q on treatment with H₂SO₄ at 0°C gives R. The reaction of R with CH₃COCl in the presence of anhydrous AlCl₃ in CH₂Cl₂ followed by treatment with H₂O produces compound S. [Et in compound P is ethyl group]

17. The product S is

(A)

(B)

(C)

(D)
1. (A, B, C)
   (A) During adiabatic expansion, the final temperature is less than the initial temperature. Therefore the final volume in adiabatic expansion will also be less than the final volume in isothermal expansion. This can be graphically shown as

   ![Diagram showing adiabatic and isothermal expansions]

   The magnitude of work done by the gas is equal to the area under the curve. As seen from the figure the area under curve in reversible isothermal is more. Hence, the magnitude of work done is lesser in adiabatic reversible expansion as compared to the corresponding work in isothermal expansion.

   (B) In free expansion, $P_{eq} = 0 \Rightarrow W = 0$
   If carried out isothermally ($\Delta U = 0 \Rightarrow q = 0$ (Adiabatic) From I law
   If carried out adiabatically ($q = 0$) $\Rightarrow \Delta U = 0$ (Isothermal) From I law

   (C) During irreversible compression, maximum work is done on the gas (corresponding to shaded area)

   (D) When $T_1 = T_2 \Rightarrow \Delta U = nC_A \Delta T = 0$
   In reversible adiabatic expansion, $T_2 < T_1$
   $\therefore \Delta T = -ve \Rightarrow \Delta U = -ve$

2. (B, D)

   ![Graph showing P vs V]

   The graph representing +ve deviation from Raoult's law therefore M – L < M – M or L – L
   $P_L > P^0_L X_L$
   but when $X_L = 1$, mixture has almost pure liquid L so
   $P_L = P^0_L$

3. (A, B, D)
   (A) In both the acids central atom is $sp^3$ hybridized.

   ![Chemical structure of ClO₄⁻ and ClO₃⁻]

   (B) $ClO_4^-$ is resonance stabilized anion
   $HClO_4$
   $ClO_4^- + H^+ \rightarrow HClO$
   $ClO_3^- + H^+ \rightarrow HCl$ 

   Hence $HClO_4$ is more acidic than $HClO$.

   (C) $ClO_3^- + H_2O \rightarrow HCl + HOCl$

   (D) $HClO_4 + H_2O \rightarrow ClO_4^- + H_3O^+$
   Acid I Base I Base I acid I

   Since $H_2O$ is accepting $H^+$ from $HClO_4$ so $H_2O$ is stronger base compared to $ClO_4^-$. 

4. (C, D)

   The colour of $X_2$ molecules of halogens is due to absorption of light in the visible region. The energy acquired in this manner excites the valence electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO), i.e., transition from $\pi^*$ to $\sigma^*$ molecular orbital.

   $\text{X}_2 : \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z, \pi 2p_x^2$

   $= \pi 2p_z^2, \pi^* 2p_x^2 = \pi^* 2p_x^2 \rightarrow \sigma^* 2p_x^0$

   (HOMO) (LUMO)

5. (B, C, D)

   [Co(H₂O)₆]Cl₂ (X) + $\text{NH}_4\text{Cl} + \text{AgNO}_3$ (aq) $\rightarrow$ [Co(NH₃)₆]Cl₃ (Y)

   Pink Solution
   HCl (excess)
   room temperature

   $[\text{CoCl}_4]^{2-}$ (Z)

   Blue colour (tetrahedral)
   $sp^3$ as $Cl^-$ is a weak field ligand

   $[\text{CoCl}_4]^{2-} + 6\text{H}_2\text{O} \rightleftharpoons \text{Co(H}_2\text{O})^2^+ + 4\text{Cl}^-$(Blue)

   $X$ and $Z$ in equilibrium at 0°C $\Rightarrow$ then equilibrium is shifted towards $X$, making colour of solution pink.
6. (A, B)

IUPAC name

(A) \[
\begin{array}{c}
\text{Cl} \\
\text{1-chloro-4-methylbenzene} \\
\text{CH}_3
\end{array}
\]

(B) \[
\begin{array}{c}
\text{Cl} \\
\text{4-chlorotoluene} \\
\text{CH}_3
\end{array}
\]

7. (B, D)

(B) Bromination proceeds through trans-addition in both the reactions.

M and N are identical, hence, M and O and N and P are two set of diastereomers.

(D)
8. (2) Density \( (d) = \frac{Z \times M}{a^3 \times N_A} \) \( (d = \text{density}) \)

For FCC, \( Z = 4 \)

Given \( a = 4 \times 10^{-8} \text{ cm} \)

\[
8 = \frac{4 \times M}{(4 \times 10^{-8})^3 \times 6 \times 10^{23}}
\]

\[
M = \frac{8 \times (4 \times 10^{-8})^3 \times 6 \times 10^{23}}{4}
\]

\[
M = 8 \times 6 \times 10^{23} \times 64 \times 10^{-24}
\]

\[
\text{No. of atoms} = \frac{\text{wt}}{\text{Molar mass}} \times N_A
\]

\[
\frac{256 \times 10^6 \times 10^{23}}{8 \times 6 \times 16} = 2 \times 10^{24}
\]

\[
\therefore \ \text{Value of} \ N = 2
\]

9. (6) The formula for conductance is \( G = \frac{\alpha}{\ell} \)

\[
5 \times 10^{-7} = \kappa \times \frac{1}{120}
\]

\[
\kappa = 6 \times 10^{-5} \text{ s cm}^{-1}
\]

\[
\Lambda_\text{m} = \frac{\kappa \times 1000}{M} = \frac{6 \times 10^{-5} \times 1000}{0.0015} = 40
\]

\[
\therefore \ \text{pH} = 4
\]

\[
\therefore \ \text{[H}^+] = 10^{-4} = \text{ca} = 0.0015 \alpha
\]

\[
\alpha = \frac{10^{-4}}{0.0015}
\]

\[
\alpha = \frac{\Lambda_\text{m}}{\Lambda_\text{m}} \Rightarrow \frac{10^{-4}}{0.0015} = 40
\]

\[
\Lambda_\text{m} = 6 \times 10^2 \text{ s cm}^2 \text{ mole}^{-1}
\]

\[
\therefore, \ z = 6
\]

10. (6) \textbf{Species} \hspace{1cm} \textbf{Number of lone pairs on central atom}

(i) \([\text{TeBr}]^-\) \hspace{1cm} 1
(ii) \([\text{BrF}_3]^+\) \hspace{1cm} 2
(iii) \([\text{SF}_3]^-\) \hspace{1cm} 0
(iv) \([\text{XeF}_3]^+\) \hspace{1cm} 3

Total number of lone pairs = 1 + 2 + 0 + 3 = 6

11. (6) \((\text{H}_2, \text{Cl}_2, \text{Be}_2, \text{C}_2, \text{N}_2, \text{F}_2, \text{H}_2, \text{be}_2, \text{c}_2, \text{b}_2, \text{f}_2)\)

\[
\text{H}_2 : \ \sigma^1 s^2 \ \ (\text{Diamagnetic})
\]

\[
\text{He}_2^+: \ \sigma^1 s^2, \sigma^1 s^1 \ \ (\text{Paramagnetic})
\]

\[
\text{Li}_2 : \ \sigma^1 s^2, \sigma^1 s^2, \sigma^2 s^2 \ \ (\text{Diamagnetic})
\]

\[
\text{Be}_2 : \ \sigma^1 s^2, \sigma^1 s^2, \sigma^2 s^2, \sigma^2 s^2 \ \ (\text{Diamagnetic})
\]

\[
\text{B}_2 : \ \sigma^1 s^2, \sigma^2 s^2, \sigma^2 s^2, \sigma^2 s^2, \pi^2 p_x = \pi^2 p_y^1 \ \ (\text{Diamagnetic})
\]

\[
\text{C}_2 : \ \sigma^1 s^2, \sigma^2 s^2, \sigma^2 s^2, \sigma^2 s^2, \pi^2 p_x^2 = \pi^2 p_y^2 \ \ (\text{Diamagnetic})
\]

12. (5) Non-aromatic Anti-aromatic Non-aromatic Anti-aromatic

\[
\text{Aromatic Aromatic Aromatic Aromatic}
\]

13. (C) \(1s\) wave function for \(\text{He}^+\) is given by

\[
\Psi_{\{1s\}} = \Psi_{n,\ell,m_r} = \frac{Z}{\sqrt{\pi a_0^3}} \exp\left(\frac{Zr}{a_0}\right)
\]

or \(\propto \left(\frac{Z}{a_0}\right)^{3/2} \exp\left[\frac{Zr}{a_0}\right]\)

i.e., it is independent of \(\cos \theta\).

The probability of finding an electron at zero distance from the nucleus is zero. The probability increases gradually as the distance increases, goes to maximum and then begins to decrease.

14. (A) For a given orbital with principal quantum number, \(n\) and azimuthal quantum number, \(\ell\).

Number of radial nodes = \(n - \ell - 1\)
CHEMISTRY

15. (C) Refer ans 13.
   Energy needed to excite from \( n = 2 \) to \( n = 4 \)
   \[
   \Delta E_{2-4} = 13.6 Z^2 \times \frac{3}{16} \text{eV}
   \]
   Similarly,
   \[
   \Delta E_{2-6} = 13.6 Z^2 \times \frac{8}{36} \text{eV}
   \]
   on dividing
   \[
   \frac{\Delta E_{2-4}}{\Delta E_{2-6}} = \frac{3}{16} \times \frac{36}{8} = \frac{27}{32}
   \]

16. (A) Alkylbenzenes when treated with Br\(_2\) at high temperature, in the presence of sunlight and absence of halogen carrier undergo halogenation in the side chain. Thus

   ![Chemical structures](image)

17. (C)

   ![Chemical structures](image)

18. (D) Perkin condensation of benzaldehyde with \((\text{CH}_3\text{CO})_2\text{O}/\text{CH}_3\text{COOK}\) yields cis and trans form of cinnamic acid.

   \[
   \text{C}_6\text{H}_5\text{CHO} + (\text{CH}_3\text{CO})_2\text{O} \rightarrow \text{C}_6\text{H}_5\text{CH} = \text{CHCOOH}
   \]

   ![Chemical structures](image)

**Paper - 2**

1. (C) As \( T \) increase, V.P. increases
   \[
   \Delta T_f = K_f \times m
   \]
   \[
   273 - T_f = 2 \times \frac{34.5 \times 1000}{46 \times 500}
   \]
   \[
   \therefore \quad T_f = 270 \text{K}
   \]

2. (B) \( \text{Zn}(s) + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu}(s) \)
   \[
   \Delta G = \Delta G^0 + 2.303 \text{RT} \log_{10} Q, \quad Q = \frac{\left[ \text{Zn}^{2+} \right]}{\left[ \text{Cu}^{2+} \right]}
   \]
   \[
   [\Delta G^0 = -nFE^0] = -2 \times F \times 1.1
   \]
   Given \([\text{Zn}^{2+}] = 10[\text{Cu}^{2+}]\)
   \[
   \therefore \quad \Delta G = -2F(1.1) + 2.303 \text{RT} \log_{10} 10 = 2.303 \text{RT} - 2.2F
   \]
3. (A) At eq. \( \Delta G = 0 \)
\( \Delta G^\circ = \frac{d\pi(DV)}{2} \)
2.9 kJ mol\(^{-1}\) = \( (P_2 - 1) \times 2 \times 10^{-6} \) m\(^3\) mol\(^{-1}\)
or
\[
2.9 \times 10^{3} \frac{\text{kg m}^2}{\text{s}^2 \text{mol}^{-1}} = (P_2 - 1) \left( 2 \times 10^{-6} \right) \frac{\text{m}^3}{\text{mol}^{-1}}
\]
\[
(P_2 - 1) = \frac{2.9 \times 10^{3} \times 10^{6}}{2} \frac{\text{kg}}{\text{ms}^2}
\]
\[
= 1.45 \times 10^9 \frac{\text{kg}}{\text{ms}^2} = 1.45 \times 10^9 \text{Pa}
\]
\[
\therefore P_2 = 1.45 \times 10^9 + 1 \text{Pa} = 14500 \times 10^5 + 1 = 14501 \times 10^5 \text{Pa} = 14501 \text{Bar}
\]
4. (C) Fe + conc. HNO\(_3\) \(\rightarrow\) Fe\(_2\)O\(_3\)
Cu + conc. HNO\(_3\) \(\rightarrow\) CuNO\(_3\) + NO\(_2\) + H\(_2\)O
4Au + 8NaCN + O\(_2\) + 2H\(_2\)O \(\rightarrow\) 4Na[Au(CN)\(_2\)] + 4NaOH
Zn + NaOH \(\rightarrow\) Na\(_2\)ZnO\(_2\) + H\(_2\)
5. (C) Correct order:
H\(_3\)PO\(_4\) > H\(_4\)PO\(_6\) > H\(_3\)PO\(_3\) > H\(_3\)PO\(_2\)
\((+5) > (+4) > (+3) > (+1)\)
6. (C)
Step 1:
\[
\text{Step 2:}
\]
Diazocoupling
7. (C)
The conjugate acid is stabilized by resonance with two different \(-\text{NH}_2\) group. Hence electron density increases on N of \(=\text{NH}\)
8. (A, B)
(A) As adsorption is spontaneous, \(\Delta G\) for the process is \(-\text{ve}\). Adsorption is accompanied by decrease in randomness. Therefore \(\Delta S\) and \(\Delta T\) for the process is also negative. As \(\Delta S\) for the process is \(-\text{ve}\) and the process is spontaneous, \(\Delta H\) for the process has to be \(-\text{ve}\) i.e., enthalpy of the system decreases.

(B) Under a given set of conditions of temperature and pressure the easily liquefiable gases e.g. C\(_2\)H\(_6\), NH\(_3\) and HCl are adsorbed more than the gases like N\(_2\), H\(_2\) and CO. The ease with which a gas can be liquefied is determined by its critical temperature.

Critical temperature is the minimum temperature above which a gas can be liquefied. This implies that gases with high critical temperature values can be easily liquefied as compared to gases with low critical temperature value.
9. (A, B, D)
10. (A, B) The Arrhenius equation is
\[
k = A e^{-E_aRT}
\]
where \(A\) = Pre-exponential factor
A is not directly related with temperature and activation energy.
Where \(A = \frac{Z \times P}{(\text{Frequency factor} \times \text{Steric factor})}\)
Hence we can say the \(E_a\) is independent of steric factor
\[
P = \frac{K_{\text{actual}}}{K_{\text{theoretical}}}
\]
So, \(A_{\text{actual}} > A_{\text{theoretical}}\)
CHEMISTRY

11. (A, B, C)
   (A) 1 is \( \text{Br}^1 \) benzyl halide and \( \text{C} - \text{C} - \text{Br}^3 \) alkylhalide. Follow \( S_n\).1.
   (B) I and II follow \( S_n\)2 also, as both are \( 1^\circ \) halide.
   (C) Compound (IV) undergoes inversion of configuration due to presence of chiral carbon atom.

12. (A, B, D)
   (A) Structure of \( \text{Al}_3(\text{CH}_3)_6 \)

   \[ \text{H}_3\text{C} \backslash \text{Al} \backslash \text{Al} \backslash \text{H}_3\text{C} \]
   \[ \text{H} \backslash \text{Al} \backslash \text{Al} \backslash \text{H} \]
   \[ 3\text{C}-2\text{e}^- \text{ Bond} \]

   (B) Structure of \( \text{B}_2\text{H}_6 \)

   \[ \text{H} \backslash \text{B} \backslash \text{B} \backslash \text{H} \]
   \[ 3\text{C}-2\text{e}^- \text{ Bond} \]

   (C) Structure of \( \text{Al}_3\text{Cl}_6 \)

   \[ \text{Cl} \backslash \text{Al} \backslash \text{Al} \backslash \text{Cl} \]
   \[ \text{Cl} \backslash \text{Al} \backslash \text{Al} \backslash \text{Cl} \]

   (D) \( \text{BCl}_3 \) is stronger lewis acid as the bond formed with the base will involve 2\( p \) orbital overlap which is stronger than 3\( p \) orbital overlap in the case of \( \text{AlCl}_3 \).

13. (A, D)
    \( \text{NO} \Rightarrow \text{Neutral} \)
    \( \text{B}_2\text{O}_3 \Rightarrow \text{Acidic} \)
    \( \text{CrO} \Rightarrow \text{Basic} \)
    All other oxides are amphoteric

14. (A, B)

   (C) \( \text{CH}_3 \backslash \text{P} \)

   \[ (\text{i}) \text{O}_2, \text{CH}_2\text{Cl}_2 \]
   \[ (\text{ii}) \text{Zn, H}_2\text{O} \]

   \[ \text{Q} (\text{C}_4\text{H}_4\text{O}), \text{i.e.,} \text{CH}_3 \]

   \[ (\text{Q}) \]

   (+ve cannizaro reaction)

   \[ \text{H} \backslash \text{C} - \text{H} \]

   (R) \( \text{CH}_3 \backslash \text{CH}_3 \)

   \[ (\text{i}) \text{O}_2, \text{CH}_2\text{Cl}_2 \]

   \[ (\text{ii}) \text{Zn, H}_2\text{O} \]

   \[ \text{O} \]

   \[ \text{S} \]

   (+ve haloform reaction)

   \[ \text{CH}_3 \backslash \text{CH}_3 \]

   \[ \text{H} - \text{C} - \text{H} \]
15. **(C) & 16. (B)**

\[
\text{KClO}_3 \xrightarrow{\Delta} \text{MnO}_2 \rightarrow \text{KCl} + \text{O}_2 \quad (W)
\]

\[
P_4 + \text{O}_2 \rightarrow P_4\text{O}_{10} \quad (X)
\]

\[
P_4\text{O}_{10} + \text{HNO}_3 \rightarrow N_2\text{O}_5 + \text{HPO}_3 \quad (Y) \quad (Z)
\]

17. **(A) & 18. (C)**

\[
\text{C(CH}_3\text{)}_3\text{C}^-\text{OEt} + \text{CH}_3\text{MgBr(\text{excess})C}_2\text{H}_5\text{O} \rightarrow \text{C(CH}_3\text{)}_3\text{C}^-\text{CH}_3 + \text{O}_\text{MgBr}
\]

\[\xrightarrow{\text{H}_2\text{O}}\]

\[
\text{C(CH}_3\text{)}_3\text{C}^-\text{CH}_3 \rightarrow \text{C(CH}_3\text{)}_3\text{C}^-\text{CH}_3
\]

\[\xrightarrow{\text{H}_2\text{O (dehydration)}}\]

\[
\text{C(CH}_3\text{)}_3\text{C}^-\text{C}^-\text{CH}_3 \rightarrow \text{C(CH}_3\text{)}_3\text{C}^-\text{C}^-\text{CH}_3
\]

\[\xrightarrow{\text{H}_2\text{SO}_4 \quad 0^\circ\text{C}}\]

\[
\text{C(CH}_3\text{)}_3\text{C}^-\text{C}^-\text{CH}_3
\]

\[\xrightarrow{\text{alkylation}}\]

\[
\text{C(CH}_3\text{)}_3\text{C}^-\text{C}^-\text{CH}_3
\]

\[\xrightarrow{\text{CH}_3\text{C}^-\text{Cl} / \text{AlCl}_3 \quad (\text{Acylation})}\]

\[
\text{C(CH}_3\text{)}_3\text{C}^-\text{C}^-\text{CH}_3\text{COCH}_3
\]
1. Which of the following compounds will form significant amount of meta product during mono-nitration reaction?

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<td>(2)</td>
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<tr>
<td><img src="image1" alt="OH" /></td>
<td><img src="image2" alt="OCOCH₃" /></td>
</tr>
<tr>
<td>(3)</td>
<td>(4)</td>
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<tr>
<td><img src="image3" alt="NH₂" /></td>
<td><img src="image4" alt="NHCOCH₃" /></td>
</tr>
</tbody>
</table>

2. \( \Delta U \) is equal to

- (1) Isochoric work
- (2) Isobaric work
- (3) Adiabatic work
- (4) Isothermal work

3. The increasing order of the reactivity of the following halides for the \( S_n \) reaction is

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<tbody>
<tr>
<td>(I)</td>
<td>(II)</td>
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<tr>
<td>( CH_3CHCH_2CH_3 Cl )</td>
<td>( CH_3CH_2CH_2Cl )</td>
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<tr>
<td>(III)</td>
<td>(III)</td>
</tr>
<tr>
<td>( p-H_3CO-C_6H_4-CH_2Cl )</td>
<td>( p-H_3CO-C_6H_4-CH_2Cl )</td>
</tr>
</tbody>
</table>

4. The radius of the second Bohr orbit for hydrogen atom is:

- (1) \( 6.6262 \times 10^{-34} \) Js; mass of electron = \( 9.1091 \times 10^{-31} \) kg; charge of electron = \( 1.60210 \times 10^{-19} \) C; permittivity of vacuum = \( 8.854185 \times 10^{-12} \) kg m\(^{-1}\) kg\(^{-1}\) m\(^{-3}\) A\(^{2}\)

- (1) 1.65Å
- (2) 4.76Å
- (3) 0.529Å
- (4) 2.12Å

5. \( pK_a \) of a weak acid (HA) and \( pK_b \) of a weak base (BOH) are 3.2 and 3.4, respectively. The pH of their salt (AB) solution is

- (1) 72
- (2) 69
- (3) 70
- (4) 1.0

6. The formation of which of the following polymers involves hydrolysis reaction?

- (1) Nylon 6
- (2) Bakelite
- (3) Nylon 6, 6
- (4) Terylene

7. The most abundant elements by mass in the body of a healthy human adult are:

- Oxygen (61.4%)
- Carbon (22.9%)
- Hydrogen (10.0%)
- Nitrogen (2.6%)

The weight which a 75 kg person would gain if all \(^{1}\)H atoms are replaced by \(^{2}\)H atoms is

- (1) 15 kg
- (2) 37.5 kg
- (3) 7.5 kg
- (4) 10 kg

8. Which of the following, upon treatment with tert-BuONa followed by addition of bromine water, fails to decolourize the colour of bromine?

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<td><img src="image5" alt="O" /></td>
<td><img src="image6" alt="Br" /></td>
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<tr>
<td>(3)</td>
<td>(4)</td>
</tr>
<tr>
<td><img src="image5" alt="O" /></td>
<td><img src="image6" alt="Br" /></td>
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</table>

9. In the following reactions, ZnO is respectively acting as a/an:

- (A) \( ZnO + Na_2O \rightarrow Na_2ZnO_2 \)
- (B) \( ZnO + CO_2 \rightarrow ZnCO_3 \)

- (1) base and acid
- (2) base and base
- (3) acid and acid
- (4) acid and base

10. Both lithium and magnesium display several similar properties due to the diagonal relationship; however, the one which is incorrect is:

- (1) Both form basic carbonates
- (2) Both form soluble bicarbonates
- (3) Both form nitrides
- (4) Nitrates of both Li and Mg yield NO₂ and O₂ on heating

11. 3-Methyl-pent-2-ene on reaction with HBr in presence of peroxide forms an addition product. The number of possible stereoisomers for the product is:

- (1) Six
- (2) Zero
- (3) Two
- (4) Four

12. A metal crystallises in a face centred cubic structure. If the edge length of its unit cell is 'a', the closest approach between two atoms in metallic crystal will be:

- (1) 2a
- (2) \( 2\sqrt{2} \) a
- (3) \( \sqrt{2} \) a
- (4) \( \frac{a}{\sqrt{2}} \)

13. Two reactions \( R_1 \) and \( R_2 \) have identical pre-exponential factors. Activation energy of \( R_1 \) exceeds that of \( R_2 \) by 10 kJ mol\(^{-1}\). If \( k_1 \) and \( k_2 \) are rate constants for reactions \( R_1 \) and \( R_2 \) respectively at 300 K, then ln\( (k_2/k_1) \) is equal to:

- (R = 8.314 J mol\(^{-1}\) K\(^{-1}\))

- (1) 8
- (2) 12
- (3) 6
- (4) 4
14. The correct sequence of reagents for the following conversion will be:

\[
\begin{align*}
(1) \ [Ag(NH_3)_2]^+OH^-, H^+/CH_3OH, CH_3MgBr \\
(2) \ CH_3MgBr, H^+/CH_3OH, [Ag(NH_3)_2]^+OH^- \\
(3) \ CH_3MgBr, [Ag(NH_3)_2]^+OH^-, H^+/CH_3OH \\
(4) \ [Ag(NH_3)_2]^+OH^-, CH_3MgBr, H^+/CH_3OH
\end{align*}
\]

15. The Tyndall effect is observed only when following conditions are satisfied:

(a) The diameter of the dispersed particles is much smaller than the wavelength of the light used.
(b) The diameter of the dispersed particle is not much smaller than the wavelength of the light used.
(c) The refractive indices of the dispersed phase and dispersion medium are almost similar in magnitude.
(d) The refractive indices of the dispersed phase and dispersion medium differ greatly in magnitude.

(1) (a) and (d) (2) (b) and (d) (3) (a) and (c) (4) (b) and (c)

16. Which of the following compounds will behave as a reducing sugar in an aqueous KOH solution?

(1) HOH₂C\[\begin{array}{c}
|\quad| \quad| \quad| \\
|\quad| \quad| \quad|
\end{array}\]CH₂OH

(2) \[\begin{array}{c}
|\quad| \quad| \quad| \\
|\quad| \quad| \quad|
\end{array}\]OH

(3) \[\begin{array}{c}
|\quad| \quad| \quad| \\
|\quad| \quad| \quad|
\end{array}\]OCOCH₃

(4) \[\begin{array}{c}
|\quad| \quad| \quad| \\
|\quad| \quad| \quad|
\end{array}\]OH

17. Given

\[
\begin{align*}
C_{(graphite)} + O_2(g) &\rightarrow CO_2(g) ; \quad \Delta H^\circ = -393.5 \text{ kJ mol}^{-1} \\
H_2(g) + \frac{1}{2} O_2(g) &\rightarrow H_2O(l) ; \quad \Delta H^\circ = -285.8 \text{ kJ mol}^{-1}
\end{align*}
\]

\[
\begin{align*}
\text{CO}_2(g) + 2H_2O(l) &\rightarrow \text{CH}_4(g) + 2O_2(g) ; \quad \Delta H^\circ = +890.3 \text{ kJ mol}^{-1}
\end{align*}
\]

Based on the above thermochemical equations, the value of \(\Delta H^\circ\) at 298 K for the reaction

\[
\begin{align*}
C_{(graphite)} + 2H_2(g) &\rightarrow CH_4(g) \text{ will be :}
\end{align*}
\]

(1) \(+74.8 \text{ kJ mol}^{-1}\) (2) \(+144.0 \text{ kJ mol}^{-1}\)

(3) \(-74.8 \text{ kJ mol}^{-1}\) (4) \(-144.0 \text{ kJ mol}^{-1}\)

18. Which of the following reactions is an example of a redox reaction?

(1) \(\text{XeF}_4 + \text{O}_2 \rightarrow \text{XeF}_6 + \text{O}_2\)

(2) \(\text{XeF}_4 + \text{F}_2 \rightarrow [\text{XeF}]^+ \cdot \text{PF}_5^-\)

(3) \(\text{XeF}_6 + \text{H}_2\text{O} \rightarrow \text{XeOF}_4 + 2\text{HF}\)

(4) \(\text{XeF}_6 + 2\text{H}_2\text{O} \rightarrow \text{XeOF}_2\text{F}_2 + 4\text{HF}\)

19. The products obtained when chlorine gas reacts with cold and dilute aqueous NaOH are:

(1) \(\text{ClO}^- \text{ and ClO}_2^-\) (2) \(\text{ClO}_2^- \text{ and ClO}_3^-\)

(3) \(\text{Cl}^- \text{ and ClO}^-\) (4) \(\text{Cl}^- \text{ and ClO}_2^-\)

20. The major product obtained in the following reaction is:

\[
\begin{align*}
\text{Br} &\rightarrow \text{H} \\
\text{C}_6\text{H}_5 &\rightarrow \text{H}
\end{align*}
\]

(1) \(\text{C}_6\text{H}_5\text{C(H(O)Bu)CH}_2\text{C}_6\text{H}_5\)

(2) \(\text{C}_6\text{H}_5\text{CH} = \text{CHC}_6\text{H}_5\)

(3) \(\text{C}_6\text{H}_5\text{CH}(\text{O}Bu)\text{CH}_2\text{C}_6\text{H}_5\)

(4) \(\text{C}_6\text{H}_5\text{CH}(\text{O}Bu)\text{CH}_2\text{C}_6\text{H}_5\)

21. Sodium salt of an organic acid 'X' produces effervescence with conc. H₂SO₄. 'X' reacts with the acidified aqueous CaCl₂ solution to give a white precipitate which decolourises acidic solution of KMnO₄. 'X' is:

(1) \(\text{C}_6\text{H}_5\text{COONa}\) (2) \(\text{HCOONa}\)

(3) \(\text{CH}_3\text{COONa}\) (4) \(\text{Na}_2\text{C}_2\text{O}_4\)

22. Which of the following species is not paramagnetic?

(1) \(\text{NO}\) (2) \(\text{CO}\)

(3) \(\text{O}_2\) (4) \(\text{B}_2\)

23. The freezing point of benzene decreases by 0.45°C when 0.2g of acetic acid is added to 20 g of benzene. If acetic acid associates to form a dimer in benzene, percentage association of acetic acid in benzene will be:

\(K_f\) for benzene = 5.12 K kg mol⁻¹

(1) 64.6% (2) 80.4%

(3) 74.6% (4) 94.6%

24. Which of the following molecules is least resonance stabilized?

(1) \(\text{C}_6\text{H}_6\) (2) \(\text{C}_6\text{H}_5\text{OCH}_3\)
27. A water sample has ppm level concentration of following anions
F^- = 10, SO_4^{2-} = 100, NO_3^- = 50
the anion/anions that make makes the water sample unsuitable for drinking is/are:
(1) only NO_3^- (2) both SO_4^{2-} and NO_3^-  
(3) only F^-  (4) only SO_4^{2-}

28. 1 gram of a carbonate (M_5CO_3) on treatment with excess HCl produces 0.01186 mole of CO_2. The molar mass of M_5CO_3 in g mol^{-1} is:
(1) 1186  (2) 84.3  
(3) 118.6 (4) 11.86

29. Given
E^o_{Cl_2/Cl^-} = 1.36 V, E^o_{Cr^{3+}/Cr} = -0.74 V,
E^o_{Cr_2O_7^{2-}/Cr^{3+}} = 1.33 V, E^o_{MnO_4^-/Mn^{2+}} = 1.51 V.

Among the following, the strongest reducing agent is:
(1) Cl^-  (2) Mn^{2+}  
(3) Cr^{3+}  (4) Cl^- 

30. The group having isoelectronic species is:
(1) O^2-, F^-, Na^+, Mg^{2+}  
(2) O^-, F^-, Na^+, Mg^+  
(3) O^2-, F^-, Na^+, Mg^{2+}  
(4) O^-, F^-, Na^+, Mg^{2+}
1. Nitrilation takes place in presence of concentrated HNO₃ + concentrated H₂SO₄.
   In strongly acidic nitrilation medium, the amine is converted into anilinium ion (−NH₃⁺); substitution is thus controlled not by −NH₂ group but by −NH₃⁺ group which, because of its positive charge, directs the entering group to the meta-position instead of ortho, and para.

2. From 1st law of thermodynamics
   \[ ΔU = q + w \]
   For adiabatic process:
   \[ q = 0 \]
   \[ ΔU = w \]

3. Since Sₙ₁ reactions involve the formation of carbocation as intermediate in the rate determining step, more is the stability of carbocation higher will be the reactivity of alkyl halides towards Sₙ₁ route.

Since stability of carbocation follows order:

\[ \text{CH₃} - \text{CH₂} - \text{CH₂} < \text{CH₃} - \text{CH} - \text{CH₂} - \text{CH₃} < \text{p-CH₃CO-CH₄} \]

Hence correct order is II < I < III

4. Radius of n\textsuperscript{th} Bohr orbit in H-atom
   \[ = 0.53 \text{ n}^2 \text{Å} \]
   Radius of II Bohr orbit = \[ 0.53 \times (2)^2 = 2.12 \text{ Å} \]

5. Given
   \[ pK_a (HA) = 3.2 \]
   \[ pK_b (BOH) = 3.4 \]
   The salt (AB) given is a salt is of weak acid and weak base. Hence the pH can be calculated by the formula
   \[ \text{pH} = 7 + \frac{1}{2} (3.2) - \frac{1}{2} (3.4) = 6.9 \]

6. Formation of Nylon-6 involves hydrolysis of caprolactam, (its monomer) in initial state.

   \[ \text{Caprolactam} \xrightarrow{\text{H₂O}} \text{H₂N(CH₂)₅COOH} \]

   α-Amino Caproic acid

   \[ \xrightarrow{\text{Polymerise}} \text{-(NH(CH₂)₅-C-NH-(CH₂)₅-CO-)}_n \]

   Nylon-6

7. Percentage (by mass) of elements given in the body of a healthy human adult is :-
   Oxygen = 61.4%, Carbon = 22.9%,
   Hydrogen = 10.0% and Nitrogen = 2.6%
   \[ \therefore \] Total weight of person = 75 kg
   \[ \therefore \] Mass due to \textsuperscript{1}H is \[ 75 \times \frac{10}{100} = 7.5 \text{ kg} \]
   If \textsuperscript{1}H atoms are replaced by \textsuperscript{2}H atoms.
   Mass gain by person would be \[ 7.5 \text{ kg} \]

8. (1)

   (1) tert-BuONa
   (2) tert-BuONa
   (3) tert-BuONa
13. (4) From Arrhenius equation,
\[ k = A e^{-\frac{E_a}{RT}} \]
so, \[ k_1 = A e^{-\frac{E_{a1}}{RT}} \] \[ \ldots (1) \]
\[ k_2 = A e^{-\frac{E_{a2}}{RT}} \] \[ \ldots (2) \]
On dividing equation (2)/(1) \[ \frac{k_2}{k_1} = e^{\frac{(E_{a1}-E_{a2})}{RT}} \]
\[ \ln \left( \frac{k_2}{k_1} \right) = \frac{E_{a1} - E_{a2}}{RT} = \frac{10,000}{8.314 \times 300} = 4 \]

14. (1) 
\[
\begin{array}{c}
\text{CHO} \\
\text{CO}_2\text{H}
\end{array}
\xrightarrow{\text{H}^+ / \text{CH}_3\text{OH}}
\begin{array}{c}
\text{CHO} \\
\text{CO}_2\text{H}
\end{array}
\]

15. (2)
16. (1)

12. (4) For a FCC unit cell
\[ r = \frac{\sqrt{2}}{4} a \]
\[ \therefore \text{closest distance} (2r) = \frac{\sqrt{2}}{4} a = \frac{a}{\sqrt{2}} \]
17. (3) Given
\[ \text{CO}_2(g) + 2\text{H}_2\text{O}(l) \rightarrow \text{CH}_4(g) + 2\text{O}_2(g), \Delta_H^\circ = 890.3\text{ kJ/mol} \quad \text{(i)} \]
\[ \text{C}_{\text{graphite}} + \text{O}_2(g) \rightarrow \text{CO}_2(g); \quad \Delta_H^\circ = -393.5\text{ kJ/mol} \quad \text{(ii)} \]
\[ \text{H}_2(g) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{H}_2\text{O}(l); \quad \Delta_H^\circ = -285.8\text{ kJ/mol} \quad \text{(iii)} \]
\[ \Delta_H^\circ = \sum (\Delta_i H^\circ)_{\text{products}} - \sum (\Delta_i H^\circ)_{\text{Reactants}} \]
\[ 890.3 = \left[ 1 \times (\Delta_f H^\circ)_{\text{CH}_4} + 2 \times 0 \right] - \left[ 1 \times (-393.5) + 2 \times (-285.8) \right] \]
\[ (\Delta_f H^\circ)_{\text{CH}_4} = 890.3 - 965.1 = -74.8\text{ kJ/mol} \]

18. (1) In the reaction
\[ \text{Oxidation} \quad \text{XeF}_4 + \text{O}_2 \text{F}_2 \rightarrow \text{XeF}_6 + \text{O}_2 \]
\[ \text{Reduction} \]

19. (3) \[ \text{Cl}_2 + \text{NaOH} \rightarrow \text{NaCl} + \text{NaClO} + \text{H}_2\text{O} \]
[cold and dilute]

20. (2) Elimination reaction is highly favoured if
(a) Bulkier base is used
(b) Higher temperature is used
Hence in given reaction biomolecular elimination reaction provides major product.

21. (4) \[ \text{Na}_2\text{C}_2\text{O}_4 + \text{H}_2\text{SO}_4 \rightarrow \text{Na}_2\text{SO}_4 + \text{CO}_2 + \text{CO}_2 + \text{H}_2\text{O} \]
[conc.]
\[ \text{Na}_2\text{C}_2\text{O}_4 + \text{CaCl}_2 \rightarrow \text{CaC}_2\text{O}_4 \downarrow + 2\text{NaCl} \]
[white ppt.]
\[ 5\text{CaC}_2\text{O}_4 \downarrow + 2\text{KMnO}_4 + 8\text{H}_2\text{SO}_4 \]
[purple]
\[ \text{K}_2\text{SO}_4 + 5\text{CaSO}_4 + 2\text{MnSO}_4 + 10\text{CO}_2 + 8\text{H}_2\text{O} \]
[colourless]

22. (2)
1. \[ \text{NO} \rightarrow \text{one unpaired electron is present in } \pi^* \text{ molecular orbit hence paramagnetic.} \]

23. (4) In benzene
\[ 2\text{CH}_3\text{COOH} \rightarrow (\text{CH}_3\text{COOH})_2 \]
\[ 1 - \alpha = \frac{\alpha}{2} \quad \therefore i = 1 - \alpha + \frac{\alpha}{2} = 1 - \frac{\alpha}{2} \]

Here \( \alpha \) is degree of association
\[ \Delta_T^f = k_{\alpha/m} \]
\[ 0.45 = \left( 1 - \frac{\alpha}{2} \right) \left( \frac{0.2}{60} \right) \]
\[ \frac{20}{1000} \]
\[ 1 - \frac{\alpha}{2} = 0.527 \]
\[ \alpha = 0.945 \]
% degree of association = 94.6%

24. (4) is nonaromatic and hence least reasonance
stabilized whereas other three are aromatic.

25. (4) Moles of complex = \[ \text{Molarity} \times \text{Volume(ml)} \]
\[ \frac{100 \times 0.1}{1000} = 0.01 \text{ mole} \]
Moles of ions precipitated with excess of
\[ \text{AgNO}_3 = \frac{1.2 \times 10^{22}}{6.02 \times 10^{23}} = 0.02 \text{ moles} \]
\[ 0.01 \times n = 0.02 \quad \therefore n = 2 \]
It means \( 2\text{Cl}^- \) ions present in ionization sphere
\[ \text{complex is } [\text{Co(H}_2\text{O})_3\text{Cl}]\text{Cl}_2\text{H}_2\text{O} \]

26. (2) DIBAL-H is an electrophilic reducing agent. It reduces both ester and carboxylic group into an aldehyde at
low temperature.

27. (3) Above 2 ppm concentration of $F^-$ in drinking water cause brown mottling of teeth.

28. (2) Given chemical eqn

$$M_2CO_3 + 2HCl \rightarrow 2MCl + H_2O + CO_2$$

From the balanced chemical eqn,

$$n_{M_2CO_3} = n_{CO_2}$$

$$\frac{1}{M_2CO_3} = 0.01186$$

$$\therefore M_2CO_3 = \frac{1}{0.01186}$$

$$\Rightarrow M = 84.3 \text{ gm/mol}$$

29. (1) $E^{\circ}_{\text{MnO}_4^-/Mn^{2+}} = 1.51V$

$$E^{\circ}_{\text{Cl}_2/Cl^{-}} = 1.36V$$

$$E^{\circ}_{\text{C}_2\text{O}_4^2-/C}_3\text{O}_4^{3-} = 1.33V$$

$$E^{\circ}_{\text{Cr}^{3+/Cr} = -0.74}$$

Since $\text{Cr}^{3+}$ is having least reducing potential, so $\text{Cr}$ is the best reducing agent.

30. (1) Isoelectronic species have same no. of electrons.

<table>
<thead>
<tr>
<th>ions</th>
<th>$O^{2-}$</th>
<th>$F^-$</th>
<th>$Na^+$</th>
<th>$Mg^{2+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>no. of $e^-$</td>
<td>8+2</td>
<td>9+1</td>
<td>11-1</td>
<td>12-2</td>
</tr>
</tbody>
</table>

Therefore, $O^{2-}$, $F^-$, $Na^+$, $Mg^{2+}$ are isoelectronic.
Chapter 1

Some Basic Concepts of Chemistry

Section-A

<table>
<thead>
<tr>
<th>A</th>
<th>Fill in the Blanks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>The modern atomic mass unit is based on ................. (1980)</td>
</tr>
<tr>
<td>2.</td>
<td>The total number of electrons present in 18 ml of water is ...................... (1980)</td>
</tr>
<tr>
<td>3.</td>
<td>3 g of a salt of molecular weight 30 is dissolved in 250 g of water. The molality of the solution is ............... (1983 - 1 Mark)</td>
</tr>
<tr>
<td>4.</td>
<td>The weight of $1 \times 10^{22}$ molecules of CuSO$_4 \cdot 5$H$_2$O is ..................... (1991 - 1 Mark)</td>
</tr>
<tr>
<td>5.</td>
<td>The compound YBa$_2$Cu$_3$O$_7$, which shows superconductivity, has copper in oxidation state ................., assume that the rare earth element yttrium is in its usual +3 oxidation state. (1994 - 1 Mark)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>C</th>
<th>MCQs with One Correct Answer</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>27 g of Al will react completely with how many grams of oxygen? (1978)</td>
</tr>
</tbody>
</table>
|   | (a) 8 g  
|   | (b) 16 g  
|   | (c) 32 g  
|   | (d) 48 g  |
| 2. | A compound was found to contain nitrogen and oxygen in the ratio 28 gm and 80 gm respectively. The formula of the compound is (1978) |
|   | (a) NO  
|   | (b) N$_2$O$_3$  
|   | (c) N$_2$O$_5$  
|   | (d) N$_2$O$_4$  |
| 3. | The largest number of molecules is in (1979) |
|   | (a) 36 g of water  
|   | (b) 28 g of carbon monoxide  
|   | (c) 46 g of ethyl alcohol  
|   | (d) 54 g of nitrogen pentoxide  |
| 4. | The total number of electrons in one molecule of carbon dioxide is (1979) |
|   | (a) 22  
|   | (b) 44  
|   | (c) 66  
|   | (d) 88  |
| 5. | A gaseous mixture contains oxygen and nitrogen in the ratio of 1 : 4 by weight. Therefore the ratio of their number of molecules is (1979) |
|   | (a) 1 : 4  
|   | (b) 1 : 8  
|   | (c) 7 : 32  
|   | (d) 3 : 16  |

6. 2.76 g of silver carbonate on being strongly heated yields a residue weighing (1979) |
   | (a) 2.16 g  
   | (b) 2.48 g  
   | (c) 2.32 g  
   | (d) 2.64 g  |

7. M is molecular weight of KMnO$_4$. The equivalent weight of KMnO$_4$ when it is converted into K$_2$MnO$_4$ is (1980) |
   | (a) M  
   | (b) M/3  
   | (c) M/5  
   | (d) M/7  |

8. If 0.50 mole of BaCl$_2$ is mixed with 0.20 mol of Na$_3$PO$_4$, the maximum number of moles of Ba$_3$(PO$_4$)$_2$ that can be formed is (1981 - 1 Mark) |
   | (a) 0.70  
   | (b) 0.50  
   | (c) 0.20  
   | (d) 0.10  |

9. One mole of N$_2$H$_4$ loses ten moles of electrons to form a new compound Y. Assuming that all the nitrogen appears in the new compound, what is the oxidation state of nitrogen in Y? (There is no change in the oxidation state of hydrogen). (1981 - 1 Mark) |
   | (a) -1  
   | (b) -3  
   | (c) +3  
   | (d) +5  |

10. The oxidation number of carbon in CH$_3$O is (1982 - 1 Mark) |
    | (a) -2  
    | (b) +2  
    | (c) 0  
    | (d) +4  |

11. A molal solution is one that contains one mole of a solute in: (1986 - 1 Mark) |
    | (a) 1000 g of the solvent  
    | (b) one litre of the solvent  
    | (c) one litre of the solution  
    | (d) 22.4 litres of the solution  |

12. The brown ring complex compound is formulated as $[Fe(H$_2$O)$_5$(NO)]SO$_4$. The oxidation state of iron is: (1987 - 1 Mark) |
    | (a) 1  
    | (b) 2  
    | (c) 3  
    | (d) 0  |

13. The equivalent weight of MnSO$_4$ is half of its molecular weight when it is converted to: (1988 - 1 Mark) |
    | (a) Mn$_2$O$_3$  
    | (b) MnO$_2$  
    | (c) MnO$_4^-$  
    | (d) MnO$_4^{2-}$  |

14. In which mode of expression, the concentration of a solution remains independent of temperature? (1988 - 1 Mark) |
    | (a) Molarity  
    | (b) Normality  
    | (c) Formality  
    | (d) Molality  |
15. The oxidation number of phosphorus in Ba(H₂PO₄)₂ is:
   (1990 - 1 Mark)
   (a) +3  (b) +2  (c) +1  (d) −1

16. The oxidation states of the most electronegative element in
   the products of the reaction, BaO₂ with dil. H₂SO₄ is:
   (1991 - 1 Mark)
   (a) 0 and −1  (b) −1 and −2  (c) −2 and 0  (d) −2 and −1

17. For the redox reaction:
   MnO₄²⁻ + C₂O₄²⁻ + H⁺ → Mn²⁺ + CO₂ + H₂O
   the correct coefficients of the reactants for the balanced
   reaction are:
   (1992 - 1 Mark)
   \[
   \begin{align*}
   \text{MnO}_4^- & : 2 \\
   \text{C}_2\text{O}_4^{2-} & : 5 \\
   \text{H}^+ & : 16
   \end{align*}
   \]
   (a) 2  (b) 5  (c) 16  (d) 2

18. The normality of 0.3 M phosphorous acid (H₃PO₄) is:
   (1999 - 2 Marks)
   (a) 0.1  (b) 0.9  (c) 0.3  (d) 0.6

19. The oxidation number of sulphur in S₈, S₆, F₂, H₂S respectively, are:
   (1999 - 2 Marks)
   (a) 0, +1 and −2  (b) +2, +1 and −2  (c) 0, +1 and +2  (d) −2, +1 and −2

20. Amongst the following identify the species with an atom in
    +6 oxidation state
   (2000S)
   (a) MnO₄⁻  (b) Cr(CN)₆³⁻  (c) NiF₂⁻  (d) CrO₂Cl₂

21. The reaction, 3ClO⁻(aq) → ClO₃⁻(aq) + 2Cl⁻(aq), is an example of:
   (2001S)
   (a) oxidation reaction  (b) reduction reaction  (c) disproportionation reaction  (d) decomposition reaction

22. An aqueous solution of 6.3 g oxalic acid dihydrate is made up to 250 ml. The volume of 0.1 N NaOH required to completely neutralize 10 ml of this solution is:
   (2001S)
   (a) 40 ml  (b) 20 ml  (c) 10 ml  (d) 4 ml

23. In the standardization of Na₂S₂O₃ using K₂Cr₂O₇ by
   iodometry, the equivalent weight of K₂Cr₂O₇ is:
   (2001S)
   (a) (molecular weight)/2  (b) (molecular weight)/6  (c) (molecular weight)/3  (d) same as molecular weight

24. How many moles of electron weigh one kilogram?
   (2002S)
   (a) \(6.023 \times 10^{23}\)  (b) \(\frac{1}{9.108} \times 10^{31}\)

25. Which has maximum number of atoms?
   (2003S)
   (a) 24g of C (12)  (b) 56g of Fe (56)  (c) 27g of Al (27)  (d) 108g of Ag (108)

26. Mixture X = 0.02 mol of [Co(NH₃)₆SO₄]Br and 0.02 mol of
   [Co(NH₃)₆Br]SO₄ was prepared in 2 litre of solution.
   (2003S)
   1 litre of mixture X + excess AgNO₃ → Y

   1 litre of mixture X + excess BaCl₂ → Z

   No. of moles of Y and Z are
   (a) 0.01, 0.01  (b) 0.02, 0.01  (c) 0.01, 0.02  (d) 0.02, 0.02

27. The pair of the compounds in which both the metals are in
    the highest possible oxidation state is:
   (2004S)
   (a) [Fe(CN)₆]³⁻, [Co(CN)₆]³⁻  (b) Cr₂O₇²⁻, MnO₄⁻  (c) TiO₃, MnO₂  (d) [Co(CN)₆]³⁻, MnO₃

28. Consider a titration of potassium dichromate solution with
   acidified Mohr’s salt solution using diphenylamine as indicator.
   The number of moles of Mohr’s salt required per mole of dichromate is:
   (2007)
   (a) 3  (b) 4  (c) 5  (d) 6

**Subjective Problems**

1. What weight of AgCl will be precipitated when a solution
   containing 4.77 g of NaCl is added to a solution of 5.77 g of
   AgNO₃?  
   (1978)

2. One gram of an alloy of aluminium and magnesium when
   treated with excess of dil. HCl forms magnesium chloride,
   aluminium chloride and hydrogen. The evolved hydrogen,
   collected over mercury at 0°C has a volume of 1.20 litres at
   0.92 atm. pressure. Calculate the composition of the alloy.
   [H = 1, Mg = 24, Al = 27]  
   (1978)

3. Igniting MnO₂ converts it quantitatively to Mn₃O₄. A sample
   of pyrolusite is of the following composition: MnO₂ 80%,
   SiO₂ and other inert constituents 15%, rest being water. The
   sample is ignited in air to constant weight. What is the
   percentage of Mn in the ignited sample?  
   [O = 16, Mn = 54.9]  
   (1978)

4. 4.215 g of a metallic carbonate was heated in a hard glass
   tube and the CO₂ evolved was found to measure 1336 ml at
   27°C and 700 mm pressure. What is the equivalent weight of
   the metal?  
   (1979)

5. (a) 5.5 g of a mixture of FeSO₄, 7H₂O and Fe₂(SO₄)₃·9H₂O
   requires 5.4 ml of 0.1 N KMnO₄ solution for complete
   oxidation. Calculate the number of gram mole of
   hydrated ferric sulphate in the mixture.
(b) The vapour density (hydrogen = 1) of a mixture consisting of NO₂ and N₂O₄ is 38.3 at 26.7°C. Calculate the number of moles of NO₂ in 100 g of the mixture.

(1979)

6. 5 ml of a gas containing only carbon and hydrogen were mixed with an excess of oxygen (30 ml) and the mixture exploded by means of an electric spark. After the explosion, the volume of the mixed gases remaining was 25 ml. On adding a concentrated solution of potassium hydroxide, the volume further diminished to 15 ml of the residual gas being pure oxygen. All volumes have been reduced to N.T.P. Calculate the molecular formula of the hydrocarbon gas.

(1979)

7. In the analysis of 0.500 g sample of feldspar, a mixture of chlorides of sodium and potassium is obtained which weighs 0.1180 g. Subsequent treatment of mixed chlorides with silver nitrate gives 0.2451 g of silver chloride. What is the percentage of sodium oxide and potassium oxide in feldspar.

(1979)

8. A compound contains 28 percent of nitrogen and 72 percent of metal by weight. 3 atoms of metal combine with 2 atoms of N. Find the atomic weight of metal.

(1980)

9. (i) A sample of MnSO₄·4H₂O is strongly heated in air. The residue is Mn₃O₄:
(ii) The residue is dissolved in 100 ml of 0.1 N FeSO₄ containing dilute H₂SO₄.
(iii) The solution reacts completely with 50 ml of KMnO₄ solution.
(iv) 25 ml of the KMnO₄ solution used in step (iii) requires 30 ml of 0.1 N FeSO₄ solution for complete reaction.

Find the amount of MnSO₄·4H₂O present in the sample.

(1980)

10. (a) One litre of a sample of hard water contains 1 mg of CaCl₂ and 1 mg of MgCl₂. Find the total hardness in terms of parts of CaCO₃ per 10⁶ parts of water by weight.
(b) A sample of hard water contains 20 mg of Ca²⁺ ions per litre. How many milli-equivalent of Na₂CO₃ would be required to soften 1 litre of the sample?
(c) 1 gm of Mg is burnt in a closed vessel which contains 0.5 gm of O₂.
(i) Which reactant is left in excess?
(ii) Find the weight of the excess reactants?
(iii) How many millilitres of 0.5 N H₂SO₄ will dissolve the residue in the vessel.

(1980)

11. A hydrocarbon contains 10.5 g of carbon per gram of hydrogen. 1 litre of the vapour of the hydrocarbon at 127°C and 1 atmosphere pressure weighs 2.8 g. Find the molecular formula.

(1980)

12. Find
(i) The total number of neutrons and
(ii) The total mass of neutron in 7 mg of ¹⁴C.

(1980)

(1979)

13. A mixture contains NaCl and unknown chloride MCl.
(i) 1 g of this is dissolved in water. Excess of acidified AgNO₃ solution is added to it. 2.567 g of white ppt. is formed.
(ii) 1 g of original mixture is heated to 300°C. Some vapours come out which are absorbed in acidified AgNO₃ solution, 1.341 g of white precipitate was obtained.

Find the molecular weight of unknown chloride.

(1980)

14. A 1.00 gm sample of H₂O₂ solution containing X per cent H₂O₂ by weight requires X ml of a KMnO₄ solution for complete oxidation under acidic conditions. Calculate the normality of the KMnO₄ solution.

(1981 - 3 Marks)

15. Balance the following equations.

(i) Cu₂O + H⁺ + NO₃⁻ → Cu²⁺ + NO + H₂O

(1981 - 1 Mark)

(ii) K₃[Fe(CN)₆] + H₂SO₄ + H₂O → K₂SO₄ + FeSO₄ + (NH₄)₂SO₄ + CO

(1981 - 1 Mark)

(iii) C₂H₂OH + I₂ + OH⁻ → CH₃ + HCO⁻ + I⁻ + H₂O

(1981 - 1 Mark)

16. Hydroxylamine reduces iron (III) according to the equation:
2NH₂OH + 4 Fe³⁺ → N₂O(g) ↑ + H₂O + 4 Fe²⁺ + 4H⁺

Iron (II) thus produced is estimated by titration with a standard permanganate solution. The reaction is:

MnO₄⁻ + 5 Fe²⁺ + 8H⁺ → Mn²⁺ + 5 Fe³⁺ + 4H₂O

(1981 - 1 Mark)

A 10 ml sample of hydroxylamine solution was diluted to 1 litre. 50 ml of this diluted solution was boiled with an excess of iron (III) solution. The resulting solution required 12 ml of 0.02 M KMnO₄ solution for complete oxidation of iron (II). Calculate the weight of hydroxylamine in one litre of the original solution. (H = 1, N = 14, O = 16, K = 39, Mn = 55, Fe = 56)

(1982 - 4 Marks)

17. The density of a 3 M sodium thiosulphate solution (Na₂S₂O₃) is 1.25 g per ml. Calculate (i) the percentage by weight of sodium thiosulphate, (ii) the molar fraction of sodium thiosulphate and (iii) the molalities of Na⁺ and S₂O₃²⁻ ions.

(1983 - 5 Marks)

18. 4.08 g of a mixture of BaO and an unknown carbonate MCO₃ was heated strongly. The residue weighed 3.64 g. This was dissolved in 100 ml of 1 N HCl. The excess acid required 16 ml of 2.5 N NaOH solution for complete neutralization. Identify the metal M.

(At. wt. H = 1, C = 12, O = 16, Cl = 35.5, Ba = 138)
19. Complete and balance the following reactions:

(i) \( \text{Zn} + \text{NO}_3^- \rightarrow \text{Zn}^{2+} + \text{NH}_4^+ \) (1983 - 1 Mark)

(ii) \( \text{Cr}_2\text{O}_7^{2-} + \text{C}_2\text{H}_5\text{H}_2\text{O} \rightarrow \text{C}_2\text{H}_4\text{O}_2 + \text{Cr}^{3+} \) (1983 - 1 Mark)

(iii) \( \text{HNO}_3 + \text{HCl} \rightarrow \text{NO} + \text{Cl}_2 \) (1983 - 1 Mark)

(iv) \( \text{Ce}^{3+} + \text{S}_2\text{O}_5^{2-} \rightarrow \text{SO}_4^{2-} + \text{Ce}^{4+} \) (1983 - 1 Mark)

(v) \( \text{Cl}_2 + \text{OH}^- \rightarrow \text{Cl}^- + \text{ClO}^- \) (1983 - 1 Mark)

(vi) \( \text{Mn}^{2+} + \text{PbO}_2 \rightarrow \text{MnO}_4^- + \text{H}_2\text{O} \) (1986 - 1 Mark)

(vii) \( \text{S} + \text{OH}^- \rightarrow \text{S}^{2-} + \text{S}_2\text{O}_3^{2-} \) (1986 - 1 Mark)

(viii) \( \text{ClO}_3^- + \text{I}^- + \text{H}_2\text{SO}_4 \rightarrow \text{Cl}^- + \text{HSO}_4^- \) (1986 - 1 Mark)

(ix) \( \text{Ag}^{+} + \text{AsH}_3 \rightarrow \text{H}_3\text{AsO}_3 + \text{H}^+ \) (1986 - 1 Mark)

20. \( 2.68 \times 10^{-3} \) moles of a solution containing an ion \( A^{n+} \) require \( 1.61 \times 10^{-3} \) moles of \( \text{MnO}_4^- \) for the oxidation of \( A^{n+} \) to \( A^{(n+1)+} \) in acid medium. What is the value of \( n \)?

(1984 - 2 Marks)

21. Five ml of 8N nitric acid, 4.8 ml of 5N hydrochloric acid and a certain volume of 17M sulphuric acid are mixed together and made up to 2 litre. Thirty ml of this acid mixture exactly neutralize 42.9 ml of sodium carbonate solution containing one gram of \( \text{Na}_2\text{CO}_3 \), 10H\(_2\text{O} \) in 100 ml of water. Calculate the amount in gram of the sulphate ions in solution.

(1985 - 4 Marks)

22. Arrange the following in increasing oxidation number of iodine.

\( \text{I}_2, \text{HI}, \text{HIO}_4, \text{ICl} \)

(1986 - 1 Mark)

23. (i) What is the weight of sodium bromate and molarity of solution necessary to prepare 85.5 ml of 0.672 N solution when the half-cell reaction is:

\[ \text{BrO}_3^- + 6\text{H}^+ + 6\text{e}^- \rightarrow \text{Br}^- + 3\text{H}_2\text{O} \]

(ii) What would be the weight as well as molarity if the half-cell reaction is:

\[ 2\text{BrO}_3^- + 12\text{H}^+ + 10\text{e}^- \rightarrow \text{Br}_2 + 6\text{H}_2\text{O} \]

(1987 - 5 Marks)

24. A sugar syrup of weight 214.2 g contains 34.2 g of sugar (\( \text{C}_{12}\text{H}_{22}\text{O}_{11} \)). Calculate: (i) molar concentration and (ii) mole fraction of sugar in the syrup.

(1988 - 2 Marks)

25. A sample of hydrazine sulphate (\( \text{N}_2\text{H}_5\text{SO}_4 \)) was dissolved in 100 ml of water, 10 ml of this solution was reacted with excess of ferric chloride solution and warmed to complete the reaction. Ferrous ion formed was estimated and it required 20 ml of M/50 potassium permanganate solution. Estimate the amount of hydrazine sulphate in one litre of the solution.

(1988 - 3 Marks)

Reaction:

\[ 4\text{Fe}^{3+} + \text{N}_2\text{H}_4 \rightarrow \text{N}_2 + 4\text{Fe}^{2+} + 4\text{H}^+ \]

\[ \text{MnO}_4^- + 5\text{Fe}^{2+} + 8\text{H}^+ \rightarrow \text{Mn}^{2+} + 5\text{Fe}^{3+} + 4\text{H}_2\text{O} \]

26. An equal volume of a reducing agent is titrated separately with 1M K\(_2\text{MnO}_4 \) in acid neutral and alkaline media. The volumes of K\(_2\text{MnO}_4 \) required are 20 ml in acid, 33.4 ml neutral and 100 ml in alkaline media. Find out the oxidation state of manganese in each reduction product. Give the balanced equations for all the three half-reactions. Find out the volume of 1M K\(_2\text{Cr}_2\text{O}_7 \) consumed; if the same volume of the reducing agent is titrated in acid medium (1989 - 5 Marks)

27. A mixture of \( \text{H}_2\text{C}_2\text{O}_4 \) (oxalic acid) and Na\(_2\text{HCO}_3 \) weighing 2.02 g was dissolved in water and solution made up to 1 litre. Ten millilitres of the solution required 3.0 ml of 0.1 N sodium hydroxide solution for complete neutralization. In another experiment, 10.0 ml of the same solution, in hot dilute sulphuric acid medium. Require 4.0 ml of 0.1 N potassium permanganate solution for complete reaction. Calculate the amount of \( \text{H}_2\text{C}_2\text{O}_4 \) and Na\(_2\text{HCO}_3 \) in the mixture.

(1990 - 5 Marks)

28. A solid mixture (5.0 g) consisting of lead nitrate and sodium nitrate was heated below 600°C until the weight of the residue was constant. If the loss in weight is 28.0 per cent, find the amount of lead nitrate and sodium nitrate in the mixture.

(1990 - 4 Marks)

29. Calculate the molality of 1 litre solution of 93% \( \text{H}_2\text{SO}_4 \) (weight/volume). The density of the solution is 1.84 g/ml.

(1990 - 1 Mark)

30. A solution of 0.2 g of a compound containing \( \text{Cu}^{2+} \) and \( \text{C}_2\text{O}_4^{2-} \) ions on titration with 0.02 M K\(_2\text{MnO}_4 \) in presence of \( \text{H}_2\text{SO}_4 \) consumes 22.6 ml of the oxidant. The resultant solution is neutralized with \( \text{Na}_2\text{CO}_3 \), acidified with dil. acetic acid and treated with excess KI. The liberated iodine requires 11.3 ml of 0.05 M \( \text{Na}_2\text{S}_2\text{O}_3 \) solution for complete reduction.

Find out the molar ratio of \( \text{Cu}^{2+} \) to \( \text{C}_2\text{O}_4^{2-} \) in the compound. Write down the balanced redox reactions involved in the above titrations.

(1991 - 5 Marks)

31. A 1.0 g sample of \( \text{Fe}_2\text{O}_3 \) solid of 55.2% purity is dissolved in acid and reduced by heating the solution with zinc dust. The resultant solution is cooled and made up to 100.0 ml. An aliquot of 25.0 ml of this solution requires 17.0 ml of 0.0167 M solution of an oxidant for titration. Calculate the number of electrons taken up by the oxidant in the reaction of the above titration.

(1991 - 4 Marks)

32. A 2.0 g sample of a mixture containing sodium carbonate, sodium bicarbonate and sodium sulphate is gently heated till the evolution of \( \text{CO}_2 \) ceases. The volume of \( \text{CO}_2 \) at 750 mm Hg pressure and at 298 K is measured to be 123.9 ml. A 1.5g of the same sample requires 150 ml of (M/10) HCl for complete neutralisation. Calculate the % composition of the components of the mixture.

(1992 - 5 Marks)
33. One gram of commercial AgNO₃ is dissolved in 50 ml of water. It is treated with 50 ml of a KI solution. The silver iodide thus precipitated is filtered off. Excess of KI in the filtrate is titrated with (M/10) KIO₃ solution in presence of 6M HCl till all I⁻ ions are converted into ICl. It requires 50 ml of (M/10) KIO₃ solution. 20 ml of the same stock solution of KI requires 30 ml of (M/10) KIO₃ under similar conditions. Calculate the percentage of AgNO₃ in the sample.

(Reaction: KIO₃ + 2KI + 6HCl → 3ICl + 3KCl + 3H₂O)

(1992 - 4 Marks)

34. Upon mixing 45.0 ml of 0.25 M lead nitrate solution with 25.0 ml of 0.10 M chromic sulphate solution, precipitation of lead sulphate takes place. How many moles of lead sulphate are formed? Also, calculate the molar concentrations of the species left behind in the final solution. Assume that lead sulphate is completely insoluble.

(1993 - 3 Marks)

35. The composition of a sample of Wustite is Fe₀.93O₁.₀₀. What percentage of the iron is present in the form of Fe (III)?

(1994 - 2 Marks)

36. 8.0575 × 10⁻² kg of Glauber's salt is dissolved in water to obtain 1 dm³ of a solution of density 1.072 kg m⁻³. Calculate the molarity, molality and mole fraction of Na₂S₂O₃ in the solution.

(1994 - 3 Marks)

37. A 3.00 g sample containing Fe₃O₄, Fe₂O₃ and an inert impure substance, is treated with excess of KI solution in presence of dilute H₂SO₄. The entire iron is converted into Fe²⁺ along with the liberation of iodine. The resulting solution is diluted to 100 ml. A 20 ml of the diluted solution requires 11.0 ml of 0.5 M Na₂S₂O₃ solution to reduce the iodine present. A 50 ml of the diluted solution, after complete extraction of the iodine requires 12.80 ml of 0.25 M KMnO₄ solution in dilute H₂SO₄ medium for the oxidation of Fe²⁺. Calculate the percentages of Fe₂O₃ and Fe₃O₄ in the original sample.

(1996 - 5 Marks)

38. An aqueous solution containing 0.10 g KIO₃ (formula weight = 214.0) was treated with an excess of KI solution. The solution was acidified with HCl. The liberated I₂ consumed 45.0 mL of thiosulphate solution to decolourise the blue starch-iodine complex. Calculate the molarity of the sodium thiosulphate solution.

(1998 - 5 Marks)

39. How many millilitres of 0.5 M H₂SO₄ are needed to dissolve 0.5 g of copper(II) carbonate?

(1999 - 3 Marks)

40. A plant virus is found to consist of uniform cylindrical particles of 150 Å in diameter and 5000 Å long. The specific volume of the virus is 0.75 cm³/g. If the virus is considered to be a single particle, find its molar mass.

(1999 - 3 Marks)

41. Hydrogen peroxide solution (20 ml) reacts quantitatively with a solution of KMnO₄ (20 ml) acidified with dilute H₂SO₄. The same volume of the KMnO₄ solution is just decolourised by 10 ml of MnSO₄ in neutral medium simultaneously forming a dark brown precipitate of hydrated MnO₂. The brown precipitate is dissolved in 10 ml of 0.2 M sodium oxalate under boiling condition in the presence of dilute H₂SO₄. Write the balanced equations involved in the reactions and calculate the molarity of H₂SO₄.

(2001 - 5 Marks)

42. Calculate the molarity of water if its density is 1000 kg/m³.

(2003 - 2 Marks)

**Assertion & Reason Type Questions**

1. Read the following statement and explanation and answer as per the options given below:

**STATEMENT(S):** In the titration of Na₂CO₃ with HCl using methyl orange indicator, the volume required at the equivalence point is twice that of the acid required using phenolphthalein indicator.

**EXPLANATION(E):** Two moles of HCl are required for the complete neutralization of one mole of Na₂CO₃.

(a) Both S and E are true, and E is the correct explanation of S.
(b) Both S and E are true, but E is not the correct explanation of S.
(c) S is true but E is false.
(d) S is false but E is true.

**Integer Value Correct Type**

1. A student performs a titration with different burettes and finds titre values of 25.2 ml, 25.25 ml, and 25.0 ml. The number of significant figures in the average titre value is

(2010)

2. Silver (atomic weight = 108 g mol⁻¹) has a density of 10.5 g cm⁻³. The number of silver atoms on a surface area 10⁻¹² m² can be expressed in scientific notation as y × 10^x. The value of x is:

(2010)

3. The difference in the oxidation numbers of the two types of sulphur atoms in Na₂S₄O₆ is

(2011)

4. If the value of Avogadro number is 6.023 × 10²³ mol⁻¹ and the value of Boltzmann constant is 1.380 × 10⁻²³ J K⁻¹, then the number of significant digits in the calculated value of the universal gas constant is

(JEE Adv. 2014)
Section-B

1. In a compound C, H and N atoms are present in 9 : 1 : 3.5 by weight. Molecular weight of compound is 108. Molecular formula of compound is [2002]
   (a) C₂H₈N₂ (b) C₃H₄N (c) C₅H₈N₂ (d) C₆H₁₂N₃.
2. With increase of temperature, which of these changes? [2002]
   (a) molality (b) weight fraction of solute (c) molarity (d) mole fraction.
3. Number of atoms in 558.5 gram Fe (at. wt. of Fe = 55.85 g mol⁻¹) is [2003]
   (a) twice that in 60 g carbon (b) 6.023 × 10²² (c) half that in 8 g He (d) 558.5 × 6.023 × 10²³
4. What volume of hydrogen gas, at 273 K and 1 atm. pressure will be consumed in obtaining 21.6 g of elemental boron (atomic mass = 10.8) from the reduction of boron trichloride by hydrogen? [2003]
   (a) 67.2 L (b) 44.8 L (c) 22.4 L (d) 89.6 L
5. 25ml of a solution of barium hydroxide on titration with a 0.1 molar solution of hydrochloric acid gave a litre value of 35ml. The molarity of barium hydroxide solution was [2003]
   (a) 0.14 (b) 0.28 (c) 0.35 (d) 0.07
6. 6.02 × 10²⁰ molecules of urea are present in 100 ml of its solution. The concentration of urea solution is [2004]
   (a) 0.02 M (b) 0.01 M (c) 0.001 M (d) 0.1 M (Avogadro constant, Nₐ = 6.02 × 10²³ mol⁻¹)
7. To neutralise completely 20 mL of 0.1 M aqueous solution of phosphorous acid (H₃PO₃), the value of 0.1 M aqueous KOH solution required is [2004]
   (a) 40 mL (b) 20 mL (c) 10 mL (d) 60 mL
8. The ammonia evolved from the treatment of 0.30 g of an organic compound for the estimation of nitrogen was passed in 100 mL of 0.1 M sulphuric acid. The excess of acid required 20 mL of 0.5 M sodium hydroxide solution for complete neutralization. The organic compound is [2004]
   (a) urea (b) benzamide (c) acetamide (d) thiourea
9. Two solutions of a substance (non electrolyte) are mixed in the following manner. 480 ml of 1.5 M first solution + 520 ml of 1.2 M second solution. What is the molarity of the final mixture? [2005]
   (a) 2.70 M (b) 1.344 M (c) 1.50 M (d) 1.20 M
10. If we consider that 1/6, in place of 1/12, mass of carbon atom is taken to be the relative atomic mass unit, the mass of one mole of the substance will [2005]
    (a) be a function of the molecular mass of the substance (b) remain unchanged (c) increase two fold (d) decrease twice
11. How many moles of magnesium phosphate, Mg₅(PO₄)₂, will contain 0.25 mole of oxygen atoms? [2006]
    (a) 1.25 × 10⁻² (b) 2.5 × 10⁻² (c) 0.02 (d) 3.125 × 10⁻²
12. Density of a 2.05M solution of acetic acid in water is 1.02 g/mL. The molality of the solution is [2006]
    (a) 2.28 mol kg⁻¹ (b) 0.44 mol kg⁻¹ (c) 1.14 mol kg⁻¹ (d) 3.28 mol kg⁻¹
13. The density (in g mL⁻¹) of a 3.60 M sulphuric acid solution that is 29% H₂SO₄ (molar mass = 98 g mol⁻¹) by mass will be [2007]
    (a) 1.45 (b) 1.64 (c) 1.88 (d) 1.22
14. In the reaction, [2007]
    2Al(s) + 6HCl(aq) → 2Al³⁺(aq) + 6Cl⁻(aq) + 3H₂(g)
    (a) 11.2 L H₂(g) at STP is produced for every mole HCl(aq) consumed
    (b) 6 L HCl(aq) is consumed for every 3 L H₂(g) produced
    (c) 33.6 L H₂(g) is produced regardless of temperature and pressure for every mole Al that reacts
    (d) 67.2 H₂(g) at STP is produced for every mole Al that reacts
15. Consider the following reaction:
    xMnO₄⁻ + yC₂O₄²⁻ + zH⁺ → xMn²⁺ + 2yCO₂ + z₁H₂O
    The value of x, y and z in the reaction are, respectively: [JEE M 2013]
    (a) 5, 2 and 16 (b) 2, 5 and 8 (c) 2, 5 and 16 (d) 5, 2 and 8
16. A gaseous hydrocarbon gives upon combustion 0.72 g of water and 3.08 g of CO₂. The empirical formula of the hydrocarbon is: [JEE M 2013]
    (a) C₂H₄ (b) C₃H₄ (c) C₆H₅ (d) C₇H₈
17. Experimentally it was found that a metal oxide has formula M₉O₉₈. Metal M, present as M²⁺ and M³⁺ in its oxide. Fraction of the metal which exists as M³⁺ would be: [JEE M 2013]
    (a) 7.01% (b) 4.08% (c) 6.05% (d) 5.08%
CHAPTER 2

Structure of Atom

Section-A

A Fill in the Blanks

1. The mass of a hydrogen atom is ............... kg. (1982 - 1 Mark)
2. Isotopes of an element differ in the number of ........... in their nuclei. (1982 - 1 Mark)
3. When there are two electrons in the same orbital, they have ............... spins. (1982 - 1 Mark)
4. Elements of the same mass number but of different atomic numbers are known as .............. (1983 - 1 Mark)
5. The uncertainty principle and the concept of wave nature of matter were proposed by .............. and .............. respectively. (Heisenberg, Schrodinger, Maxwell, de Broglie) (1988 - 1 Mark)
6. The light radiations with discrete quantities of energy are called ............... (1993 - 1 Mark)
7. Wave functions of electrons in atoms and molecules are called ............... (1993 - 1 Mark)
8. The 2px, 2py, and 2pz orbitals of an atom have identical shapes but differ in their ............... (1993 - 1 Mark)
9. The outermost electronic configuration of Cr is ............... (1994 - 1 Mark)

B True / False

1. The outer electronic configuration of the ground state chromium atom is 3d^64s^2. (1982 - 1 Mark)
2. Gamma rays are electromagnetic radiations of wavelengths of 10^{-6} cm to 10^{-5} cm. (1983 - 1 Mark)
3. The energy of the electron in the 3d-orbital is less than that in the 4s-orbital in the hydrogen atom. (1983 - 1 Mark)
4. The electron density in the XY plane in 3d x^2 - y^2 orbital is zero. (1986 - 1 Mark)
5. In a given electric field, β-particles are deflected more than α-particles in spite of α-particles having larger charge. (1993 - 1 Mark)

C MCQs with One Correct Answer

1. The number of neutrons in dipositive zinc ion with mass number 70 is (1979)
   (a) 34  (b) 36  (c) 38  (d) 40
2. Rutherford’s experiment on scattering of α-particles showed for the first time that the atom has (1981 - 1 Mark)
   (a) electrons  (b) protons  (c) nucleus  (d) neutrons
3. Any p-orbital can accommodate upto (1983 - 1 Mark)
   (a) four electrons  (b) six electrons  (c) two electrons with parallel spins  (d) two electrons with opposite spins
4. The principal quantum number of an atom is related to the (1983 - 1 Mark)
   (a) size of the orbital  (b) spin angular momentum  (c) orbital angular momentum  (d) orientation of the orbital in space
5. Rutherford’s scattering experiment is related to the size of the (1983 - 1 Mark)
   (a) nucleus  (b) atom  (c) electron  (d) neutron
6. The increasing order (lowest first) for the values of e/m (charge/mass) for electron (e), proton (p), neutron (n) and alpha particle (α) is : (1984 - 1 Mark)
   (a) e, p, n, α  (b) n, p, e, α  (c) n, p, α, e  (d) n, α, p, e
7. Correct set of four quantum numbers for the valence (outermost) electron of rubidium (Z = 37) is : (1984 - 1 Mark)
   (a) 5, 0, 0, +1/2  (b) 5, 1, 0, +1/2  (c) 5, 1, 1, +1/2  (d) 6, 0, 0, +1/2
8. Which electronic level would allow the hydrogen atom to absorb a photon but not to emit a photon? (1984 - 1 Mark)
   (a) 3s  (b) 2p  (c) 2s  (d) 1s
9. Bohr model can explain:
(a) the spectrum of hydrogen atom only
(b) spectrum of an atom or ion containing one electron only
(c) the spectrum of hydrogen molecule
(d) the solar spectrum

10. The radius of an atomic nucleus is of the order of:
(a) $10^{-10}$ cm  
(b) $10^{-13}$ cm
(c) $10^{-15}$ cm  
(d) $10^{-8}$ cm

11. Electromagnetic radiation with maximum wavelength is:
(a) ultraviolet  
(b) radiowave
(c) X-ray  
(d) infrared

12. Rutherford’s alpha particle scattering experiment eventually led to the conclusion that:
(a) mass and energy are related
(b) electrons occupy space around the nucleus
(c) neutrons are buried deep in the nucleus
(d) the point of impact with matter can be precisely determined.

13. Which one of the following sets of quantum numbers represents an impossible arrangement?:

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<th>$m_s$</th>
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<tr>
<td>d)</td>
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</table>

14. The ratio of the energy of a photon of 2000Å wavelength radiation to that of 4000Å radiation is:
(a) $\frac{1}{4}$  
(b) 4
(c) $\frac{1}{2}$  
(d) 2

15. The triad of nuclei that is isotonic is:

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<th>n=9</th>
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<tr>
<td>b)</td>
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<td>c)</td>
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</tr>
<tr>
<td>d)</td>
<td>C, N, F</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

16. The wavelength of a spectral line for an electronic transition is inversely related to:
(a) the number of electrons undergoing the transition
(b) the nuclear charge of the atom
(c) the difference in the energy of the energy levels involved in the transition
(d) the velocity of the electron undergoing the transition.

17. The orbital angular momentum of an electron in 2s orbital is:
(a) $\frac{1}{2}h$  
(b) Zero
(c) $h$  
(d) $\frac{h}{2\pi}$

18. The outermost electronic configuration of the most electronegative element is:
(a) ns$^2$ np$^3$  
(b) ns$^2$ np$^4$
(c) ns$^2$ np$^5$  
(d) ns$^2$ np$^6$

19. The correct ground state electronic configuration of chromium atom is:
(a) [Ar] 3d$^5$ 4s$^1$  
(b) [Ar] 3d$^4$ 4s$^2$
(c) [Ar] 3d$^6$ 4s$^0$  
(d) [Ar] 4d$^2$ 4s$^1$

20. The correct set of quantum numbers for the unpaired electron of chlorine atom is:

<table>
<thead>
<tr>
<th>n</th>
<th>l</th>
<th>m</th>
</tr>
</thead>
<tbody>
<tr>
<td>a)</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>b)</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>c)</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>d)</td>
<td>3</td>
<td>0</td>
</tr>
</tbody>
</table>

21. Which of the following does not characterise X-rays?
(a) The radiation can ionise gases
(b) It causes ZnS to fluorescence
(c) Deflected by electric and magnetic fields
(d) Have wavelengths shorter than ultraviolet rays

22. Which of the following relates to photons both as wave motion and as a stream of particles?
(a) Interference  
(b) $E = mc^2$
(c) Diffraction  
(d) $E = h\nu$

23. A 3p orbital has:
(a) two non-spherical nodes
(b) two spherical nodes
(c) one spherical & one non-spherical node
(d) one spherical and two non-spherical nodes

24. The orbital angular momentum of an electron in 2s orbital is:
(a) $\frac{1}{2}h$  
(b) Zero
(c) $h$  
(d) $\frac{h}{2\pi}$

25. For a d-electron, the orbital angular momentum is
(a) $\sqrt{6}(h/2\pi)$  
(b) $\sqrt{2}(h/2\pi)$
(c) $(h/2\pi)$  
(d) 2(h/2π)

26. The electrons, identified by quantum numbers n and l, are
(i) n=4, l=1, (ii) n=4, l=0, (iii) n=3, l=2, and (iv) n=3, l=1 can be placed in order of increasing energy, from the lowest to highest, as
(a) (iv)<(ii)<(iii)<(i)  
(b) (ii)<(iv)<(i)<(iii)
(c) (i)<(iii)<(ii)<(iv)  
(d) (iii)<(i)<(iv)<(ii)
27. The number of nodal planes in a $p_z$ orbital is \textbf{(2000S)}
   (a) one (b) two (c) three (d) zero

28. The electronic configuration of an element is $1s^2 \ 2s^2 \ 2p^6 \ 3s^2 \ 3p^6 \ 3d^5 \ 4s^1$. This represents its \textbf{(2000S)}
   (a) excited state (b) ground state (c) cationic form (d) anionic form

29. The wavelength associated with a golf ball weighing 200 g and moving at a speed of 5 m/s is of the order \textbf{(2001S)}
   (a) $10^{-10}$ m (b) $10^{-20}$ m (c) $10^{-30}$ m (d) $10^{-40}$ m

30. The quantum numbers $+\frac{1}{2}$ and $-\frac{1}{2}$ for the electron spin represent \textbf{(2001S)}
   (a) rotation of the electron in clockwise and anticlockwise direction respectively
   (b) rotation of the electron in anticlockwise and clockwise direction respectively
   (c) magnetic moment of the electron pointing up and down respectively
   (d) two quantum mechanical spin states which have no classical analogue

31. Rutherford’s experiment, which established the nuclear model of the atom, used a beam of \textbf{(2002S)}
   (a) $\beta$-particles, which impinged on a metal foil and got absorbed
   (b) $\gamma$-rays, which impinged on a metal foil and ejected electrons
   (c) helium atoms, which impinged on a metal foil and got scattered
   (d) helium nuclei, which impinged on a metal foil and got scattered

32. If the nitrogen atom has electronic configuration $1s^2$, it would have energy lower than that of the normal ground state configuration $1s^2 2s^2 2p^3$, because the electrons would be closer to the nucleus. Yet $1s^2$ is not observed because it violates. \textbf{(2002S)}
   (a) Heisenberg uncertainty principle
   (b) Hund’s rule
   (c) Pauli exclusion principle
   (d) Bohr postulate of stationary orbits

33. The radius of which of the following orbit is same as that of the first Bohr’s orbit of hydrogen atom? \textbf{(2004S)}
   (a) He$^+$ ($n=2$) (b) Li$^{2+}$ ($n=2$) (c) Li$^+$ ($n=3$) (d) Be$^{2+}$ ($n=2$)

34. The number of radial nodes of $3s$ and $2p$ orbitals are respectively \textbf{(2005S)}
   (a) 2, 0 (b) 0, 2 (c) 1, 2 (d) 2, 1

35. Given that the abundances of isotopes $^{54}$Fe, $^{56}$Fe and $^{57}$Fe are 5%, 90% and 5%, respectively, the atomic mass of Fe is \textbf{(2009S)}
   (a) 55.85 (b) 55.95 (c) 55.75 (d) 56.05

36. The kinetic energy of an electron in the second Bohr orbit of a hydrogen atom is $[a_0$ is Bohr radius] \textbf{(2012)}
   (a) $\frac{\hbar^2}{4\pi^2 ma_0^2}$ (b) $\frac{\hbar^2}{16\pi^2 ma_0^2}$
   (c) $\frac{\hbar^2}{32\pi^2 ma_0^2}$ (d) $\frac{\hbar^2}{64\pi^2 ma_0^2}$

37. $P$ is the probability of finding the 1s electron of hydrogen atom in a spherical shell of infinitesimal thickness, $dr$, at a distance $r$ from the nucleus. The volume of this shell is $4\pi r^2 dr$. The qualitative sketch of the dependence of $P$ on $r$ is \textbf{(JEE Adv. 2016)}

D. MCQs with One or More Than One Correct

1. An isotope of $^{76}_{32}$Ge is : \textbf{(1984 - 1 Mark)}
   (a) $^{77}_{32}$Ge (b) $^{77}_{33}$As (c) $^{77}_{34}$Se (d) $^{78}_{34}$Se

2. Many elements have non-integral atomic masses because : \textbf{(1984 - 1 Mark)}
   (a) they have isotopes (b) their isotopes have non-integral masses (c) their isotopes have different masses (d) the constituents, neutrons, protons and electrons, combine to give fractional masses

3. When alpha particles are sent through a thin metal foil, most of them go straight through the foil because : \textbf{(1984 - 1 Mark)}
   (a) alpha particles are much heavier than electrons (b) alpha particles are positively charged (c) most part of the atom is empty space (d) alpha particle move with high velocity
4. The sum of the number of neutrons and protons in the isotope of hydrogen is: \(1986 - 1 \text{ Mark}\)
   (a) 6 (b) 2 (c) 4 (d) 3

5. The energy of an electron in the first Bohr orbit of H atom is \(-13.6 \text{ eV}\). The possible energy value(s) of the excited state(s) for electrons in Bohr orbits of hydrogen is (are) \(1986 - 2 \text{ Marks}\)
   (a) \(-3.4 \text{ eV}\) (b) \(-4.2 \text{ eV}\) (c) \(-6.8 \text{ eV}\) (d) \(-7.5 \text{ eV}\)

6. Which of the following statement(s) is (are) correct? \(1986 - 2 \text{ Marks}\)
   (a) The electronic configuration of Cr is \([Ar] 3d^3 4s^1\). (Atomic Number of Cr = 24)
   (b) The magnetic quantum number may have a negative value.
   (c) In silver atom, 23 electrons have a spin of one type and 24 of the opposite type. (Atomic Number of Ag = 47)
   (d) The oxidation state of nitrogen in HN\(_3\) is \(-3\).

7. Decrease in atomic number is observed during \(1986 - 2 \text{ Marks}\)
   (a) alpha emission (b) beta emission (c) positron emission (d) electron capture.

8. Ground state electronic configuration of nitrogen atom can be represented by \(1999 - 3 \text{ Marks}\)
   (a) \(\uparrow \downarrow \downarrow \uparrow \uparrow \uparrow \)
   (b) \(\downarrow \downarrow \uparrow \uparrow \uparrow \)
   (c) \(\uparrow \downarrow \uparrow \uparrow \downarrow \downarrow \)
   (d) \(\uparrow \downarrow \uparrow \downarrow \downarrow \downarrow \)

9. \[E_n = \frac{-21.76 \times 10^{-19}}{n^2} \text{ J}\]. Calculate the longest wavelength of light that will be needed to remove an electron from the third Bohr orbit of the He\(^+\) ion. \(1990 - 3 \text{ Marks}\)

10. What transition in the hydrogen spectrum would have the same wavelength as the Balmer transition \(n = 4\) to \(n = 2\) of He\(^+\) spectrum? \(1993 - 5 \text{ Marks}\)

11. Iodine molecule dissociates into atoms after absorbing light of 4500 Å. If one quantum of radiation is absorbed by each molecule, calculate the kinetic energy of iodine atoms. (Bond energy of I\(_2\) = 240 kJ mol\(^{-1}\)) \(1995 - 2 \text{ Marks}\)

12. Calculate the wave number for the shortest wavelength transition in the Balmer series of atomic hydrogen. \(1996 - 1 \text{ Mark}\)

13. Consider the hydrogen atom to be a proton embedded in a cavity of radius \(a_0\) (Bohr radius) whose charge is neutralised by the addition of an electron to the cavity in vacuum, infinitely slowly. Estimate the average total energy of an electron in its ground state in a hydrogen atom as the work done in the above neutralisation process. Also, if the magnitude of the average kinetic energy is half the magnitude of the average potential energy, find the average potential energy. \(1996 - 2 \text{ Marks}\)

14. Calculate the energy required to excite one litre of hydrogen gas at 1 atm and 298 K to the first excited state of atomic hydrogen. The energy for the dissociation of H\(_2\) bond is 436 kJ mol\(^{-1}\). \(2000 - 4 \text{ Marks}\)
15. Wavelength of high energy transition of H–atoms is 91.2 nm. Calculate the corresponding wavelength of He atoms.

\[ \psi_{2s} = \frac{1}{4\sqrt{2\pi}} \left( \frac{1}{a_0} \right)^{3/2} \left( 2 - \frac{r_0}{a_0} \right) e^{-r_0/a_0} \]

Where \( a_0 \) is Bohr’s radius. If the radial node in 2s be at \( r_0 \), then find \( r_0 \) in terms of \( a_0 \).

16. The Schrödinger wave equation for hydrogen atom is

\[ \psi_{2s} = \frac{1}{4\sqrt{2\pi}} \left( \frac{1}{a_0} \right)^{3/2} \left( 2 - \frac{r_0}{a_0} \right) e^{-r_0/a_0} \]

Where \( a_0 \) is Bohr’s radius. If the radial node in 2s be at \( r_0 \), then find \( r_0 \) in terms of \( a_0 \).

17. A ball of mass 100 g is moving with 100 m/s\(^{-1}\). Find its wavelength.

18. Find the velocity (m/s\(^{-1}\)) of electron in first Bohr’s orbit of radius \( a_0 \). Also find the de Broglie’s wavelength (in m). Find the orbital angular momentum of 2p orbital of hydrogen atom in units of \( h/2\pi \).

**F** Match the Following

Each question contains statements given in two columns, which have to be matched. The statements in Column-I are labelled A, B, C and D, while the statements in Column-II are labelled p, q, r and s. Any given statement in Column-I can have correct matching with ONE OR MORE statement(s) in Column-II. The appropriate bubbles corresponding to the answers to these questions have to be darkened as illustrated in the following example:

If the correct matches are A-p, s and t; B-q and r; C-p and q; and D-s then the correct darkening of bubbles will look like the given.

1. According to Bohr’s theory,
   \[ E_n = \text{Total energy} \]
   \[ K_n = \text{Kinetic energy} \]
   \[ V_n = \text{Potential energy} \]
   \[ r_n = \text{Radius of } n\text{th orbit} \]

Match the following:

<table>
<thead>
<tr>
<th>Column I</th>
<th>Column II</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A) ( V_n / K_n )</td>
<td>p</td>
</tr>
<tr>
<td>(B) If radius of ( n\text{th orbit} ) ( \propto E_n^x ) ( x = ? )</td>
<td>q</td>
</tr>
<tr>
<td>(C) Angular momentum in lowest orbital</td>
<td>r</td>
</tr>
<tr>
<td>(D) ( \frac{1}{r_n} \propto Z^y ) ( y = ? )</td>
<td>s</td>
</tr>
</tbody>
</table>

2. Match the entries in Column I with the correctly related quantum number(s) in Column II. Indicate your answer by darkening the appropriate bubbles of the 4 × 4 matrix given in the ORS

<table>
<thead>
<tr>
<th>Column I</th>
<th>Column II</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A) Orbital angular momentum of the electron in a hydrogen-like atomic orbital</td>
<td>(p) Principal quantum number</td>
</tr>
<tr>
<td>(B) A hydrogen-like one-electron wave function obeying Pauli principle</td>
<td>(q) Azimuthal quantum number</td>
</tr>
<tr>
<td>(C) Shape, size and orientation of hydrogen-like atomic orbitals</td>
<td>(r) Magnetic quantum number</td>
</tr>
<tr>
<td>(D) Probability density of electron at the nucleus in hydrogen-like atom</td>
<td>(s) Electron spin quantum number</td>
</tr>
</tbody>
</table>

**G** Comprehension Based Questions

The hydrogen-like species Li\(^{2+}\) is in a spherically symmetric state \( S_1 \) with one radial node. Upon absorbing light the ion undergoes transition to a state \( S_2 \). The state \( S_2 \) has one radial node and its energy is equal to the ground state energy of the hydrogen atom.

1. The state \( S_1 \) is:
   (a) 1s \quad (b) 2s \quad (c) 2p \quad (d) 3s

2. Energy of the state \( S_1 \) in units of the hydrogen atom ground state energy is:
   (a) 0.75 \quad (b) 1.50 \quad (c) 2.25 \quad (d) 4.50

**H** Assertion & Reason Type Questions

1. Assertion: Nuclide \( ^{30}_{13} \text{Al} \) is less stable than \( ^{40}_{20} \text{Ca} \)

Reason: Nuclides having odd number of protons and neutrons are generally unstable.

(a) If both assertion and reason are correct, and reason is the correct explanation of the assertion.

(b) If both assertion and reason are correct, but reason is not the correct explanation of the assertion.
(c) If assertion is correct but reason is incorrect.
(d) If assertion is incorrect but reason is correct.

2. This question contains STATEMENT-1 (Assertion) and STATEMENT-2 (Reason) and has 4 choices (a), (b), (c) and (d) out of which ONLY ONE is correct.

**STATEMENT-1**: Band gap in germanium is small. because **STATEMENT-2**: The energy gap of each germanium atomic energy level is infinitesimally small. (2007)

(a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1
(b) Statement-1 is True, Statement-2 is True; Statement-2 is not a correct explanation for Statement-1
(c) Statement-1 is True, Statement-2 is False
(d) Statement-1 is False, Statement-2 is True

3. **STATEMENT-1**: The plot of atomic number (y-axis) versus number of neutrons (x-axis) for stable nuclei shows a curvature towards x-axis from the line of 45° slope as the atomic number is increased.

**STATEMENT-2**: Proton-proton electrostatic repulsions begin to overcome attractive forces involving protons and neutrons in heavier nuclides. (2008)

(a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
(b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.
(c) Statement-1 is True, Statement-2 is False
(d) Statement-1 is False, Statement-2 is True

---

### Section-B

**JEE Main / AIEEE**

1. In a hydrogen atom, if energy of an electron in ground state is 13.6. ev, then that in the 2\textsuperscript{nd} excited state is [2002]

(a) 1.51 eV  
(b) 3.4 eV  
(c) 6.04 eV  
(d) 13.6 eV.

2. Uncertainty in position of a minute particle of mass 25 g in space is 10\textsuperscript{-5} m. What is the uncertainty in its velocity (in m/s\textsuperscript{-1})? \[ h = 6.6 \times 10\textsuperscript{-34} \text{Js} \] [2002]

(a) 2.1 \times 10\textsuperscript{-34}  
(b) 0.5 \times 10\textsuperscript{-34}  
(c) 2.1 \times 10\textsuperscript{-28}  
(d) 0.5 \times 10\textsuperscript{-23}.

3. The number of d-electrons retained in Fe\textsuperscript{2+} (At. no. of Fe = 26) ion is [2003]

(a) 4  
(b) 5  
(c) 6  
(d) 3.

4. The orbital angular momentum for an electron revolving in an orbit is given by \[ \sqrt{l(l+1)} \frac{h}{2\pi} \]. This momentum for an s-electron will be given by [2003]

(a) zero  
(b) \[ \frac{h}{2\pi} \]  
(c) \[ \sqrt{2} \frac{h}{2\pi} \]  
(d) \[ \frac{1}{2} \frac{h}{2\pi} \] .

5. Which one of the following groupings represents a collection of isoelectronic species?(At. nos.: Cs: 55, Br: 35) [2003]

(a) N\textsuperscript{3−}, F\textsuperscript{−}, Na\textsuperscript{+}  
(b) Be, Al\textsuperscript{3+}, Cl\textsuperscript{−}  
(c) Ca\textsuperscript{2+}, Cs\textsuperscript{+}, Br  
(d) Na\textsuperscript{+}, Ca\textsuperscript{2+}, Mg\textsuperscript{2+}

6. In Bohr series of lines of hydrogen spectrum, the third line from the red end corresponds to which one of the following inter-orbit jumps of the electron for Bohr orbits in an atom of hydrogen [2003]

(a) 5 → 2  
(b) 4 → 1  
(c) 2 → 5  
(d) 3 → 2.

7. The de Broglie wavelength of a tennis ball of mass 60 g moving with a velocity of 10 metres per second is approximately [2003]

(a) 10\textsuperscript{-31} metres  
(b) 10\textsuperscript{-16} metres  
(c) 10\textsuperscript{-25} metres  
(d) 10\textsuperscript{-33} metres

Planck’s constant, \( h = 6.63 \times 10\textsuperscript{-34} \text{Js} \)

8. Which of the following sets of quantum numbers is correct for an electron in 4f orbital? [2004]

(a) \( n = 4, \ell = 3, m = +1, s = +\frac{1}{2} \)  
(b) \( n = 4, \ell = 4, m = -4, s = -\frac{1}{2} \)  
(c) \( n = 4, \ell = 3, m = +4, s = +\frac{1}{2} \)  
(d) \( n = 3, \ell = 2, m = -2, s = +\frac{1}{2} \)
9. Consider the ground state of Cr atom (X = 24). The number of electrons with the azimuthal quantum numbers, \( \ell = 1 \) and \( \ell = 2 \) are, respectively \[2004\]
(a) 16 and 4  (b) 12 and 5  (c) 12 and 4  (d) 16 and 5

10. The wavelength of the radiation emitted, when in a hydrogen atom electron falls from infinity to stationary state 1, would be (Rydberg constant = \( 1.097 \times 10^7 \) m\(^{-1} \)) \[2004\]
(a) 406 nm  (b) 192 nm  (c) 91 nm  (d) \( 9.1 \times 10^{-8} \) nm

11. Which one of the following sets of ions represents the collection of isoelectronic species? \[2004\]
(a) \( K^+, Cl^-, Mg^{2+}, Sc^{3+} \)  (b) \( Na^+, Ca^{2+}, Sc^{3+}, F^- \)  (c) \( K^+, Ca^{2+}, Sc^{3+}, Cl^- \)  (d) \( Na^+, Mg^{2+}, Al^{3+}, Cl^- \)  
(Atomic nos. : F = 9, Cl = 17, Na = 11, Mg = 12, Al = 13, K = 19, Ca = 20, Sc = 21)

12. In a multi-electron atom, which of the following orbitals described by the three quantum numbers will have the same energy in the absence of magnetic and electric fields? \[2005\]
(A) \( n = 1, l = 0, m = 0 \)  (B) \( n = 2, l = 0, m = 0 \)  (C) \( n = 2, l = 1, m = 1 \)  (D) \( n = 3, l = 2, m = 0 \)  
(a) (D) and (E)  (b) (C) and (D)  (c) (B) and (C)  (d) (A) and (B)

13. Of the following sets which one does NOT contain isoelectronic species? \[2005\]
(a) \( BO_3^{3-}, CO_3^{2-}, NO_3^- \)  (b) \( SO_3^{2-}, CO_3^{2-}, NO_3^- \)  (c) \( CN^-, N_2, C_2^{-} \)  (d) \( PO_4^{3-}, SO_4^{2-}, ClO_4^{-} \)

14. According to Bohr's theory, the angular momentum of an electron in 5th orbit is \[2006\]
(a) \( 10 \ h / \pi \)  (b) \( 2.5 \ h / \pi \)  (c) \( 25 \ h / \pi \)  (d) \( 1.0 \ h / \pi \)

15. Uncertainty in the position of an electron (mass = \( 9.1 \times 10^{-31} \) kg) moving with a velocity 300 ms\(^{-1} \), accurate up to 0.001% will be \[2006\]
(a) \( 1.92 \times 10^{-2} \) m  (b) \( 3.84 \times 10^{-2} \) m  (c) \( 19.2 \times 10^{-2} \) m  (d) \( 5.76 \times 10^{-2} \) m  
\( (h = 6.63 \times 10^{-34} \text{Js}) \)

16. Which one of the following sets of ions represents a collection of isoelectronic species? \[2006\]
(a) \( N^3-, O^2-, F^-, S^2- \)  (b) \( Li^+, Na^+, Mg^{2+}, Ca^{2+} \)  (c) \( K^+, Cl^-, Ca^{2+}, Se^{3+} \)  (d) \( Ba^{2+}, Sr^{2+}, K^+, Ca^{2+} \)

17. Which of the following sets of quantum numbers represents the highest energy of an atom? \[2007\]
(a) \( n = 3, l = 0, m = 0, s = +1/2 \)  (b) \( n = 3, l = 1, m = 1, s = +1/2 \)  (c) \( n = 3, l = 2, m = 1, s = +1/2 \)  (d) \( n = 4, l = 0, m = 0, s = +1/2 \)

18. Which one of the following constitutes a group of the isoelectronic species? \[2008\]
(a) \( C_2^{2-}, O_2^-, CO, NO \)  (b) \( NO^+, C_2^{2-}, CN^-, N_2 \)  (c) \( CN^-, N_2, O_2^{2-}, C_2^{2-} \)  (d) \( N_2, O_2^-, NO^+, CO \)

19. The ionization enthalpy of hydrogen atom is \( 1.312 \times 10^6 \) J mol\(^{-1} \). The energy required to excite the electron in the atom from \( n = 1 \) to \( n = 2 \) is \[2008\]
(a) \( 8.51 \times 10^5 \) J mol\(^{-1} \)  (b) \( 6.56 \times 10^5 \) J mol\(^{-1} \)  (c) \( 7.56 \times 10^5 \) J mol\(^{-1} \)  (d) \( 9.84 \times 10^5 \) J mol\(^{-1} \)

20. Calculate the wavelength (in nanometer) associated with a proton moving at 1.0 \times 10^3 m s\(^{-1} \).
(Mass of proton = \( 1.67 \times 10^{-27} \) kg and \( h = 6.63 \times 10^{-34} \) Js) \[2009\]
(a) 0.40 nm  (b) 2.5 nm  (c) 14.0 nm  (d) 0.32 nm

21. In an atom, an electron is moving with a speed of 600 m/s with an accuracy of 0.005%. Certainty with which the position of the electron can be located is \( (h = 6.6 \times 10^{-34} \) kg m\(^2\)s\(^{-1} \), mass of electron, \( e_m = 9.1 \times 10^{-31} \) kg) \[2009\]
(a) \( 5.10 \times 10^{-3} \) m  (b) \( 1.92 \times 10^{-3} \) m  (c) \( 3.84 \times 10^{-3} \) m  (d) \( 1.52 \times 10^{-4} \) m

22. The energy required to break one mole of Cl – Cl bonds in Cl\(_2\) is 242 kJ mol\(^{-1} \). The longest wavelength of light capable of breaking a single Cl – Cl bond is \[2010\]
\( c = 3 \times 10^8 \) m s\(^{-1} \) and \( N_A = 6.02 \times 10^{23} \) mol\(^{-1} \).
(a) \( 594 \) nm  (b) \( 640 \) nm  (c) \( 700 \) nm  (d) \( 494 \) nm

23. Ionisation energy of He\(^+\) is 19.6 \times 10^{-18} \) J atom\(^{-1} \). The energy of the first stationary state (\( n = 1 \)) of Li\(^{2+}\) is \[2010\]
(a) \( 4.41 \times 10^{-16} \) J atom\(^{-1} \)  (b) \( -4.41 \times 10^{-17} \) J atom\(^{-1} \)  (c) \( -2.2 \times 10^{-15} \) J atom\(^{-1} \)  (d) \( 8.82 \times 10^{-17} \) J atom\(^{-1} \)

24. A gas absorbs a photon of 355 nm and emits at two wavelengths. If one of the emissions is at 680 nm, the other is at: \[2011\]
(a) \( 1035 \) nm  (b) \( 325 \) nm  (c) \( 743 \) nm  (d) \( 518 \) nm
25. The electrons identified by quantum numbers \( n \) and \( \ell \) :

(A) \( n = 4, \ell = 1 \)  
(B) \( n = 4, \ell = 0 \)  
(C) \( n = 3, \ell = 2 \)  
(D) \( n = 3, \ell = 1 \)

can be placed in order of increasing energy as: [2012]

(a) \((C) < (D) < (B) < (A)\)
(b) \((D) < (B) < (C) < (A)\)
(c) \((B) < (D) < (A) < (C)\)
(d) \((A) < (C) < (B) < (D)\)

26. Energy of an electron is given by \( E = -2.178 \times 10^{-18} \left( \frac{Z^2}{n^2} \right) \). Wavelength of light required to excite an electron in an hydrogen atom from level \( n = 1 \) to \( n = 2 \) will be: [JEE M 2013]

(h = 6.62 \times 10^{-34} \text{ Js and } c = 3.0 \times 10^8 \text{ ms}^{-1})

(a) \( 1.214 \times 10^{-7} \text{ m} \)
(b) \( 2.816 \times 10^{-7} \text{ m} \)
(c) \( 6.500 \times 10^{-7} \text{ m} \)
(d) \( 8.500 \times 10^{-7} \text{ m} \)

27. The correct set of four quantum numbers for the valence electrons of rubidium atom (\( Z = 37 \)) is: [JEE M 2014]

\begin{align*}
\text{(a)} & \quad 5,0,0,\frac{1}{2} \\
\text{(b)} & \quad 5,1,0,\frac{1}{2} \\
\text{(c)} & \quad 5,1,1,\frac{1}{2} \\
\text{(d)} & \quad 5,0,1,\frac{1}{2}
\end{align*}

28. Which of the following is the energy of a possible excited state of hydrogen? [JEE M 2015]

(a) \(-3.4 \text{ eV}\)
(b) \(+6.8 \text{ eV}\)
(c) \(+13.6 \text{ eV}\)
(d) \(-6.8 \text{ eV}\)

29. A stream of electrons from a heated filaments was passed two charged plates kept at a potential difference \( V \) esu. If \( e \) and \( m \) are charge and mass of an electron, respectively, then the value of \( \frac{h}{\lambda} \) (where \( \lambda \) is wavelength associated with electron wave) is given by: [JEE M 2016]

\begin{align*}
\text{(a)} & \quad \sqrt{meV} \\
\text{(b)} & \quad \sqrt{2meV} \\
\text{(c)} & \quad meV \\
\text{(d)} & \quad 2meV
\end{align*}
CHAPTER 3
Classification of Elements and Periodicity in Properties

Section-A

A Fill in the Blanks

1. The energy released when an electron is added to a neutral gaseous atom is called ........... of the atom.  (1982 - 1 Mark)
2. On Mulliken scale, the average of ionization potential and electron affinity is known as ...............  (1985 - 1 Mark)

B True / False

1. In group IA, of alkali metals, the ionisation potential decreases on moving down the group. Therefore, lithium is a strongest reducing agent.  (1987 - 1 Mark)
2. The decreasing order of electron affinity of F, Cl, Br is F > Cl > Br.  (1993 - 1 Mark)
3. The basic nature of the hydroxides of group 13 (Gr. III B) decreases progressively down the group. (1993 - 1 Mark)

C MCQs with One Correct Answer

1. The correct order of second ionisation potential of carbon, nitrogen, oxygen and fluorine is  (1981 - 1 Mark)
   (a) C > N > O > F  (b) O > N > F > C
   (c) O > F > N > C  (d) F > O > N > C
2. The element with the highest first ionization potential is  (1982 - 1 Mark)
   (a) boron  (b) carbon
   (c) nitrogen  (d) oxygen
3. The first ionisation potential in electron volts of nitrogen and oxygen atoms are respectively given by  (1987 - 1 Mark)
   (a) 14.6, 13.6  (b) 13.6, 14.6
   (c) 13.6, 13.6  (d) 14.6, 14.6
4. Atomic radii of fluorine and neon in Ångstrom units are respectively given by  (1987 - 1 Mark)
   (a) 0.72, 1.60  (b) 1.60, 1.60
   (c) 0.72, 0.72  (d) None of these values
5. The electronegativity of the following elements increases in the order  (1987 - 1 Mark)
   (a) C, N, Si, P  (b) N, Si, C, P
   (c) Si, P, C, N  (d) P, Si, N, C
6. The first ionisation potential of Na, Mg, Al and Si are in the order  (1988 - 1 Mark)
   (a) Na < Mg > Al < Si  (b) Na > Mg > Al > Si
   (c) Na < Mg < Al < Si  (d) Na > Mg > Al < Si
7. Which one of the following is the strongest base?  (1989 - 1 Mark)
   (a) AsH₃  (b) NH₃
   (c) PH₃  (d) SbH₃
8. Which one of the following is the smallest in size?  (1989 - 1 Mark)
   (a) N³⁻  (b) O²⁻
   (c) F⁻  (d) Na⁺
9. Amongst the following elements (whose electronic configurations are given below), the one having the highest ionization energy is :  (1990 - 1 Mark)
   (a) [Ne] 3s²3p¹  (b) [Ne] 3s²3p³
   (c) [Ne] 3s²3p²  (d) [Ne] 3d⁰4s²⁴p³
10. The statement that is not correct for the periodic classification of element is  (1992 - 1 Mark)
    (a) The properties of elements are the periodic functions of their atomic numbers
    (b) Non-metallic elements are lesser in number than metallic elements
    (c) The first ionisation energies of elements along a period do not vary in a regular manner with increase in atomic number
    (d) For transition elements the d-subshells are filled with electrons monotonically with increase in atomic number
    (a) Sn  (b) Pb
    (c) Fe  (d) Ag
12. Which of the following has the maximum number of unpaired electrons? (1996 - 1 Mark)
   (a) Mg$^{2+}$  (b) Ti$^{3+}$  (c) V$^{3+}$  (d) Fe$^{2+}$

13. The correct order of radii is (2000S)
   (a) N < Be < B  (b) F$^- < O^{2-} < N^{3-}$
   (c) Na < Li < K  (d) Fe$^{3+} < Fe^{2+} < Fe^{4+}$

14. The correct order of acidic strength is (2000S)
   (a) Cl$_2$O$_7$ > SO$_2$ > P$_2$O$_5$  (b) CO$_2$ > N$_2$O$_5$ > SO$_3$
   (c) Na$_2$O > MgO > Al$_2$O$_3$  (d) K$_2$O > CaO > MgO

15. Amongst H$_2$O, H$_2$S, H$_2$Se and H$_2$Te, the one with the highest boiling point is (2000S)
   (a) H$_2$O because of hydrogen bonding
   (b) H$_2$Te because of higher molecular weight
   (c) H$_2$S because of hydrogen bonding
   (d) H$_2$Se because of lower molecular weight

16. Identify the correct order of acidic strengths of CO$_2$, CuO, CaO, H$_2$O (2002S)
   (a) CaO < CuO < H$_2$O < CO$_2$  (b) H$_2$O < CuO < CaO < CO$_2$
   (c) CaO < H$_2$O < CuO < CO$_2$  (d) H$_2$O < CO$_2$ < CuO < CaO

D  MCQs with One or More Than One Correct

1. The statements that are true for the long form of the periodic table are: (1988 - 1 Mark)
   (a) it reflects the sequence of filling the electrons in the order of sub-energy level s, p, d and f.
   (b) it helps to predict the stable valency states of the elements
   (c) it reflects trends in physical and chemical properties of the elements
   (d) it helps to predict the relative ionicity of the bond between any two elements.

2. Sodium sulphate is soluble in water whereas barium sulphate is sparingly soluble because: (1989 - 1 Mark)
   (a) the hydration energy of sodium sulphate is more than its lattice energy
   (b) the lattice energy of barium sulphate is more than its hydration energy
   (c) the lattice energy has no role to play in solubility
   (d) the hydration energy of sodium sulphate is less than its lattice energy.

3. Ionic radii of (1999 - 3 Marks)
   (a) Ti$^{4+} <$ Mn$^{7+}$  (b) $^{35}$Cl$^- < $ $^{37}$Cl$^-$
   (c) K$^+ >$ Cl$^-$  (d) P$^{3+} >$ P$^{5+}$

E  Subjective Problems

1. Arrange the following in:
   (i) Decreasing ionic size : Mg$^{2+}$, O$^{2-}$, Na$^+$, F$^-$ (1985 - 1 Mark)
   (ii) Increasing acidic property : ZnO, Na$_2$O$_2$, P$_2$O$_5$, MgO (1985 - 1 Mark)
   (iii) Increasing first ionization potential : Mg, Al, Si, Na (1985 - 1 Mark)
   (iv) Increasing size : Cl$^-$, S$^{2-}$, Ca$^{2+}$, Ar (1986 - 1 Mark)
   (v) Increasing order of ionic size : N$^{3-}$, Na$^+$, F$^-$, O$^{2-}$, Mg$^{2+}$ (1991 - 1 Mark)
   (vi) Increasing order of basic character : MgO, SrO, K$_2$O, NiO, Ca$$_2$$O (1991 - 1 Mark)
   (vii) Arrange the following ions in order of their increasing radii : Li$^+$, Mg$^{2+}$, K$^+$, Al$^{3+}$ (1989 - 2 Marks)

2. The first ionization energy of carbon atom is greater than that of boron atom whereas, the reverse is true for the second ionization energy. (1989 - 2 Marks)

H  Assertion & Reason Type Questions

1. Read the following statement and explanation and answer as per the options given below:
   ASSERTION : The first ionization energy of Be is greater than that of B. (2000S)
   REASON : 2p orbital is lower in energy than 2s
   (a) If both assertion and reason are CORRECT, and reason is the CORRECT explanation of the assertion.
   (b) If both assertion and reason are CORRECT, but reason is NOT the CORRECT explanation of the assertion.
   (c) If assertion is CORRECT, but reason is INCORRECT.
   (d) If assertion is INCORRECT, but reason is CORRECT.

I  Integer Value Correct Type

1. Among the following, the number of elements showing only one non-zero oxidation state is: O, Cl, F, N, P, Sn, Ti, Na, Ti (2010)
Classification of Elements and Periodicity in Properties

Section-B

JEE Main / AIEEE

1. According to the Periodic Law of elements, the variation in properties of elements is related to their
(a) nuclear masses
(b) atomic numbers
(c) nuclear neutron-proton number ratios
(d) atomic masses

2. Which one of the following is an amphoteric oxide?
(a) Na₂O
(b) SO₂
(c) B₂O₃
(d) ZnO

3. Which one of the following ions has the highest value of ionic radius?
(a) O²⁻
(b) B³⁺
(c) Li⁺
(d) F⁻

4. Among Al₂O₃, SiO₂, P₂O₅ and SO₂ the correct order of acid strength is
(a) Al₂O₃ < SiO₂ < P₂O₅ < SO₂
(b) SiO₂ < Al₂O₃ < P₂O₅ < SO₂
(c) SO₂ < P₂O₅ < SiO₂ < Al₂O₃
(d) Al₂O₃ < SiO₂ < P₂O₅ < SO₂

5. The formation of the oxide ion O²⁻(g) requires first an exothermic and then an endothermic step as shown below
O₂(g) + e⁻ = O²⁻(g) \[ ΔH^o = -142 \text{ kJmol}^{-1} \]
O²⁻(g) + e⁻ = O²⁻(g) \[ ΔH^o = 844 \text{ kJmol}^{-1} \]
This is because
(a) O²⁻ ion will tend to resist the addition of another electron
(b) Oxygen has high electron affinity
(c) Oxygen is more electronegative
(d) O²⁻ ion has comparatively larger size than oxygen atom

6. Which of the following oxides is amphoteric in character?
(a) SnO₂
(b) SiO₂
(c) CO₂
(d) CaO

7. In which of the following arrangements, the order is NOT according to the property indicated against it?
(a) Li < Na < K < Rb:
Increasing metallic radius
(b) I < Br < F < Cl:
Increasing electron gain enthalpy (with negative sign)
(c) B < C < N < O:
Increasing first ionization enthalpy
(d) Al³⁺ < Mg²⁺ < Na⁺ < F⁻:
Increasing ionic size

8. Following statements regarding the periodic trends of chemical reactivity of the alkali metals and the halogens are given. Which of these statements gives the correct picture?
(a) Chemical reactivity increases with increase in atomic number down the group in both the alkali metals and halogens
(b) In alkali metals the reactivity increases but in the halogens it decreases with increase in atomic number down the group
(c) The reactivity decreases in the alkali metals but increases in the halogens with increase in atomic number down the group
(d) In both the alkali metals and the halogens the chemical reactivity decreases with increase in atomic number down the group

9. In which of the following arrangements, the sequence is not strictly according to the property written against it?
(a) HF < HCl < HBr, HI: increasing acid strength
(b) NH₃ < PH₃ < AsH₃ < SbH₃: increasing basic strength
(c) B < C < O < N: increasing first ionization enthalpy
(d) CO₂ < SiO₂ < SnO₂ < PbO₂: increasing oxidising power

10. The correct sequence which shows decreasing order of the ionic radii of the elements is
(a) Al³⁺ > Mg²⁺ > Na⁺ > F⁻ > O²⁻
(b) Na⁺ > Mg²⁺ > Al³⁺ > O²⁻ > F⁻
(c) Na⁺ > F⁻ > Mg²⁺ > O²⁻ > Al³⁺
(d) O²⁻ > F⁻ > Na⁺ > Mg²⁺ > Al³⁺

11. Which one of the following orders presents the correct sequence of the increasing basic nature of the given oxides?
(a) Al₂O₃ < MgO < Na₂O < K₂O
(b) MgO < K₂O < Al₂O₃ < Na₂O
(c) Na₂O < K₂O < MgO < Al₂O₃
(d) K₂O < Na₂O < Al₂O₃ < MgO

12. The increasing order of the ionic radii of the given iso-electronic species is:
(a) Cl⁻, Ca²⁺, K⁺, S²⁻
(b) S²⁻, Cl⁻, Ca²⁺, K⁺
(c) Ca²⁺, K⁺, Cl⁻, S²⁻
(d) K⁺, S²⁻, Ca²⁺, Cl⁻
13. Which of the following represents the correct order of increasing first ionization enthalpy for Ca, Ba, S, Se and Ar?

(a) Ca < S < Ba < Se < Ar  
(b) S < Se < Ca < Ba < Ar  
(c) Ba < Ca < Se < S < Ar  
(d) Ca < Ba < S < Se < Ar  

[JEE M 2013]

14. The first ionisation potential of Na is 5.1 eV. The value of electron gain enthalpy of Na⁺ will be:

(a) 1.71, 1.40 and 1.36  
(b) 1.71, 1.36 and 1.40  
(c) 1.36, 1.40 and 1.71  
(d) 1.36, 1.71 and 1.40  

[JEE M 2013]

15. The ionic radii (in Å) of N³⁻, O²⁻ and F⁻ are respectively:

(a) 2.55 eV  
(b) 10.2 eV  
(c) 10.2 eV  
(d) 2.55 eV  

[JEE M 2015]
CHAPTER 4

Chemical Bonding and Molecular Structure

Section-A

A Fill in the Blanks

1. The angle between two covalent bonds is maximum in .......... . (CH₄, H₂O, CO₂) (1981 - 1 Mark)

2. Pair of molecules which forms strongest intermolecular hydrogen bond is .......... .
   \[ \text{SiH}_4 \text{ and SiF}_4, \text{CH}_3—\text{C}—\text{CH}_3 \text{ and CHCl}_3, \text{H}—\text{C}—\text{OH} \]
   and \[ \text{CH}_3—\text{C}—\text{OH} \] (1981 - 1 Mark)

3. There are .......... π bonds in a nitrogen molecule. (1982 - 1 Mark)

4. .......... hybrid orbitals of nitrogen atom are involved in the formation of ammonium ion. (1982 - 1 Mark)

5. The shape of \[ \text{[CH}_3]^+ \] is .......... . (1990 - 1 Mark)

6. The two types of bonds present in \[ \text{B}_2\text{H}_6 \] are covalent and ....... . (1994 - 1 Mark)

7. When \[ \text{N}_2 \] goes to \[ \text{N}_2^2- \], the N–N bond distance ..., and when \[ \text{O}_2 \] goes to \[ \text{O}_2^+ \] the O–O bond distance ....... . (1996 - 1 Mark)

B True / False

1. Linear overlap of two atomic p-orbitals leads to a sigma bond. (1983 - 1 Mark)

2. All molecules with polar bonds have dipole moment. (1985 - ½ Mark)

3. SnCl₂ is a non-linear molecule. (1985 - ½ Mark)

4. In benzene, carbon uses all the three p-orbitals for hybridisation. (1987 - 1 Mark)

5. \[ sp^2 \] hybrid orbitals have equal s and p character. (1987 - 1 Mark)

6. The presence of polar bonds in a polyatomic molecule suggests that the molecule has non-zero dipole moment. (1990 - 1 Mark)

7. The dipole moment of \[ \text{CH}_3\text{F} \] is greater than that of \[ \text{CH}_3\text{Cl} \]. (1993 - 1 Mark)

C MCQs with One Correct Answer

1. The compound which contains both ionic and covalent bonds is (1979)
   (a) \[ \text{CH}_4 \] (b) \[ \text{H}_2 \] (c) \[ \text{KCN} \] (d) \[ \text{KCl} \]

2. The octet rule is not valid for the molecule (1979)
   (a) \[ \text{CO}_2 \] (b) \[ \text{H}_2\text{O} \] (c) \[ \text{O}_2 \] (d) \[ \text{CO} \]

3. Element X is strongly electropositive and element Y is strongly electronegative. Both are univalent. The compound formed would be (1980)
   (a) \[ X^+Y^- \] (b) \[ X^+Y^+ \] (c) \[ X—Y \] (d) \[ X \rightarrow Y \]

4. Which of the following compounds are covalent? (1980)
   (a) \[ \text{H}_2 \] (b) \[ \text{CaO} \] (c) \[ \text{KCl} \] (d) \[ \text{Na}_2\text{S} \]

5. The total number of electrons that take part in forming the bond in \[ \text{N}_2 \] is (1980)
   (a) 2 (b) 4 (c) 6 (d) 10

6. Which of the following is soluble in water (1980)
   (a) \[ \text{CS}_2 \] (b) \[ \text{C}_2\text{H}_5\text{OH} \] (c) \[ \text{CCl}_4 \] (d) \[ \text{CHCl}_3 \]

7. If a molecule \[ \text{MX}_3 \] has zero dipole moment, the sigma bonding orbitals used by M (atomic number < 21) are (1981 - 1 Mark)
   (a) pure \[ p \] (b) \[ sp \] hybrid (c) \[ sp^2 \] hybrid (d) \[ sp^3 \] hybrid

8. The ion that is isoelectronic with \[ \text{CO} \] is (1982 - 1 Mark)
   (a) \[ \text{CN}^- \] (b) \[ \text{O}_2^+ \] (c) \[ \text{O}_2^- \] (d) \[ \text{N}_2^+ \]

9. Among the following, the molecule that is linear is (1982 - 1 Mark)
   (a) \[ \text{CO}_2 \] (b) \[ \text{NO}_2 \] (c) \[ \text{SO}_2 \] (d) \[ \text{ClO}_2 \]

10. The compound with no dipole moment is (1982 - 1 Mark)
    (a) methyl chloride (b) carbon tetrachloride (c) methylene chloride (d) chloroform

11. Carbon tetrachloride has no net dipole moment because of (1983 - 1 Mark)
    (a) its planar structure (b) its regular tetrahedral structure (c) similar sizes of carbon and chlorine (d) similar electron affinities of carbon and chlorine

12. Which one among the following does not have the hydrogen bond? (1983 - 1 Mark)
    (a) phenol (b) liquid \[ \text{NH}_3 \] (c) water (d) liquid \[ \text{HCl} \]

13. The types of bonds present in \[ \text{CuSO}_4 \cdot 5\text{H}_2\text{O} \] are only (1983 - 1 Mark)
    (a) electrovalent and covalent (b) electrovalent and coordinate covalent (c) electrovalent, covalent and coordinate covalent (d) covalent and coordinate covalent
14. On hybridization of one s and one p orbitals we get:
   (a) two mutually perpendicular orbitals (1984 - 1 Mark)
   (b) two orbitals at 180°
   (c) four orbitals directed tetrahedrally
   (d) three orbitals in a plane

15. The molecule having one unpaired electron is:
   (1985 - 1 Mark)
   (a) NO  (b) CO  (c) CN−  (d) O2

16. The bond between two identical non-metal atoms has a pair of electrons:
   (1986 - 1 Mark)
   (a) unequally shared between the two
   (b) transferred fully from one atom to another
   (c) with identical spins
   (d) equally shared between them

17. The hydrogen bond is strongest in:
   (1986 - 1 Mark)
   (a) O−H…S  (b) S−H…O
   (c) F−H…F  (d) F−H…O

18. The hybridization of sulphur in sulphur dioxide is:
   (1986 - 1 Mark)
   (a) sp  (b) sp3  (c) sp2  (d) dsp2

19. Hydrogen bonding is maximum in:
   (1987 - 1 Mark)
   (a) Ethanol  (b) Diethyl ether
   (c) Ethyl chloride  (d) Triethylamine

20. The species in which the central atom uses sp2 hybrid orbitals in its bonding is:
   (1988 - 1 Mark)
   (a) PH3  (b) NH3  (c) CH3+  (d) SbH3

21. The molecule that has linear structure is:
   (1988 - 1 Mark)
   (a) CO2  (b) NO2  (c) SO2  (d) SiO2

22. The molecule which has zero dipole moment is:
   (1989 - 1 Mark)
   (a) CH2Cl2  (b) BF3
   (c) NF3  (d) ClO2

23. The molecule which has pyramidal shape is:
   (1989 - 1 Mark)
   (a) PCl3  (b) SO3
   (c) CO32−  (d) NO3−

24. The compound in which C uses its sp3 hybrid orbitals for bond formation is:
   (1989 - 1 Mark)
   (a) HCOOH  (b) (H2N)2CO
   (c) (CH3)2COH  (d) CH3CHO

25. Which of the following is paramagnetic? (1989 - 1 Mark)
   (a) O2−  (b) CN−  (c) CO  (d) NO+

26. The type of hybrid orbitals used by the chlorine atom in ClO2− is:
   (1992 - 1 Mark)
   (a) sp3  (b) sp2
   (c) sp  (d) none of these

27. The maximum possible number of hydrogen bonds a water molecule can form is
   (1992 - 1 Mark)
   (a) 2  (b) 4  (c) 3  (d) 1

28. The cyanide ion, CN− and N2 are isoelectronic. But in contrast to CN−, N2 is chemically inert, because of
   (1992 - 1 Mark)
   (a) low bond energy  (b) absence of bond polarity

29. Pick out the isoelectronic structures from the following:
   (1993 - 1 Mark)
   I. CH3+  II. H3O+
   III. NH3  IV. CH3
   (a) I and II  (b) III and IV
   (c) I and III  (d) II, III and IV

30. Which one is most ionic? (1995S)
   (a) P2O5  (b) CrO4  (c) MnO  (d) Mn2O7

31. Number of paired electrons in O2 molecule is: (1995S)
   (a) 7  (b) 8  (c) 16  (d) 14

32. Among the following species, identify the isostructural pairs.
   NF3, NO3−, BF3, H3O+, HN3
   (1996 - 1 Mark)
   (a) [NF3, NO3−] and[BF3, H3O+]  
   (b) [NF3, HN3] and[NO3−, BF3]
   (c) [NF3, H3O+] and[NO3−, BF3]
   (d) [NF3, H3O+] and[HN3, BF3]

33. The number and type of bonds between two carbon atoms in CaC2 are:
   (1996 - 1 Mark)
   (a) one sigma (σ) and one pi (π) bonds
   (b) one sigma (σ) and two pi (π) bonds
   (c) one sigma (σ) and one and a half pi (π) bonds
   (d) one sigma (σ) bond.

34. Which contains both polar and non-polar bonds?
   (a) NH4Cl  (b) HCN  
   (c) H2O2  (d) CH4

35. The critical temperature of water is higher than that of O2 because the H2O molecule has
   (1997 - 1 Mark)
   (a) fewer electrons than O2
   (b) two covalent bonds
   (c) V-shape (d) dipole moment.

36. Which one of the following compounds has sp2 hybridization? (1997 - 1 Mark)
   (a) CO2  (b) SO2  (c) N2O  (d) CO

37. The geometry and the type of hybrid orbital present about the central atom in BF3 is
   (1998 - 2 Marks)
   (a) linear, sp  (b) trigonal planar, sp2
   (c) tetrahedral, sp3  (d) pyramidal, sp3.

38. The correct order of increasing C—O bond length of CO, CO32−, CO2 is
   (1999 - 2 Marks)
   (a) CO32− < CO2 < CO  
   (b) CO2 < CO32− < CO
   (c) CO < CO32− < CO2  (d) CO < CO2 < CO32−

39. The geometry of H2S and its dipole moment are
   (1999 - 2 Marks)
   (a) angular and non-zero  (b) angular and zero
   (c) linear and non-zero  (d) linear and zero
40. Molecularshapes of SF₄, CF₃ and XeF₂ are (2000S) 
   (a) the same, with 2, 0 and 1 lone pairs of electrons respectively 
   (b) the same, with 1, 1 and 1 lone pairs of electrons respectively 
   (c) different, with 0, 1 and 2 lone pairs of electrons respectively 
   (d) different, with 1, 0 and 2 lone pairs of electrons respectively

41. The hybridisation of atomic orbitals of nitrogen in NO₂⁻, NO₃⁻ and NH₄⁺ are (2000S) 
   (a) sp, sp³ and sp² respectively 
   (b) sp, sp² and sp³ respectively 
   (c) sp², sp and sp³ respectively 
   (d) sp², sp³ and sp respectively

42. The common features among the species CN⁻, CO and NO⁺ are (2001S) 
   (a) bond order three and isoelectronic 
   (b) bond order three and weak field ligands 
   (c) bond order two and π-acceptors 
   (d) isoelectronic and weak field ligands

43. The correct order of hybridization of the central atom in the following species NH₃, PtCl₄²⁻, PCl₅ and BCl₃ is (2001S) 
   (a) sp², sp³, sp³ and sp² (b) sp³, sp³, sp³, sp² (c) sp³, sp³, sp³, sp² (d) sp³, sp³, sp³, sp³

44. Specify the coordination geometry around and hybridisation of N and B atoms in a : 1 complex of BF₃ and NH₃ 
   (a) N : tetrahedral, sp³; B : tetrahedral, sp³ (2002S) 
   (b) N : pyramidal, sp³; B : pyramidal, sp³ 
   (c) N : pyramidal, sp³; B : planar, sp² 
   (d) N : pyramidal, sp³; B : tetrahedral, sp³

45. Identify the least stable ion amongst the following : (2002S) 
   (a) Li⁺ (b) Be⁺ (c) B⁺ (d) C⁺

46. Which of the following molecular species has unpaired electron(s) ? (2002S) 
   (a) N₂ (b) F₂ (c) O₂⁻ (d) O₂²⁻

47. Which of the following are isoelectronic and isostructural? NO₃⁻, CO₃²⁻, ClO₃⁻, SO₃⁻ (2003S) 
   (a) NO₃⁻, CO₃²⁻ (b) SO₃⁻, NO₃⁻ (c) ClO₃⁻, CO₃²⁻ (d) CO₂⁻, SO₃⁻

48. According to molecular orbital theory which of the following statement about the magnetic character and bond order is correct regarding O₂⁺ (2004S) 
   (a) Paramagnetic and Bond order < O₂ 
   (b) Paramagnetic and Bond order > O₂ 
   (c) Diamagnetic and Bond order < O₂ 
   (d) Diamagnetic and Bond order > O₂

49. Which species has the maximum number of lone pair of electrons on the central atom? (2005S) 
   (a) [ClO₃]⁻ (b) XeF₄ (c) SF₄ (d) I₃⁻

50. Among the following, the paramagnetic compound is (2007) 
   (a) Na₂O₂ (b) O₃ (c) N₂O (d) KO₂

51. The species having bond order different from that in CO is (2007) 
   (a) NO⁻ (b) NO⁺ (c) CN⁻ (d) N₂

52. Assuming that Hund’s rule is violated, the bond order and magnetic nature of the diatomic molecule B₂ is (2010) 
   (a) 1 and diamagnetic (b) 0 and diamagnetic (c) 1 and paramagnetic (d) 0 and paramagnetic

53. The species having pyramidal shape is : (2010) 
   (a) SO₃⁻ (b) BrF₃ (c) SiO₂⁻ (d) OSF₂

54. Geometricalshapes of the complexes formed by the reaction of Ni²⁺ with Cl⁻, CN⁻ and H₂O, respectively, are (2011) 
   (a) octahedral, tetrahedral and square planar 
   (b) tetrahedral, square planar and octahedral 
   (c) square planar, tetrahedral and octahedral 
   (d) octahedral, square planar and octahedral

55. Assuming 2s-2p mixing is NOT operative, the paramagnetic species among the following is (JEE Adv. 2014) 
   (a) Be₂⁺ (b) B₂⁺ (c) C₂⁺ (d) N₂⁺

56. The geometries of the ammonia complexes of Ni²⁺, Pt²⁺ and Zn²⁺ respectively, are (JEE Adv. 2016) 
   (a) octahedral, square planar and tetrahedral 
   (b) square planar, octahedral and tetrahedral 
   (c) tetrahedral, square planar and octahedral 
   (d) octahedral, tetrahedral and square planar

D. MCQs with One or More Than One Correct

1. CO₂ is isostructural with : (1986 - 1 Mark) 
   (a) HgCl₂ (b) SnCl₂ (c) C₃H₆ (d) NO₂

2. The linear structure is assumed by : (1991 - 1 Mark) 
   (a) SnCl₂ (b) NCO⁻ (c) CS₂ (d) NO₂⁺

3. Which of the following have identical bond order? (1992 - 1 Mark) 
   (a) CN⁻ (b) O₂⁻ (c) NO⁺ (d) CN⁺

4. The molecules that will have dipole moment are (1992 - 1 Mark) 
   (a) 2,2-dimethylpropane (b) trans-2-pentene (c) cis-3-hexene (d) 2,2,3,3-tetramethylbutane

5. The compound(s) with TWO lone pairs of electrons on the central atom is(are) (JEE Adv. 2016) 
   (a) BrF₃ (b) ClF₃ (c) XeF₄ (d) SF₄

   (a) C₂⁻ is expected to be diamagnetic 
   (b) O₂²⁺ is expected to have a longer bond length than O₂ 
   (c) N₂⁺ and N₂⁻ have the same bond order 
   (d) He2⁺ has the same energy as two isolated He atoms

E. Subjective Problems

1. Water is liquid while H₂S is a gas at room temperature. (1978)

2. Write the Lewis dot structural formula for each of the following. Give, also, the formula of a neutral molecule, which has the same geometry and the same arrangement of the bonding electrons as in each of the following. An example is
given below in the case of $H_3O^+$:

\[
\begin{array}{ccc}
& H & \\
H & : & O : H^+ \\
\text{Lewis dot structure} & & \\
& H & \\
H & : & N : H
\end{array}
\]

Neutral molecule

(i) $O_2^{2-}$; (ii) $CO_2^{3-}$; (iii) $CN^{-}$; (iv) $NCS^{-}$

\[(1983 - 1 \times 4 = 4 \text{ Marks})\]

3. How many sigma bonds and how many pi-bonds are present in a benzene molecule? \[(1985 - 1 \text{ Mark})\]

4. Write the Lewis dot structure of the following:

\[O_3COC_2\] \[(1986 - 1 \text{ Mark})\]

5. Arrange the following:

(i) $N_2$, $O_2$, $F_2$, $Cl_2$ in increasing order of bond dissociation energy. \[(1988 - 1 \text{ Mark})\]

(ii) Increasing strength of hydrogen bonding ($X-\text{H}\cdots X$):

\[O, S, F, Cl, N\] \[(1991 - 1 \text{ Mark})\]

(iii) In the decreasing order of the $O-\text{O}$ bond length present in them

\[O_2, KO_2, and O_2 [\text{AsF}_4]\] \[(2004 - 4 \text{ Marks})\]

6. The dipole moment of KCl is $3.336 \times 10^{-29}$ Coulomb meters which indicates that it is a highly polar molecule. The interatomic distance between $K^+$ and $Cl^-$ in this molecule is $2.6 \times 10^{-10}$ m. Calculate the dipole moment of KCl molecule if there were opposite charges of one fundamental unit located at each nucleus. Calculate the percentage ionic character of KCl. \[(1993 - 2 \text{ Marks})\]

7. Using the VSEPR theory, identify the type of hybridization and draw the structure of $\text{OF}_2$. What are the oxidation states of O and F? \[(1994 - 3 \text{ Marks})\]

8. A compound of vanadium has a magnetic moment of 1.73 BM. Work out the electronic configuration of the vanadium ion in the compound. \[(1997 - 2 \text{ Marks})\]

9. Interpret the non-linear shape of $H_2S$ molecule and non-planar shape of $\text{PCL}_3$ using valence shell electron pair repulsion (VSEPR) theory. (Atomic numbers: H = 1, P = 15, S = 16, Cl = 17.) \[(1998 - 4 \text{ Marks})\]

10. Write the M.O. electron distribution of $\text{O}_2$. Specify its bond order and magnetic property. \[(2000 - 3 \text{ Marks})\]

11. Using VSEPR theory, draw the shape of $\text{PCL}_3$ and $\text{BrF}_5$. \[(2003 - 2 \text{ Marks})\]

12. Draw the structure of $\text{XeF}_4$ and $\text{OSF}_4$ according to VSEPR theory, clearly indicating the state of hybridisation of the central atom and lone pair of electrons (if any) on the central atom. \[(2004 - 2 \text{ Marks})\]

**F** Match the Following

1. Match the orbital overlap figures shown in List-I with the description given in List-II and select the correct answer using the code given below the lists. \[(JEE \text{ Adv. 2014})\]

**H** Assertion & Reason Type Questions

1. Read the following Assertion and Reason and answer as per the options given below: \[(1998 - 2 \text{ Marks})\]

**Assertion**: The electronic structure of $O_3$ is

\[\text{structure is not allowed because octet around O cannot be expanded.} \]

**Reason**: (a) If both **assertion** and **reason** are correct, and **reason** is the correct explanation of the **assertion**.

(b) If both **assertion** and **reason** are correct, but **reason** is not the correct explanation of the **assertion**.

(c) If **assertion** is correct but **reason** is incorrect.

(d) If **assertion** is incorrect but **reason** is correct.

2. Read the following Assertion and Reason and answer as per the options given below: \[(1998 - 2 \text{ Marks})\]

**Assertion**: LiCl is predominantly a covalent compound.

**Reason**: Electronegativity difference between Li and Cl is too small.

(a) If both **assertion** and **reason** are correct, and **reason** is the correct explanation of the **assertion**.

(b) If both **assertion** and **reason** are correct, but **reason** is not the correct explanation of the **assertion**.

(c) If **assertion** is correct but **reason** is incorrect.

(d) If **assertion** is incorrect but **reason** is correct.

**I** Integer Value Correct Type

1. Based on VSEPR theory, the number of 90 degree $F-\text{Br}-F$ angles in $\text{BrF}_5$ is \[(2010)\]

2. The total number of lone-pairs of electrons in melamine is \[(JEE \text{ Adv. 2013})\]
3. A list of species having the formula $XZ_4$ is given below. $\text{XeF}_4$, $\text{SF}_4$, $\text{SiF}_4$, $\text{BF}_4^-$, $\text{BrF}_4^-$, $[\text{Cu(NH}_3]_4]^2^+$, $[\text{FeCl}_4]^{2^-}$, $[\text{CoCl}_4]^2^-$ and $[\text{PtCl}_4]^2^-$.

Defining shape on the basis of the location of $X$ and $Z$ atoms, the total number of species having a square planar shape is

(\textit{JEE Adv. 2014})

4. Among the triatomic molecules/ions, $\text{BeCl}_2$, $\text{N}_2^-$, $\text{N}_2\text{O}$, $\text{NO}_2^-$, $\text{O}_3$, $\text{SCl}_2$, $\text{ICl}_2^-$, $\text{I}_2^-$ and $\text{XeF}_2$, the total number of linear molecule(s)/ion(s) where the hybridization of the central atom does not have contribution from the d-orbital(s) is

[Atomic number : $S = 16$, $\text{Cl} = 17$, $I = 53$ and $\text{Xe} = 54$]

(\textit{JEE Adv. 2015})

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**Section B**

1. In which of the following species the interatomic bond angle is $109^\circ 28'$? [2002]
   (a) $\text{NH}_3$, $(\text{BF}_4^-)^1$  
   (b) $(\text{NH}_4)^+$, $\text{BF}_3$
   (c) $\text{NH}_3$, $\text{BF}_4$
   (d) $(\text{NH}_4)^+$, $\text{BF}_3$

2. Which of the following are arranged in an increasing order of their bond strengths? [2002]
   (a) $\text{O}_2^- < \text{O}_2^- < \text{O}_2^- < \text{O}_2^- < \text{O}_2^- < \text{O}_2^-$
   (b) $\text{O}_2^- < \text{O}_2^- < \text{O}_2^- < \text{O}_2^- < \text{O}_2^- < \text{O}_2^-$
   (c) $\text{O}_2^- < \text{O}_2^- < \text{O}_2^- < \text{O}_2^- < \text{O}_2^- < \text{O}_2^-$
   (d) $\text{O}_2^- < \text{O}_2^- < \text{O}_2^- < \text{O}_2^- < \text{O}_2^- < \text{O}_2^-$

3. Hybridisation of the underline atom changes in: [2002]
   (a) $\text{AlH}_3$ changes to $\text{AlH}_4^+$
   (b) $\text{H}_2\text{O}$ changes to $\text{H}_2\text{O}^+$
   (c) $\text{NH}_3$ changes to $\text{NH}_4^+$
   (d) in all cases

4. An ether is more volatile than an alcohol having the same molecular formula. This is due to [2003]
   (a) alcohols having resonance structures
   (b) inter-molecular hydrogen bonding in ethers
   (c) inter-molecular hydrogen bonding in alcohols
   (d) dipolar character of ethers

5. Which one of the following pairs of molecules will have permanent dipole moments for both members? [2003]
   (a) $\text{NO}_2$ and $\text{CO}_2$
   (b) $\text{NO}_2$ and $\text{O}_3$
   (c) $\text{SiF}_4$ and $\text{CO}_2$
   (d) $\text{SiF}_4$ and $\text{NO}_2$

6. Which one of the following compounds has the smallest bond angle in its molecule? [2003]
   (a) $\text{OH}_2$
   (b) $\text{SH}_2$
   (c) $\text{NH}_3$
   (d) $\text{SO}_2$

7. The pair of species having identical shapes for molecules of both species is [2003]
   (a) $\text{XeF}_4$, $\text{CO}_2$
   (b) $\text{BF}_3$, $\text{PCL}_3$
   (c) $\text{PF}_3$, $\text{IF}_5$
   (d) $\text{CF}_4$, $\text{SF}_4$

8. The correct order of bond angles (smallest first) in $\text{H}_2\text{S}$, $\text{NH}_3$, $\text{BF}_3$, and $\text{SiH}_4$ is [2004]
   (a) $\text{H}_2\text{S} < \text{NH}_3 < \text{SiH}_4 < \text{BF}_3$
   (b) $\text{NH}_3 < \text{H}_2\text{S} < \text{SiH}_4 < \text{BF}_3$
   (c) $\text{H}_2\text{S} < \text{SiH}_4 < \text{NH}_3 < \text{BF}_3$
   (d) $\text{H}_2\text{S} < \text{NH}_3 < \text{BF}_3 < \text{SiH}_4$

9. The bond order in NO is 2.5 while that in NO$^+$ is 3. Which of the following statements is true for these two species? [2004]
   (a) Bond length in NO$^+$ is equal to that in NO
   (b) Bond length in NO is greater than in NO$^+$
   (c) Bond length in NO$^+$ is greater than in NO
   (d) Bond length is unpredictable

10. The states of hybridization of boron and oxygen atoms in boric acid ($\text{H}_3\text{BO}_3$) are respectively [2004]

11. Which one of the following has the regular tetrahedral structure? [2004]
   (a) $\text{BF}_4^-$
   (b) $\text{SF}_4$
   (c) $\text{XeF}_4$
   (d) $[\text{Ni(CN)}_4]^2^-$

(Atomic nos : $B = 5$, $S = 16$, $\text{Ni} = 28$, $\text{Xe} = 54$)

12. The maximum number of $90^\circ$ angles between bond pair-bond pair of electrons is observed in [2004]
   (a) dsp$^2$ hybridization
   (b) sp$^2$d hybridization
   (c) dsp$^3$ hybridization
   (d) sp$^3$d$^2$ hybridization

13. Lattice energy of an ionic compound depends upon [2005]
   (a) Charge on the ion and size of the ion
   (b) Packing of ions only
   (c) Size of the ion only
   (d) Charge on the ion only

14. Which of the following molecules/ions does not contain unpaired electrons? [2006]
   (a) $\text{N}_2^+$
   (b) $\text{O}_2$
   (c) $\text{O}_2^-$
   (d) $\text{B}_2$

15. In which of the following molecules/ions are all the bonds not equal? [2006]
   (a) $\text{XeF}_4$
   (b) $\text{BF}_4^-$
   (c) $\text{SF}_4$
   (d) $\text{SiF}_4$

16. The decreasing values of bond angles from $\text{NH}_3$ (106°) to $\text{SbH}_3$ (101°) down group-15 of the periodic table is due to [2006]
   (a) decreasing lp-bp repulsion
   (b) decreasing electronegativity
   (c) increasing bp-bp repulsion
   (d) increasing p-orbital character in sp$^3$

17. Which of the following species exhibits the diamagnetic behaviour? [2007]
   (a) NO
   (b) $\text{O}_2^-$
   (c) $\text{O}_2^+$
   (d) $\text{O}_2$

18. The charge/size ratio of a cation determines its polarizing power. Which one of the following sequences represents the increasing order of the polarizing power of the cationic
species, $K^+, Ca^{2+}, Mg^{2+}, Be^{2+}$

(a) $Ca^{2+} < Mg^{2+} < Be^{2+} < K^+$
(b) $Mg^{2+} < Be^{2+} < K^+ < Ca^{2+}$
(c) $Be^{2+} < K^+ < Ca^{2+} < Mg^{2+}$
(d) $K^+ < Ca^{2+} < Mg^{2+} < Be^{2+}$.

19. In which of the following ionization processes, the bond order has increased and the magnetic behaviour has changed? [2007]

(a) $N_2 \rightarrow N_2^+$
(b) $C_2 \rightarrow C_2^+$
(c) $NO \rightarrow NO^+$
(d) $O_2 \rightarrow O_2^+$.

20. Which of the following hydrogen bonds is the strongest? [2007]

(a) $O - H \cdots F$
(b) $O - H \cdots H$
(c) $F - H \cdots F$
(d) $O - H \cdots O$.

21. Which one of the following pairs of species have the same bond order? [2008]

(a) $CN^- \text{ and } NO^+$
(b) $CN^- \text{ and } CN^+$
(c) $O_2^- \text{ and } CN^-$
(d) $NO^+ \text{ and } CN^+$.

22. The bond dissociation energy of $B - F$ in BF$_3$ is 646 kJ mol$^{-1}$ whereas that of C - F in CF$_4$ is 515 kJ mol$^{-1}$. The correct reason for higher B - F bond dissociation energy as compared to that of C - F is [2008]

(a) stronger $\sigma$ bond between B and F in BF$_3$ as compared to that between C and F in CF$_4$.
(b) significant $\pi$ interaction between B and F in BF$_3$ whereas there is no possibility of such interaction between C and F in CF$_4$.
(c) lower degree of $\pi$ interaction between B and F in BF$_3$ than that between C and F in CF$_4$.
(d) smaller size of B atom as compared to that of C atom.

23. Using MO theory, predict which of the following species has the shortest bond length? [2008]

(a) $O_2^+$
(b) $O_2^-$
(c) $O_2^{2-}$
(d) $O_2^{2+}$.

24. Among the following the maximum covalent character is shown by the compound [2011]

(a) FeCl$_2$
(b) SnCl$_2$
(c) AlCl$_3$
(d) MgCl$_2$.

25. The hybridization of orbitals of N atom in NO$_3^-$, NO$_2^+$ and NH$_4^+$ are respectively: [2011]

(a) sp, sp$^2$, sp$^3$
(b) sp$^2$, sp, sp$^3$
(c) sp, sp$^3$, sp$^2$
(d) sp$^2$, sp$^3$, sp

26. The structure of IF$_7$ is: [2011]

(a) square pyramidal
(b) trigonal bipyramidal
(c) octahedral
(d) pentagonal bipyramidal

27. Ortho-Nitrophenol is less soluble in water than $m$- and $p$-Nitrophenols because:

(a) o-Nitrophenol is more volatile steam than those of $m$- and $p$-isomers.
(b) o-Nitrophenol shows intramolecular H-bonding
(c) o-Nitrophenol shows intermolecular H-bonding
(d) Melting point of o-Nitrophenol is lower than that of $m$- and $p$-isomers.

28. In which of the following pairs the two species are not isomeric? [2012]

(a) CO$_3^{2-}$ and NO$_3^-$
(b) PCl$_4^-$ and SiCl$_4$
(c) PF$_5$ and BrF$_5$
(d) AlF$_3^-$ and SF$_6$

29. Which one of the following molecules is expected to exhibit diamagnetic behaviour? [JEE M 2013]

(a) C$_2$
(b) N$_2$
(c) O$_2$
(d) S$_2$

30. Which of the following is the wrong statement? [JEE M 2013]

(a) ONCl and ONO$^-$ are not isoelectronic.
(b) $O_2$ molecule is bent
(c) Ozone is violet-black in solid state
(d) Ozone is diamagnetic gas.

31. In which of the following pairs of molecules/ions, both the species are not likely to exist? [JEE M 2013]

(a) H$_2^+$, He$_2^{2-}$
(b) H$_2$, He$_2^{2-}$
(c) H$_2^+$, He$_2$
(d) H$_2$, He$_2^{2+}$

32. Stability of the species Li$_2^-$, Li$_2^-$ and Li$_2^+$ increases in the order of: [JEE M 2013]

(a) Li$_2$ < Li$_2^-$ < Li$_2^+$
(b) Li$_2^-$ < Li$_2^+$ < Li$_2$
(c) Li$_2$ < Li$_2^-$ < Li$_2^+$
(d) Li$_2^-$ < Li$_2$ < Li$_2^+$

33. For which of the following molecule significant $\mu \neq 0$? [JEE M 2014]

(a) Only (i)
(b) (i) and (ii)
(c) Only (iii)
(d) (iii) and (iv)

34. The species in which the N atom is in a state of $sp$ hybridization is: [JEE M 2016]

(a) NO$_3^-$
(b) NO$_2$
(c) NO$_2^-$
(d) NO$_2^+$

CHAPTER 5

States of Matter

Section-A

A Fill in the Blanks

1. The total energy of one mole of an ideal monatomic gas at 27°C is ............ calories. (1984 - 1 Mark)
2. \( C_p - C_v \) for an ideal gas is ............. (1984 - 1 Mark)
3. The rate of diffusion of gas is .............. proportional to both ................. and square root of molecular mass. (1986 - 1 Mark)
4. The value of \( PV \) for 5.6 litres of an ideal gas is ............ \( RT \), at N.T.P. (1987 - 1 Mark)
5. Eight gram each of oxygen and hydrogen at 27°C will have the total kinetic energy in the ratio of ............ (1989 - 1 Mark)

B True / False

1. Kinetic energy of a molecule is zero at 0°C. (1985 - \( \frac{1}{2} \) Mark)
2. A gas in a closed container will exert much higher pressure due to gravity at the bottom than at the top. (1985 - \( \frac{1}{2} \) Mark)
3. In the van der Waal’s equation \( \left( P + \frac{n^2a}{V^2} \right) (V - nb) = nRT \) the constant ‘a’ reflects the actual volume of the gas molecules. (1993 - 1 Mark)
4. A mixture of ideal gases is cooled upto liquid helium temperature (4.22 K) to form an ideal solution. (1996 - 1 Mark)

C MCQs with One Correct Answer

1. Equal weights of methane and oxygen are mixed in an empty container at 25°C. The fraction of the total pressure exerted by oxygen is (1981 - 1 Mark)
   (a) \( \frac{1}{3} \)  (b) \( \frac{1}{2} \)  (c) \( \frac{2}{3} \)  (d) \( \frac{1}{3} \times \frac{273}{298} \)
2. The temperature at which a real gas obeys the ideal gas laws over a wide range of pressure is (1981 - 1 Mark)
   (a) \( V - b \)  (b) \( RT \)  (c) \( \left( P + \frac{a}{V^2} \right) \)  (d) \( (RT)^{-1} \)
3. The ratio of root mean square velocity to average velocity of a gas molecule at a particular temperature is (1981 - 1 Mark)
   (a) 1.086 : 1  (b) 1 : 1.086  (c) 2 : 1.086  (d) 1.086 : 2
4. Helium atom is two times heavier than a hydrogen molecule. At 298 K, the average kinetic energy of a helium atom is (1982 - 1 Mark)
   (a) two times that of a hydrogen molecule.  (b) same as that of a hydrogen molecule.
   (c) four times that of a hydrogen molecule.  (d) half that of a hydrogen molecule.
5. Equal weights of methane and hydrogen are mixed in an empty container at 25°C. The fraction of the total pressure exerted by hydrogen is : (1984 - 1 Mark)
   (a) \( \frac{1}{2} \)  (b) \( \frac{8}{9} \)  (c) \( \frac{1}{9} \)  (d) \( \frac{16}{17} \)
6. Rate of diffusion of a gas is : (1985 - 1 Mark)
   (a) directly proportional to its density.
   (b) directly proportional to its molecular weight.
   (c) directly proportional to the square root of its molecular weight.
   (d) inversely proportional to the square root of its molecular weight.
7. The average velocity of an ideal gas molecule at 27°C is 0.3 m/sec. The average velocity at 927°C will be: (1986 - 1 Mark)
   (a) 0.6 m/sec  (b) 0.3 m/sec  (c) 0.9 m/sec  (d) 3.0 m/sec
8. In van der Waals equation of state for a non-ideal gas, the term that accounts for intermolecular forces is (1988 - 1 Mark)
   (a) \( V - b \)  (b) \( RT \)  (c) \( \left( P + \frac{a}{V^2} \right) \)  (d) \( (RT)^{-1} \)
9. A bottle of dry ammonia and a bottle of dry hydrogen chloride connected through a long tube are opened simultaneously at both ends the white ammonium chloride ring first formed will be \( \text{(1988 - 1 Mark)} \)
(a) at the centre of the tube.
(b) near the hydrogen chloride bottle.
(c) near the ammonia bottle.
(d) throughout the length of the tube.

10. The values of van der Waals constant \( \alpha \) for the gases \( \text{O}_2, \text{N}_2, \text{NH}_3 \) and \( \text{CH}_4 \) are 1.360, 1.390, 4.170 and 2.253 L^2 atm mol^{-2} \) respectively. The gas which can most easily be liquified is: \( \text{(1989 - 1 Mark)} \)
(a) \( \text{O}_2 \)  (b) \( \text{N}_2 \)
(c) \( \text{NH}_3 \)  (d) \( \text{CH}_4 \)

11. The density of neon will be highest at \( \text{(1990 - 1 Mark)} \)
(a) S.T.P.  (b) 0°C, 2 atm
(c) 273°C, 1 atm.  (d) 273°C, 2 atm.

12. The rate of diffusion of methane at a given temperature is twice that of a gas \( X \). The molecular weight of \( X \) is \( \text{(1990 - 1 Mark)} \)
(a) 64.0  (b) 32.0
(c) 4.0  (d) 8.0

13. According to kinetic theory of gases, for a diatomic molecule \( \text{(1991 - 1 Mark)} \)
(a) the pressure exerted by the gas is proportional to mean velocity of the molecule
(b) the pressure exerted by the gas is proportional to the root mean square velocity of the molecule
(c) the root mean square velocity of the molecule is inversely proportional to the temperature
(d) the mean translational kinetic energy of the molecule is proportional to the absolute temperature.

14. At constant volume, for a fixed number of moles of a gas, the pressure of the gas increases with rise in temperature due to \( \text{(1992 - 1 Mark)} \)
(a) Increase in average molecular speed
(b) Increased rate of collisions amongst molecules
(c) Increase in molecular attraction
(d) Decrease in mean free path

15. Longest mean free path stands for: \( \text{(1995S)} \)
(a) \( \text{H}_2 \)  (b) \( \text{N}_2 \)
(c) \( \text{O}_2 \)  (d) \( \text{Cl}_2 \)

16. Arrange the van der Waals constant for the gases: \( \text{(1995S)} \)

<table>
<thead>
<tr>
<th></th>
<th>( \text{C}<em>6\text{H}</em>{10(g)} )</th>
<th>( \text{C}_4\text{H}_6\text{CH}_3(g) )</th>
<th>( \text{Ne}_g )</th>
<th>( \text{H}_2\text{O}_g )</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>A 0.217</td>
<td>B 5.464</td>
<td>C 18.000</td>
<td>D 24.060</td>
</tr>
</tbody>
</table>

17. The ratio between the root mean square speed of \( \text{H}_2 \) at 50 K and that of \( \text{O}_2 \) at 800 K is, \( \text{(1996 - 1 Mark)} \)
(a) 4  (b) 2
(c) 1  (d) \( \frac{1}{4} \)

18. X mL of \( \text{H}_2 \) gas effuses through a hole in a container in 5 seconds. The time taken for the effusion of the same volume of the gas specified below under identical conditions is: \( \text{(1996 - 1 Mark)} \)
(a) 10 seconds : He  (b) 20 seconds : \( \text{O}_2 \)
(c) 25 seconds : CO  (d) 55 seconds : \( \text{CO}_2 \)

19. One mole of \( \text{N}_2\text{O}_4(g) \) at 300 K is kept in a closed container under one atmosphere. It is heated to 600 K when 20% by mass of \( \text{N}_2\text{O}_4(g) \) decomposes to \( \text{NO}_2(g) \). The resultant pressure is: \( \text{(1996 - 1 Mark)} \)
(a) 1.2 atm (b) 2.4 atm
(c) 2.0 atm (d) \( \frac{1}{2} \) atm

20. The compressibility factor for an ideal gas is \( \text{(1997 - 1 Mark)} \)
(a) 1.5  (b) 1.0
(c) 2.0  (d) \( \infty \)

21. A gas will approach ideal behaviour at \( \text{(1999 - 2 Marks)} \)
(a) low temperature and low pressure.
(b) low temperature and high pressure.
(c) high temperature and low pressure.
(d) high temperature and high pressure.

22. The rms velocity of hydrogen is \( \sqrt{7} \) times the rms velocity of nitrogen. If \( T \) is the temperature of the gas, then \( \text{(2000S)} \)
(a) \( T(\text{H}_2)=T(\text{N}_2) \)  (b) \( T(\text{H}_2)\gt T(\text{N}_2) \)
(c) \( T(\text{H}_2)\lt T(\text{N}_2) \)  (d) \( T(\text{H}_2)=\sqrt{7} T(\text{N}_2) \)

23. The compressibility of a gas is less than unity at STP. Therefore, \( \text{(2000S)} \)
(a) \( V_m\gt 22.4 \text{ litres} \)  (b) \( V_m\lt 22.4 \text{ litres} \)
(c) \( V_m= 22.4 \text{ litres} \)  (d) \( V_m= 44.8 \text{ litres} \)

24. At 100°C and 1 atm, if the density of liquid water is 1.0 g cm^{-3} and that of water vapour is 0.0006 g cm^{-3}, then the volume occupied by water molecules in 1 litre of steam at that temperature is \( \text{(2000S)} \)
(a) 6 cm^{3}  (b) 60 cm^{3}
(c) 0.6 cm^{3}  (d) 0.06 cm^{3}

25. The root mean square velocity of an ideal gas at constant pressure varies with density (d) as \( \text{(2001S)} \)
(a) \( d^2 \)  (b) \( d \)
(c) \( \sqrt{d} \)  (d) \( 1/\sqrt{d} \)

26. Which of the following volume \( (V) \) - temperature \( (T) \) plots represents the behaviour of one mole of an ideal gas at one atmospheric pressure? \( \text{(2002S)} \)
27. When the temperature is increased, surface tension of water increases.

(a) increases  
(b) decreases  
(c) remains constant  
(d) shows irregular behaviour

28. Positive deviation from ideal behaviour takes place because of

(a) Molecular interaction between atoms and $PV/nRT > 1$  
(b) Molecular interaction between atoms and $PV/nRT < 1$  
(c) Finite size of atoms and $PV/nRT > 1$  
(d) Finite size of atoms and $PV/nRT < 1$

29. The root mean square velocity of one mole of a monoatomic gas having molar mass $M$ is $v_{r.m.s.}$. The relation between the average kinetic energy $E$ of the gas and $v_{r.m.s.}$ is

(a) $v_{r.m.s.} = \sqrt{\frac{3E}{2M}}$  
(b) $v_{r.m.s.} = \sqrt{\frac{2E}{3M}}$

(c) $v_{r.m.s.} = \sqrt{\frac{2E}{M}}$  
(d) $v_{r.m.s.} = \sqrt{\frac{E}{3M}}$

30. The ratio of the rate of diffusion of helium and methane under identical condition of pressure and temperature will be

(a) 4  
(b) 2  
(c) 1  
(d) 0.5

31. When one mole of monoatomic ideal gas at T K undergoes adiabatic change under a constant external pressure of 1 atm volume changes from 1 litre to 2 litre. The final temperature in Kelvins would be

(a) $T = \frac{2}{(2/3)}$  
(b) $T + \frac{2}{3} \times 0.0821$  
(c) $T$  
(d) $T - \frac{2}{3} \times 0.0821$

32. A mono-atomic ideal gas undergoes a process in which the ratio of $P$ to $V$ at any instant is constant and equals to 1. What is the molar heat capacity of the gas

(a) $\frac{3R}{2}$  
(b) $2R$  
(c) 0  
(d) $\frac{5R}{2}$

33. The term that corrects for the attractive forces present in a real gas in the van der Waals equation is

(a) $nb$  
(b) $\frac{an^2}{V^2}$  
(c) $\frac{an^2}{V^2}$  
(d) $-nb$

34. For one mole of a van der Waal’s gas when $b = 0$ and $T = 300$ K, the PV vs. $1/V$ plot is shown below. The value of the van der Waal’s constant $a$ (atm. liter$^2$ mol$^{-2}$) is:

(2012)

35. The qualitative sketches I, II and III given below show the variation of surface tension with molar concentration of three different aqueous solutions of KCl, CH$_3$OH and CH$_3$(CH$_2$)$_n$OSO$_3^-$ Na$^+$ at room temperature. The correct assignment of the sketches is

(JEE Adv. 2016)

(a) I: KCl  II: CH$_3$OH  III: CH$_3$(CH$_2$)$_n$OSO$_3^-$ Na$^+$  
(b) I: CH$_3$(CH$_2$)$_n$OSO$_3^-$ Na$^+$  II: CH$_3$OH  III: KCl  
(c) I: KCl  II: CH$_3$(CH$_2$)$_n$OSO$_3^-$ Na$^+$  III: CH$_3$OH  
(d) I: CH$_3$OH  II: KCl  III: CH$_3$(CH$_2$)$_n$OSO$_3^-$ Na$^+$
1. When an ideal gas undergoes unrestrained expansion, no cooling occurs because the molecules: *(1984 - 1 Mark)*
   (a) are above the inversion temperature
   (b) exert no attractive forces on each other
   (c) do work equal to loss in kinetic energy
   (d) collide without loss of energy

2. If a gas is expanded at constant temperature:
   (a) the pressure decreases *(1986 - 1 Mark)*
   (b) the kinetic energy of the molecules remains the same
   (c) the kinetic energy of the molecules decreases
   (d) the number of molecules of the gas increases

3. Equal weights of ethane and hydrogen are mixed in an empty container at 25°C. The fraction of the total pressure exerted by hydrogen is *(1993 - 1 Mark)*
   (a) 1:2
   (b) 1:1
   (c) 1:16
   (d) 15:16

4. According to Graham’s law, at a given temperature the ratio of the rates of diffusion \( r_A/r_B \) of gases A and B is given by *(1998 - 2 Marks)*
   (a) \((P_A/P_B)(M_A/M_B)^{1/2}\)
   (b) \((M_A/M_B)(P_A/P_B)^{1/2}\)
   (c) \((P_A/P_B)(M_B/M_A)^{1/2}\)
   (d) \((M_A/M_B)(P_B/P_A)^{1/2}\)
   (Where P and M are pressures and molecular weights of gases A and B respectively.)

5. Refer to the figure given: *(2006 - 5M; -1)*
   Which of the following statements is wrong?
   (a) For gas A, \( a = 0 \) and Z will linearly depend on pressure
   (b) For gas B, \( b = 0 \) and Z will linearly depend on pressure
   (c) Gas C is a real gas and we can find ‘a’ and ‘b’ if intersection data is given
   (d) All van der Waal gases will behave like gas C and give positive slope at high pressure

6. A gas described by van der Waals equation – *(2008 - 1 Mark)*
   (a) behave similar to an ideal gas in the limit of large molar volumes
   (b) behaves similar to an ideal gas is in limit of large pressures

7. According to kinetic theory of gases *(2011)*
   (a) collisions are always elastic
   (b) heavier molecules transfer more momentum to the wall of the container
   (c) only a small number of molecules have very high velocity
   (d) between collisions, the molecules move in straight lines with constant velocities

8. One mole of a monoatomic real gas satisfies the equation \( p(V - b) = RT \) where \( b \) is a constant. The relationship of interatomic potential \( V(r) \) and interatomic distance \( r \) for the gas is given by *(JEE Adv: 2015)*

![Graph of V(r) vs r]
E Subjective Problems

1. Calculate density of NH₃ at 30°C and 5 atm pressure. (1978)
2. 3.7 g of a gas at 25°C occupied the same volume as 0.184 g of hydrogen at 17°C and at the same pressure. What is the molecular weight of the gas? (1979)
3. A straight glass tube has two inlets X and Y at two ends. The length of tube is 200 cm. HCl gas through inlets X and NH₃ gas through inlet Y are allowed to enter the tube at the same time. What fumes appear at point P inside the tube. Find distance of P from X. (1980)
4. 1 litre of mixture of CO and CO₂ is taken. The mixture is passed through a tube containing red hot charcoal. The volume now becomes 1.6 litre. The volumes are measured under the same conditions. Find the composition of mixture by volume. (1980)
5. At room temperature, ammonia gas at 1 atm pressure and hydrogen chloride gas at P atm pressure are allowed to effuse through identical pin holes from opposite ends of a glass tube of one metre length and of uniform cross-section. Ammonium chloride is first formed at a distance of 60 cm from the end through which HCl gas is sent in. What is the value of P? (1982 - 4 Marks)
6. Calculate the average of kinetic energy, in Joules of the molecules in 8.0 g of methane at 27°C. (1982 - 2 Marks)
7. Oxygen is present in 1 litre flask at a pressure of 7.6 × 10⁻¹⁰ mm of Hg. Calculate the number of oxygen molecules in the flask at 0°C. (1983 - 2 Marks)
8. When 2 gm of a gas A is introduced into an evaluated flask kept at 25°C, the pressure is found to be one atmosphere. If 3 gm of another gas B is then added to the same flask, the total pressure becomes 1.5 atm. Assuming ideal gas behaviour, calculate the ratio of the molecular weights M_A : M_B. (1983 - 2 Marks)
9. Calculate the root mean square velocity of ozone kept in a closed vessel at 20°C and 82 cm mercury pressure. (1985 - 2 Marks)
10. A spherical balloon of 21 cm diameter is to be filled up with hydrogen at N.T.P. from a cylinder containing the gas at 20 atmospheres at 27°C. If the cylinder can hold 2.82 litres of water, calculate the number of balloons that can be filled up. (1987 - 5 Marks)
11. The average velocity at T₁K, and the most probable velocity at T₂K of CO₂ gas is 9.0 × 10⁴ cm sec⁻¹. Calculate the value of T₁ and T₂. (1990 - 4 Marks)
12. Calculate the volume occupied by 5.0 g of acetylene gas at 50°C and 740 mm pressure. (1991 - 2 Marks)
13. At 27°C, hydrogen is leaked through a tiny hole into a vessel for 20 minutes. Another unknown gas at the same temperature and pressure as that of H₂ is leaked through the same hole for 20 minutes. After the effusion of the gases the mixture exerts a pressure of 6 atmosphere. The hydrogen content of the mixture is 0.7 mole. If the volume of the container is 3 litres, what is the molecular weight of the unknown gas? (1992 - 3 Marks)
14. At room temperature the following reactions proceed nearly to completion:

\[ 2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2 \rightarrow \text{N}_2\text{O}_4 \]

The dimer, N₂O₄, solidifies at 262 K. A 250 ml flask and a 100 ml flask are separated by a stop-cock. At 300 K, the nitric oxide in the larger flask exerts a pressure of 1.053 atm. and the smaller one contains oxygen at 0.789 atm. The gases are mixed by opening the stopcock and after the end of the reaction the flasks are cooled at 220K. Neglecting the vapour pressure of the dimer, find out the pressure and composition of the gas remaining at 220 K. (Assume the gases to behave ideally). (1992 - 4 Marks)
15. A gas bulb of 1 litre capacity contains \(2.0 \times 10^{21}\) molecules of nitrogen exerting a pressure of \(7.57 \times 10^3\) Nm⁻². Calculate the root mean square (r.m.s) speed and the temperature of the gas molecules. If the ratio of the most probable speed to the root mean square speed is 0.82, calculate the most probable speed for these molecules at this temperature. (1993 - 4 Marks)
16. A 4 : 1 molar mixture of He and CH₄ is contained in a vessel at 20 bar pressure. Due to a hole in the vessel, the gas mixture leaks out. What is the composition of the mixture effusing out initially? (1994 - 2 Marks)
17. An LPG (liquefied petroleum gas) cylinder weighs 14.8 kg when empty. When full, it weighs 29.0 kg and shows a pressure of 2.5 atm. In the course of use at 27°C, the weight of the full cylinder reduces to 23.2 kg. Find out the volume of the gas in cubic meters used up at the normal usage conditions, find the final pressure inside the cylinder. Assume LPG to be n-butane with normal boiling point of 0°C. (1994 - 3 Marks)
18. A mixture of ethane (C₂H₆) and ethene (C₂H₄) occupies 40 litres at 1.00 atm and at 400 K. The mixture reacts completely with 130 g of O₂ to produce CO₂ and H₂O. Assuming ideal gas behaviour, calculate the mole fractions of C₂H₆ and C₂H₄ in the mixture. (1995 - 4 Marks)
19. The composition of the equilibrium mixture (Cl₂ ⇌ 2Cl), which is attained at 1200°C, is determined by measuring the rate of effusion through a pin–hole. It is observed that at 1.80 mmHg pressure, the mixture effuses 1.16 times as fast as krypton effuses under the same conditions. Calculate the fraction of the chlorine molecules dissociated into atoms. (Relative atomic mass of Kr = 84.) (1995 - 4 Marks)
20. A 20.0 cm³ mixture of CO, CH₄ and He gases is exploded by an electric discharge at room temperature with excess of oxygen. The volume contraction is found to be 13.0 cm³. A further contraction of 14.0 cm³ occurs when the residual gas is treated with KOH solution. Find out the composition of the gaseous mixture in terms of volume percentage. (1995 - 4 Marks)
21. An evacuated glass vessel weighs 50.0 g when empty, 148.0 g when filled with a liquid of density 0.98 g mL⁻¹ and 50.5 g
when filled with an ideal gas at 760 mmHg at 300 K. Determine
the molar mass of the gas.

(1998 - 3 Marks)

22. The degree of dissociation is 0.4 at 400 K and 1.0 atm for
the gaseous reaction \( \text{PCl}_3 \rightleftharpoons \text{PCl}_2 + \text{Cl}_2 \). Assuming ideal
behaviour of all gases, calculate the density of equilibrium
mixture at 400 K and 1.0 atmosphere. (Relative atomic mass
of \( \text{P} = 31 \) and \( \text{Cl} = 35.5 \))

(1998 - 3 Marks)

23. Using van der Waal’s equation, calculate the constant, \( a \)
when two moles of a gas confined in a four litre flask exerts
a pressure of 11.0 atmospheres at a temperature of 300 K.
The value of \( b \) is 0.05 L mol\(^{-1}\).\n
(1998 - 4 Marks)

24. For the reaction, \( \text{N}_2\text{O}_4(g) \rightarrow 2\text{NO}_2(g) + 0.5 \text{O}_2(g) \), calculate
the molar fraction of \( \text{N}_2\text{O}_4(g) \) decomposed at a constant
volume and temperature, if the initial pressure is 600 mm Hg
and the pressure at any time is 960 mm Hg. Assume ideal
gas behaviour.

(1998 - 3 Marks)

25. One mole of nitrogen gas at 0.8 atm takes 38 s to diffuse
through a pinhole, whereas one mole of an unknown
compound of xenon with fluorine at 1.6 atm takes 57 s to
diffuse through the same hole. Calculate the molecular
formula of the compound.

(1999 - 5 Marks)

26. The pressure exerted by 12 g of an ideal gas at temperature
t\(^\circ\)C in a vessel of volume \( V \) litre is one atm. When
the temperature is increased by 10 degrees at the same volume,
the pressure increases by 10\%. Calculate the temperature \( t \)
and volume \( V \). (Molecular weight of the gas = 120.)

(1999 - 5 Marks)

27. Calculate the pressure exerted by one mole of \( \text{CO}_2 \) gas at
273 K if the van der Waal’s constant \( a = 3.592 \text{ dm}^6 \text{ atm mol}^{-2} \). Assume that the volume occupied by \( \text{CO}_2 \) molecules
is negligible.

(2000 - 2 Marks)

28. The compression factor (compressibility factor) for one mole
of a van der Waals gas at 0°C and 100 atmospheric pressure
is found to be 0.5. Assuming that the volume of a gas
molecule is negligible, calculate the van der Waals constant
\( a \).

(2001 - 5 Marks)

29. The density of the vapour of a substance at 1 atm pressure
and 500 K is 0.36 kg m\(^{-3}\). The vapour effuses through a
small hole at a rate of 1.33 times faster than oxygen under
the same condition.

(2002 - 5 Marks)

(a) Determine
(i) molecular weight,
(ii) molar volume,
(iii) compression factor \( Z \) of the vapour and
(iv) which forces among the gas molecules are
   dominating, the attractive or the repulsive?

(b) If the vapour behaves ideally at 1000 K, determine
   the average translational kinetic energy of a molecule.

(2003 - 2 Marks)

30. The average velocity of gas molecules is 400 m/sec. Calculate
its rms velocity at the same temperature.

(2004 - 2 Marks)

31. A graph is plotted between \( PV_m \) along \( Y \)-axis and \( P \) along
\( X \)-axis, where \( V_m \) is the molar volume of a real gas. Find the
intercept along \( Y \)-axis.

(2005 - 4 Marks)

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**F** Match The Following

Each question contains statements given in two columns, which have to be matched. The statements
in Column-I are labelled A, B, C and D, while the statements in Column-II are labelled p, q, r, s and
t. Any given statement in Column-I can have correct matching with ONE OR MORE statement(s) in
Column-II. The appropriate bubbles corresponding to the answers to these questions have to be
darkened as illustrated in the following example:

If the correct matches are A-p, s and t; B-q and r; C-p and q; and D-s then the correct darkening of
bubbles will look like the given.

1. Match gases under specified conditions listed in Column I with their properties/laws in Column II. Indicate your answer by
darkening the appropriate bubbles of the 4 \times 4 matrix given in the ORS.

(2007)

<table>
<thead>
<tr>
<th>Column I</th>
<th>Column II</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A) Hydrogen gas (( P = 200 \text{ atm}, T = 273 \text{ K} ))</td>
<td>(p) Compressibility factor ( \neq 1 )</td>
</tr>
<tr>
<td>(B) Hydrogen gas (( P \sim 0, T = 273 \text{ K} ))</td>
<td>(q) Attractive forces are dominant</td>
</tr>
<tr>
<td>(C) ( \text{CO}_2(P = 1 \text{ atm}, T = 273 \text{ K} ))</td>
<td>(r) ( PV = nRT )</td>
</tr>
<tr>
<td>(D) Real gas with very large molar volume</td>
<td>(s) ( P(V - nb) = nRT )</td>
</tr>
</tbody>
</table>

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**G** Comprehension Based Questions

\( X \) and \( Y \) are two volatile liquids with molar weights of 10 g mol\(^{-1}\)
and 40 g mol\(^{-1}\) respectively. Two cotton plugs, one soaked in \( X \)
and the other soaked in \( Y \), are simultaneously placed at the ends
of a tube of length \( L = 24 \text{ cm} \), as shown in the figure. The tube is
filled with an inert gas at 1 atmosphere pressure and a temperature
of 300 K. Vapours of \( X \) and \( Y \) react to form a product which is first
observed at a distance \( d \) cm from the plug soaked in \( X \). Take \( X \) and
\( Y \) to have equal molecular diameters and assume ideal behaviour
for the inert gas and the two vapoours.
1. The value of $d$ in cm (shown in the figure), as estimated from Graham’s law, is \textit{(JEE. Adv. 2014)}
   (a) 8 \hspace{1cm} (b) 12 \hspace{1cm} (c) 16 \hspace{1cm} (d) 20

2. The experimental value of $d$ is found to be smaller than the estimate obtained using Graham’s law. This is due to \textit{(JEE. Adv. 2014)}
   (a) Larger mean free path for $X$ as compared to that of $Y$ 
   (b) Larger mean free path for $Y$ as compared to that of $X$ 
   (c) Increased collision frequency of $Y$ with the inert gas as compared to that of $X$ with the inert gas 
   (d) Increased collision frequency of $X$ with the inert gas as compared to that of $Y$ with the inert gas 

H Assertion & Reason Type Questions

1. Read the following statement and explanation and answer as per the options given below:
   \textbf{Assertion} : The value of van der Waals’ constant ‘a’ is larger for ammonia than for nitrogen.
   \textbf{Reason} : Hydrogen bonding is present in ammonia. \textit{(1998 - 2 Marks)}
   (a) If both assertion and reason are correct, and reason is the correct explanation of the assertion.
   (b) If both assertion and reason are correct, but reason is not the correct explanation of the assertion.
   (c) If assertion is correct but reason is incorrect.
   (d) If assertion is incorrect but reason is correct.

I Integer Value Correct Type

1. At 400 K, the root mean square (rms) speed of a gas X (molecular weight = 40) is equal to the most probable speed of gas Y at 60 K. The molecular weight of the gas Y is \textit{(2009)}
2. To an evacuated vessel with movable piston under external pressure of 1 atm, 0.1 mol of He and 1.0 mol of an unknown compound (vapour pressure 0.68 atm at 0°C) are introduced. Considering the ideal gas behaviour, the total volume (in litre) of the gases at 0°C is close to \textit{(2011)}
3. The diffusion coefficient of an ideal gas is proportional to its mean free path and mean speed. The absolute temperature of an ideal gas is increased 4 times and its pressure is increased 2 times. As a result, the diffusion coefficient of this gas increases x times. The value of x is \textit{(JEE. Adv. 2016)}

Section-B JEE Main / AIEEE

1. For an ideal gas, number of moles per litre in terms of its pressure $P$, gas constant $R$ and temperature $T$ is \textit{(2002)}
   (a) $PT/R$ \hspace{1cm} (b) $PRT$ \hspace{1cm} (c) $P/R$ \hspace{1cm} (d) $RT/P$.
2. Value of gas constant $R$ is \textit{(2002)}
   (a) 0.082 litre atm \hspace{1cm} (b) 0.987 cal mol$^{-1}$ K$^{-1}$ \hspace{1cm} (c) 8.3 J mol$^{-1}$ K$^{-1}$ \hspace{1cm} (d) 83 erg mol$^{-1}$ K$^{-1}$.
3. Kinetic theory of gases proves \textit{(2002)}
   (a) only Boyle’s law \hspace{1cm} (b) only Charles’ law \hspace{1cm} (c) only Avogadro’s law \hspace{1cm} (d) All of these.
4. According to the kinetic theory of gases, in an ideal gas, between two successive collisions a gas molecule travels \textit{(2003)}
   (a) in a wavy path \hspace{1cm} (b) in a straight line path \hspace{1cm} (c) with an accelerated velocity \hspace{1cm} (d) in a circular path.
5. As the temperature is raised from 20°C to 40°C, the average kinetic energy of neon atoms changes by a factor of which of the following? \textit{(2004)}
   (a) $\frac{313}{293}$ \hspace{1cm} (b) $\sqrt{\frac{313}{293}}$ \hspace{1cm} (c) $\frac{1}{2}$ \hspace{1cm} (d) 2
6. In van der Waals equation of state of the gas law, the constant ‘b’ is a measure of \textit{(2004)}
   (a) volume occupied by the molecules \hspace{1cm} (b) intermolecular attraction \hspace{1cm} (c) intermolecular repulsions \hspace{1cm} (d) intermolecular collisions per unit volume.
7. Which one of the following statements is NOT true about the effect of an increase in temperature on the distribution of molecular speeds in a gas? \textit{(2005)}
   (a) The area under the distribution curve remains the same as under the lower temperature \hspace{1cm} (b) The distribution becomes broader \hspace{1cm} (c) The fraction of the molecules with the most probable speed increases \hspace{1cm} (d) The most probable speed increases.
8. If $10^{-4}$ dm$^3$ of water is introduced into a 1.0 dm$^3$ flask at 300 K, how many moles of water are in the vapour phase when equilibrium is established? \textit{(2010)}
(Given: Vapour pressure of H₂O at 300 K is 3170 Pa; 
R = 8.314 J K⁻¹ mol⁻¹)
(a) 5.56 × 10⁻³ mol   (b) 1.53 × 10⁻² mol
(c) 4.46 × 10⁻² mol   (d) 1.27 × 10⁻³ mol

9. ‘a’ and ‘b’ are van der Waals’ constants for gases. Chlorine is 
more easily liquefied than ethane because [2011]
(a) a and b for Cl₂ > a and b for C₂H₆
(b) a and b for Cl₂ < a and b for C₂H₆
(c) a for Cl₂ < a for C₂H₆ but b for Cl₂ > b for C₂H₆
(d) a for Cl₂ > a for C₂H₆ but b for Cl₂ < b for C₂H₆

10. The compressibility factor for a real gas at high pressure is:
(a) 1 + \( \frac{RT}{pb} \)    (b) 1    [2012]
(c) 1 + \( \frac{pb}{RT} \)    (d) 1 - \( \frac{pb}{RT} \)

11. For gaseous state, if most probable speed is denoted by C*, 
average speed by C and mean square speed by C, then for 
a large number of molecules the ratios of these speeds are:
   [JEE M 2013]
(a) C*: \( \frac{C}{C} = 1.225 : 1.128 : 1 \)
(b) C*: \( \frac{C}{C} = 1.128 : 1.225 : 1 \)
(c) C*: \( \frac{C}{C} = 1 : 1.128 : 1.225 \)
(d) C*: \( \frac{C}{C} = 1 : 1.225 : 1.128 \)

12. If Z is a compressibility factor, van der Waals equation at low 
pressure can be written as:  [JEE M 2014]
(a) \( Z = 1 + \frac{RT}{Pb} \)    (b) \( Z = 1 - \frac{a}{VRT} \)
(c) \( Z = 1 - \frac{Pb}{RT} \)    (d) \( Z = 1 + \frac{Pb}{RT} \)

13. The ratio of masses of oxygen and nitrogen in a particular 
gaseous mixture is 1 : 4. The ratio of number of their molecule 
is:   [JEE M 2014]
(a) 1 : 4    (b) 7 : 32
(c) 1 : 8    (d) 3 : 16

14. The intermolecular interaction that is dependent on the 
inverse cube of distance between the molecules is:  [JEE M 2015]
(a) London force    (b) hydrogen bond
(c) ion - ion interaction    (d) ion - dipole interaction

15. Two closed bulbs of equal volume (V) containing an ideal gas 
initially at pressure \( p_i \) and temperature \( T_i \) are connected 
through a narrow tube of negligible volume as shown in the 
figure below. The temperature of one of the bulbs is then 
raised to \( T_x \). The final pressure \( p_f \) is:  [JEE M 2016]
(a) \( 2p_i \left( \frac{T_2}{T_1 + T_2} \right) \)    (b) \( 2p_i \left( \frac{T_1 T_2}{T_1 + T_2} \right) \)
(c) \( p_i \left( \frac{T_1 T_2}{T_1 + T_2} \right) \)    (d) \( 2p_i \left( \frac{T_1}{T_1 + T_2} \right) \)
Section-A

A Fill in the Blanks

1. A system is said to be ................. if it can neither exchange matter nor energy with the surroundings. (1993 - 1 Mark)
2. The heat content of the products is more than that of the reactants in an ................. reaction. (1993 - 1 Mark)
3. Enthalpy is an ................. property. (1997 - 1 Mark)

B True / False

1. First law of thermodynamics is not adequate in predicting the direction of a process. (1982 - 1 Mark)
2. Heat capacity of a diatomic gas is higher than that of a monoatomic gas. (1985 - 1/2 Mark)

C MCQs with One Correct Answer

1. The difference between heats of reaction at constant pressure and constant volume for the reaction:
   \[ 2 \text{C}_3\text{H}_8(l) + 15\text{O}_2(g) \rightarrow 12\text{CO}_2(g) + 6\text{H}_2\text{O}(l) \text{ at } 25^\circ\text{C} \] is (kJ)
   \( \Delta H \) (1991 - 1 Mark)
   (a) -7.43
   (b) +3.72
   (c) -3.72
   (d) +7.43

2. For which change \( \Delta H \neq \Delta E \)? (1995S)
   (a) \( \text{H}_2(g) + \text{I}_2(g) \rightarrow 2\text{HI}(g) \)
   (b) \( \text{HCl} + \text{NaOH} \rightarrow \text{NaCl} \)
   (c) \( \text{C}_6\text{H}_{12}(s) + 3\text{O}_2(g) \rightarrow 3\text{CO}_2(g) + 3\text{H}_2\text{O}(g) \)
   (d) \( \text{N}_2(g) + 3\text{H}_2(g) \rightarrow 2\text{NH}_3(g) \)

3. The \( \Delta H^\circ \) for \( \text{CO}_2(g) \), \( \text{CO}(g) \) and \( \text{H}_2\text{O}(g) \) are -393.5, -110.5 and -241.8 kJ mol\(^{-1}\) respectively. The standard enthalpy change (in kJ) for the reaction \( \text{CO}_2(g) + \text{H}_2(g) \rightarrow \text{CO}(g) + \text{H}_2\text{O}(g) \) is (2000S)
   (a) 524.1
   (b) 41.2
   (c) -262.5
   (d) -41.2

4. In thermodynamics, a process is called reversible when
   (2001S)
   (a) surroundings and system change into each other.
   (b) there is no boundary between system and surroundings.
   (c) the surroundings are always in equilibrium with the system.
   (d) the system changes into the surroundings spontaneously.

5. Which one of the following statements is false? (2001S)
   (a) Work is a state function.
   (b) Temperature is a state function.
   (c) Change in the state is completely defined when the initial and final states are specified.
   (d) Work appears at the boundary of the system.

6. One mole of a non-ideal gas undergoes a change of state
   (2.0 atm, 3.0 L, 95(K) \rightarrow (4.0 atm, 5.0 L, 245K) with a change in internal energy, \( \Delta U = 30.0 \text{ L atm} \)). The change in enthalpy (\( \Delta H \)) of the process in L atm is (2002S)
   (a) 40.0
   (b) 42.3
   (c) 44.0
   (d) not defined, because pressure is not constant

7. Which of the reaction defines \( \Delta H^\circ? \) (2003S)
   (a) \( \text{C}_6\text{H}_{12}(s) + 3\text{O}_2(g) \rightarrow 3\text{CO}_2(g) + 3\text{H}_2\text{O}(g) \)
   (b) \( \frac{1}{2}\text{H}_2(g) + \frac{1}{2}\text{F}_2(g) \rightarrow \text{HF}(g) \)
   (c) \( \text{N}_2(g) + 3\text{H}_2(g) \rightarrow 2\text{NH}_3(g) \)
   (d) \( \text{CO}_2(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{CO}_2(g) \)

8. Two moles of an ideal gas is expanded isothermally and reversibly from 1 litre to 10 litre at 300 K. The enthalpy change (in kJ) for the process is (2004S)
   (a) 11.4 kJ
   (b) -11.4 kJ
   (c) 0 kJ
   (d) 4.8 kJ

9. The enthalpy of vaporization of liquid is 30 kJ mol\(^{-1}\) and entropy of vaporization is 75 J mol\(^{-1}\) K. The boiling point of the liquid at 1 atm is (2004S)
   (a) 250 K
   (b) 400 K
   (c) 450 K
   (d) 600 K

10. The direct conversion of A to B is difficult, hence it is carried out by the following shown path:

\[ \text{C} \rightarrow \text{D} \]

Given
\[ \Delta S(A \rightarrow C) = 50 \text{ e.u.}, \Delta S(C \rightarrow D) = 30 \text{ e.u.}, \Delta S(B \rightarrow D) = 20 \text{ e.u.} \]
where e.u. is the entropy unit, then \( \Delta S(A \rightarrow B) \) is (2006 - 3M, -1)
   (a) +60 e.u.
   (b) +100 e.u.
   (c) -60 e.u.
   (d) -100 e.u.
11. The value of $\log_{10} K$ for a reaction $A \underset{B}{\longrightarrow}$ is

\[ \Delta H_{298K}^{\text{o}} = -54.07 \text{ kJ mol}^{-1}, \quad \Delta S_{298K}^{\text{o}} = 10 \text{ JK}^{-1} \text{ mol}^{-1} \text{ and} \quad R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}; \]
\[ 2.303 \times 8.314 \times 298 = 5705 \]

(a) 5  
(b) 10  
(c) 95  
(d) 100  

(2007)

12. For the process $\text{H}_2\text{O}(l)$ (1 bar, 373 K) $\rightarrow \text{H}_2\text{O}(g)$ (1 bar, 373 K), the correct set of thermodynamic parameters is (2007)

(a) $\Delta G = 0$, $\Delta S = +ve$  
(b) $\Delta G = 0$, $\Delta S = -ve$  
(c) $\Delta G = +ve$, $\Delta S = 0$  
(d) $\Delta G = -ve$, $\Delta S = +ve$  

(2010)

13. The species which by definition has ZERO standard molar enthalpy of formation at 298 K is

(a) Br$_2$ (g)  
(b) Cl$_2$ (g)  
(c) H$_2$O (g)  
(d) CH$_4$ (g)  

(2013-I)

14. The standard enthalpies of formation of CO$_2$(g), H$_2$O(l) and glucose(s) at 25°C are $-390$ kJ/mol, $-286$ kJ/mol and $-1300$ kJ/mol, respectively. The standard enthalpy of combustion per gram of glucose at 25°C is (2013-I)

(a) $+2900$ kJ  
(b) $-2900$ kJ  
(c) $-161.11$ kJ  
(d) $+161.11$ kJ  

(2016)

15. For the process $\text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(g)$

(a) $\Delta S_{\text{system}} > 0$ and $\Delta S_{\text{surroundings}} > 0$  
(b) $\Delta S_{\text{system}} > 0$ and $\Delta S_{\text{surroundings}} < 0$  
(c) $\Delta S_{\text{system}} < 0$ and $\Delta S_{\text{surroundings}} > 0$  
(d) $\Delta S_{\text{system}} < 0$ and $\Delta S_{\text{surroundings}} < 0$  

(2014)

16. One mole of an ideal gas at 300 K in thermal contact with surroundings expands isothermally from 1.0 L to 2.0 L against a constant pressure of 3.0 atm. In this process, the change in entropy of surroundings ($\Delta S_{\text{sur}}$) in JK$^{-1}$ is

(a) 5.763  
(b) 1.013  
(c) $-1.013$  
(d) $-5.763$  

(2016)

6. The reversible expansion of an ideal gas under adiabatic and isothermal conditions is shown in the figure. Which of the following statement(s) is (are) correct?

(a) $T_1 = T_2$  
(b) $T_2 > T_1$  
(c) $w_{\text{isothermal}} > w_{\text{adiabatic}}$  
(d) $\Delta U_{\text{isothermal}} > \Delta U_{\text{adiabatic}}$  

(2014)

7. An ideal gas in a thermally insulated vessel at internal pressure $P_1$, volume $V_1$, and absolute temperature $T_1$ expands irreversibly against zero external pressure, as shown in the diagram. The final internal pressure, volume, and absolute temperature of the gas are $P_2$, $V_2$ and $T_2$, respectively. For this expansion,

(a) $q = 0$  
(b) $T_2 = T_1$  
(c) $P_2 V_2 = P_1 V_1$  
(d) $P_2 V_2 = P_1 V_1$  

(2014)

D | MCQs with One or More Than One Correct

1. Identify the intensive quantities from the following: (1993 - 1 Mark)

(a) Enthalpy  
(b) Temperature  
(c) Volume  
(d) Refractive Index  

2. The following is (are) endothermic reaction(s): (1999 - 3 Marks)

(a) Combustion of methane  
(b) Decomposition of water  
(c) Dehydrogenation of ethane to ethylene  
(d) Conversion of graphite to diamond  

3. Among the following state function(s) is (are) (2009)

(a) Internal energy  
(b) Irreversible expansion work  
(c) Reversible expansion work  
(d) Molar enthalpy  

4. Among the following, the intensive property is (properties are) (2010)

(a) molar conductivity  
(b) electromotive force  
(c) resistance  
(d) heat capacity  

5. For an ideal gas, consider only P–V work in going from an initial state X to the final state Z. The final state Z can be reached by either of the two paths shown in the figure. Which of the following choice(s) is (are) correct?

(2007)

E | Subjective Problems

1. The enthalpy for the following reaction ($\Delta H^\circ$) at 25°C are given below: (1981 - 2 Marks)

(i) $\frac{1}{2} \text{H}_2(g) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{OH}(g)$ 10.06 kcal  
(ii) $\text{H}_2(g) \rightarrow 2\text{H}(g)$ 104.18 kcal  
(iii) $\text{O}_2(g) \rightarrow 2\text{O}(g)$ 118.32 kcal  

Calculate the O–H bond energy in the hydroxyl radical.
2. The molar heats of combustion of C₂H₂(g), C(graphite) and H₂(g) are 310.62 kcal, 94.05 kcal and 68.32 kcal, respectively. Calculate the standard heat of formation of C₂H₂(g).

   \[ \Delta H_f \] (1983 - 2 Marks)

3. The heat energy, q, absorbed by a gas \( \Delta H \), is true at what condition(s).

   \[ \text{(1984 - 1 Mark)} \]

4. Given the following standard heats of reactions:
   (i) heat of formation of water = −68.3 kcal;
   (ii) heat of combustion of acetylene = −310.6 kcal;
   (iii) heat of combustion of ethylene = −337.2 kcal;
   Calculate the heat of reaction for the hydrogenation of acetylene at constant volume (25°C).

   \[ \text{(1984 - 4 Marks)} \]

5. The bond dissociation energies of gaseous \( \text{H}_2, \text{Cl}_2 \) and \( \text{HCl} \) are 104, 58 and 103 kcal/mole respectively. Calculate the enthalpy of formation of \( \text{HCl} \) gas.

   \[ \text{(1985 - 2 Marks)} \]

6. The standard molar heats of formation of ethane, carbon dioxide and liquid water are −21.1, −94.1 and −68.3 kcal respectively. Calculate the standard molar heat of combustion of ethane.

   \[ \text{(1986 - 2 Marks)} \]

7. An intimate mixture of ferric oxide, \( \text{Fe}_2\text{O}_3 \), and aluminium, \( \text{Al} \), is used in solid fuel rockets. Calculate the fuel value per gram and fuel value per cc of the mixture. Heats of formation and densities are as follows:

   \[ \text{(1988 - 2 Marks)} \]

8. An athlete is given 100 gm of glucose \( (\text{C}_6\text{H}_12\text{O}_6) \) of energy equivalent to 1560 kJ. He utilizes 50 per cent of this gained energy in the event. In order to avoid storage of energy in the body, calculate the weight of water he would need to perspire. The enthalpy of vaporization of water is 44 kJ/mole.

   \[ \text{(1989 - 2 Marks)} \]

9. The standard enthalpy of combustion at 25°C of hydrogen, cyclohexene \( \text{(C}_6\text{H}_{10}) \) and cyclohexane \( \text{(C}_6\text{H}_{12}) \) are −241, −3800 and −3920 kJ/mole respectively. Calculate the heat of hydrogenation of cyclohexene.

   \[ \text{(1989 - 2 Marks)} \]

10. Using the data (all values are in kcal mol\(^{-1}\)) at 25°C given below, calculate the bond energy of C–C and C–H bonds.

    \[ \text{(1990 - 5 Marks)} \]

11. A gas mixture of 3.67 litres of ethylene and methane on complete combustion at 25°C produces 6.11 litres of CO₂. Find out the amount of heat evolved on burning one litre of the gas mixture. The heats of combustion of ethylene and methane are −1423 and −891 kJ mol\(^{-1}\) at 25°C.

    \[ \text{(1991 - 5 Marks)} \]

12. Determine the enthalpy change of the reaction:

    \[ \text{C}_2\text{H}_4(g) + \text{H}_2(g) \rightarrow \text{C}_2\text{H}_5(g) + \text{CH}_4(g), \text{at } 25^\circ \text{C, using the given heat of combustion values under standard conditions:} \]

    \[ \text{Compound} \quad \text{H}_2(g) \quad \text{CH}_4(g) \quad \text{C}_2\text{H}_2(g) \quad \text{C(graphite)} \]

    \[ \Delta H_f \text{(kJ/mol)} \quad -285.8 \quad -890.0 \quad -1560.0 \quad -393.5 \]

    The standard heat of formation of \( \text{C}_2\text{H}_4(g) \) is −103.8 kJ mol\(^{-1}\).

    \[ \text{(1992 - 3 Marks)} \]

13. In order to get maximum calorific output, a burner should have an optimum fuel to oxygen ratio which corresponds to 3 times as much oxygen as is required theoretically for complete combustion of the fuel. A burner which has been adjusted for methane as fuel (with x litre/hour of \( \text{CH}_4 \) and 6x litre/hour of \( \text{O}_2 \)) is to be readjusted for butane, \( \text{C}_4\text{H}_{10} \). In order to get the same calorific output, what should be the rate of supply of butane and oxygen? Assume that losses due to incomplete combustion, etc, are the same for both the fuels and the gases behave ideally.

    \[ \text{(1993 - 3 Marks)} \]

    Heats of combustion:

    \[ \text{CH}_4 = 809 \text{ kJ/mol; } \text{C}_4\text{H}_{10} = 2878 \text{ kJ/mol} \]

14. The polymerisation of ethylene to linear polyethylene is represented by the reaction

    \[ n\text{CH}_2 = \text{CH}_2 \xrightarrow{\Delta} \text{CH}_2 - \text{CH}_2 - \text{H} \]

    where \( n \) has a large integral value. Given that the average enthalpies of bond dissociation for \( \text{C} = \text{C} \) and \( \text{C} = \text{C} \) at 298 K are +590 and +331 kJ mol\(^{-1}\) respectively, calculate the enthalpy of polymerisation per mole of ethylene at 298 K.

    \[ \text{(1994 - 2 Marks)} \]

15. The standard molar enthalpies of formation of cyclohexene(\( \text{C}_6\text{H}_{10} \)) and benzene(\( \text{C}_6\text{H}_6 \)) at 25°C are −156 and +49 kJ mol\(^{-1}\) respectively. The standard enthalpy of hydrogenation of cyclohexene(\( \text{C}_6\text{H}_{10} \)) at 25°C is −119 kJ mol\(^{-1}\). Use these data to estimate the magnitude of the resonance energy of benzene.

    \[ \text{(1996 - 2 Marks)} \]

16. Compute the heat of formation of liquid methyl alcohol in kilojoules per mole, using the following data. Heat of vaporization of liquid methyl alcohol = 38 kJ/mol. Heat of formation of gaseous atoms from the elements in their standard states; H, 218 kJ/mol; C, 715 kJ/mol; O, 249 kJ/mol.

    Average bond energies:

    \[ \text{C} = \text{H} = 415 \text{kJ/mol; } \text{C} = \text{O} = 365 \text{kJ/mol, } \text{O} = \text{H} = 463 \text{kJ/mol} \]

    \[ \text{(1997 - 5 Marks)} \]

17. Anhydrous \( \text{AlCl}_3 \) is covalent. From the data given below, predict whether it would remain covalent or become ionic in aqueous solution. (Ionisation energy for \( \text{Al} = 5137 \text{kJ mol}^{-1} \), \( \Delta H_{\text{hydration}} \) for \( \text{Al}^{3+} = -4665 \text{kJ mol}^{-1} \), \( \Delta H_{\text{hydration}} \) for \( \text{Cl}^- = -381 \text{kJ mol}^{-1} \).)

    \[ \text{(1997 - 2 Marks)} \]

18. From the following data, calculate the enthalpy change for the combustion of cyclopropane at 298 K. The enthalpy of formation of \( \text{CO}_2(g) \), \( \text{H}_2\text{O}(l) \) and propene(\( g \)) are −393.5, −285.8 and 20.42 kJ mol\(^{-1}\) respectively. The enthalpy of isomerisation of cyclopropane to propene is −33.0 kJ mol\(^{-1}\).

    \[ \text{(1998 - 5 Marks)} \]
19. Estimate the average S–F bond energy in SF₆. The values of standard enthalpy of formation of SF₆(g), S(g) and F(g) are: -1100, 275 and 80 kJ mol⁻¹ respectively. 

(1999 - 3 Marks)

20. A sample of argon gas at 1 atm pressure and 27°C expands reversibly and adiabatically from 1.25 dm³ to 2.50 dm³. Calculate the enthalpy change in this process. Cᵥₘ for argon is 12.48 J K⁻¹ mol⁻¹. 

(2000 - 4 Marks)

21. Show that the reaction CO(g) + \( \frac{1}{2} \) O₂(g) \( \rightarrow \) CO₂(g) at 300 K is spontaneous and exothermic, when the standard entropy change is -0.094 kJ mol⁻¹ K⁻¹. The standard Gibbs free energies of formation for CO₂ and CO are -394.4 and -137.2 kJ mol⁻¹, respectively. 

(2000 - 3 Marks)

22. Diborane is a potential rocket fuel which undergoes combustion according to the reaction: B₃H₆(g) + 3 O₂(g) \( \rightarrow \) B₂O₃(s) + 3H₂O(g) 

From the following data, calculate the enthalpy change for the combustion of diborane: 

\[ 2B(s) + \frac{3}{2} O₂(g) \rightarrow B₂O₃(s) \quad \Delta H = -1273 \text{ kJ mol}⁻¹ \]

\[ H₂(g) + \frac{1}{2} O₂(g) \rightarrow H₂O(l) \quad \Delta H = -286 \text{ kJ mol}⁻¹ \]

\[ H₂O(l) \rightarrow H₂O(g) \quad \Delta H = 44 \text{ kJ mol}⁻¹ \]

\[ 2B(s) + 3H₂(g) \rightarrow B₂H₆(g) \quad \Delta H = 36 \text{ kJ mol}⁻¹ \]

(2000 - 2 Marks)

23. When 1-pentyne (A) is treated with 4 N alcoholic KOH at 175°C, it is converted slowly into an equilibrium mixture of 1.3% 1-pentyne (A), 95.2% 2-pentyne (B) and 3.5% of 1, 2-pentadiene (C). The equilibrium was maintained at 175°C. Calculate \( \Delta G^o \) for the following equilibria:

\[ B \underset{A}{\overset{G_1^o}{\rightleftharpoons}} \quad B \underset{C}{\overset{G_2^o}{\rightleftharpoons}} \]

From the calculated value of \( \Delta G_1^o \) and \( \Delta G_2^o \) indicate the order of stability of (A), (B) and (C). Write a reasonable reaction mechanism showing all intermediates leading to (A), (B) and (C). 

(2001 - 10 Marks)

24. Two moles of a perfect gas undergo the following processes:

(a) a reversible isobaric expansion from (1.0 atm, 20.0 L) to (1.0 atm, 40.0 L); 

(b) a reversible isochoric change of state from (1.0 atm, 40.0 L) to (0.5 atm, 40.0 L); 

(c) a reversible isothermal compression from (0.5 atm, 40.0 L) to (1.0 atm, 20.0 L). 

(i) Sketch with labels each of the processes on the same P-V diagram. 

(ii) Calculate the total work (w) and the total heat change (q) involved in the above processes. 

(iii) What will be the values of \( \Delta U \), \( \Delta H \) and \( \Delta S \) for the overall process?

(2002 - 5 Marks)

25. Cᵥ value of He is always 3R/2 but Cᵥ value of H₂ is 3R/2 at low temperature and 5R/2 at moderate temperature and more than 5R/2 at higher temperature explain in two to three lines. 

(2003 - 2 Marks)

26. An insulated container contains 1 mol of a liquid, molar volume 100 ml, at 1 bar. When liquid is steeply pressed to 100 bar, volume decreases to 99 ml. Find \( \Delta H \) and \( \Delta U \) for the process. 

(2004 - 2 Marks)

27. In the following equilibrium N₂O₄(g) \( \rightarrow \) 2NO₂(g) 

When 5 moles of each is taken and the temperature is kept at 298 K, the total pressure was found to be 20 bar. 

Given: \( \Delta G^o_f(N₂O₄) = 100kJ; \Delta G^o_f(NO₂) = 50 kJ \)

(i) Find \( \Delta G \) of the reaction at 298 K. 

(ii) Find the direction of the reaction 

(2004 - 2 Marks)

28. For the reaction, 2CO + O₂ \( \rightarrow \) 2CO₂; \( \Delta H = -560kJ \). Two moles of CO and one mole of O₂ are taken in a container of volume 1 L. They completely form two moles of CO₂, the gases deviate appreciably from ideal behaviour. If the pressure in the vessel changes from 70 to 40 atm, find the magnitude (absolute value) of \( \Delta U \) at 500 K. (1 L atm = 0.1 kJ) 

(2006 - 6M)

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Match The Following

**F**

**DIRECTION (Q. 1 & 2): Each question contains statements given in two columns, which have to be matched. The statements in Column-I are labelled A, B, C and D, while the statements in Column-II are labelled p, q, r and s. Any given statement in Column-I can have correct matching with ONE OR MORE statement(s) in Column-II. The appropriate bubbles corresponding to the answers to these questions have to be darkened as illustrated in the following example:

If the correct matches are A-p, s and t; B-q and r; C-p and q; and D-s then the correct darkening of bubbles will look like the given.

(2011)

<table>
<thead>
<tr>
<th>Column-I</th>
<th>Column-II</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A) CO₂(g) ( \rightarrow ) CO₂(g)</td>
<td>(p) phase transition</td>
</tr>
<tr>
<td>(B) CaCO₃(s) ( \rightarrow ) CaO(s) + CO₂(g)</td>
<td>(q) allotropic change</td>
</tr>
<tr>
<td>(C) 2H₂(g) ( \rightarrow ) H₂(g)</td>
<td>(r) ( \Delta H ) is positive</td>
</tr>
<tr>
<td>(D) P₄(white, solid) ( \rightarrow ) P₄(red, solid)</td>
<td>(s) ( \Delta S ) is positive</td>
</tr>
<tr>
<td></td>
<td>(t) ( \Delta S ) is negative</td>
</tr>
</tbody>
</table>
2. Match the thermodynamic processes given under Column-I with the expressions given under Column-II.

<table>
<thead>
<tr>
<th>Column-I</th>
<th>Column-II</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A) Freezing of water at 273 K and 1 atm</td>
<td>(p) ( q = 0 )</td>
</tr>
<tr>
<td>(B) Expansion of 1 mol of an ideal gas into a vacuum under isolated conditions</td>
<td>(q) ( w = 0 )</td>
</tr>
<tr>
<td>(C) Mixing of equal volumes of two ideal gases at constant temperature and pressure in an isolated container</td>
<td>(r) ( \Delta S_{sys} &lt; 0 )</td>
</tr>
<tr>
<td>(D) Reversible heating of ( \text{H}_2(g) ) at 1 atm from 300 K to 600 K, followed by reversible cooling to 300 K at 1 atm</td>
<td>(s) ( \Delta U = 0 )</td>
</tr>
<tr>
<td>(t) ( \Delta G = 0 )</td>
<td></td>
</tr>
</tbody>
</table>

(c) If assertion is CORRECT, but reason is INCORRECT.
(d) If assertion is INCORRECT, but reason is CORRECT.

Statement - 1: There is a natural asymmetry between converting work to heat and converting heat to work and
Statement - 2: No process is possible in which the sole result is the absorption of heat from a reservoir and its complete conversion into work. (2008S)
(a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
(b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.
(c) Statement-1 is True, Statement-2 is False
(d) Statement-1 is False, Statement-2 is True

I Integer Value Correct Type

1. In a constant volume calorimeter, 3.5 g of a gas with molecular weight 28 was burnt in excess oxygen at 298.0 K. The temperature of the calorimeter was found to increase from 298.0 K to 298.45 K due to the combustion process. Given that the heat capacity of the calorimeter is 2.5 kJ K\(^{-1}\), the numerical value for the enthalpy of combustion of the gas in kJ mol\(^{-1}\) is (2009 - 6M)

2. One mole of an ideal gas is taken from \( a \) to \( b \) along two paths denoted by the solid and the dashed lines as shown in the graphs below. If the work done along the solid line path \( w_s \) and that along the dotted line path is \( w_d \), then the integer closest to the ratio \( w_d / w_s \) is : (2010)
Section-B

JEE Main / AIEEE

1. If an endothermic reaction is non-spontaneous at freezing point of water and becomes feasible at its boiling point, then
(a) \( \Delta H \) is –ve, \( \Delta S \) is +ve [2002]
(b) \( \Delta H \) and \( \Delta S \) both are +ve
(c) \( \Delta H \) and \( \Delta S \) both are –ve
(d) \( \Delta H \) is +ve, \( \Delta S \) is –ve

2. A heat engine absorbs heat \( Q_1 \) at temperature \( T_1 \) and heat \( Q_2 \) at temperature \( T_2 \). Work done by the engine is \( J (Q_1 + Q_2) \). This data violates 1st law of thermodynamics [2002]
(a) violates 1st law of thermodynamics [2002]
(b) violates 1st law of thermodynamics if \( Q_1 \) is –ve
(c) violates 1st law of thermodynamics if \( Q_2 \) is –ve
(d) does not violate 1st law of thermodynamics.

3. For the reactions, [2002]
\[ 2C + O_2 \rightarrow 2CO_2 ; \quad \Delta H = -393 \text{ J} \]
\[ 2Zn + O_2 \rightarrow 2ZnO ; \quad \Delta H = -412 \text{ J} \]
(a) carbon can oxidise Zn
(b) oxidation of carbon is not feasible
(c) oxidation of Zn is not feasible
(d) Zn can oxidise carbon.

4. The heat required to raise the temperature of body by 1 K is called [2002]
(a) specific heat
(b) thermal capacity
(c) water equivalent
(d) none of these.

5. The internal energy change when a system goes from state A to B is 40 kJ/mole. If the system goes from A to B by a reversible path and returns to state A by an irreversible path what would be the net change in internal energy? [2003]
(a) > 40 kJ
(b) < 40 kJ
(c) Zero
(d) 40 kJ

6. If at 298 K the bond energies of \( \text{C} \rightarrow \text{H}, \text{C} \rightarrow \text{C}, \text{C} \rightarrow \text{H} \) and \( \text{H} \) are 414, 347, 615 and 435 kJ mol\(^{-1}\), the value of enthalpy change for the reaction
\[ \text{H}_2 \text{C} = \text{CH}_2 (g) + \text{H}_2 (g) \rightarrow \text{H}_2 \text{C} \rightarrow \text{CH}_3 (g) \] at 298 K will be [2003]
(a) -250 kJ
(b) +125 kJ
(c) -125 kJ
(d) +250 kJ

7. In an irreversible process taking place at constant T and P and in which only pressure-volume work is being done, the change in Gibbs free energy (\( dG \)) and change in entropy (\( dS \)), satisfy the criteria [2003]
(a) \( (dS)_{V,E} > 0, (dG)_{T,P} < 0 \)
(b) \( (dS)_{V,E} = 0, (dG)_{T,P} = 0 \)
(c) \( (dS)_{V,E} = 0, (dG)_{T,P} > 0 \)
(d) \( (dS)_{V,E} < 0, (dG)_{T,P} < 0 \)

8. The correct relationship between free energy change in a reaction and the corresponding equilibrium constant \( K_c \) is [2003]
(a) \( -\Delta G = RT \ln K_c \)
(b) \( \Delta G^0 = RT \ln K_c \)
(c) \( -\Delta G^0 = RT \ln K_c \)
(d) \( \Delta G = RT \ln K_c \)

9. The enthalpy change for a reaction does not depend upon [2003]
(a) use of different reactants for the same product
(b) the nature of intermediate reaction steps
(c) the differences in initial or final temperatures of involved substances
(d) the physical states of reactants and products

10. An ideal gas expands in volume from \( 1 \times 10^{-2} \) to \( 1 \times 10^{-2} \) m\(^3\) at 300 K against a constant pressure of \( 1 \times 10^5 \) N m\(^{-2}\). The work done is [2004]
(a) 270 kJ
(b) -900 kJ
(c) -900
(d) 900 kJ

11. The enthalpies of combustion of carbon and carbon monoxide are -393.5 and -283 kJ mol\(^{-1}\) respectively. The enthalpy of formation of carbon monoxide per mole is [2004]
(a) -676.5 kJ
(b) 676.5 kJ
(c) 110.5 kJ
(d) -110.5 kJ

12. Consider an endothermic reaction \( X \rightarrow Y \) with the activation energies \( E_b \) and \( E_f \) for the backward and forward reactions, respectively. In general [2005]
(a) there is no definite relation between \( E_b \) and \( E_f \)
(b) \( E_b = E_f \)
(c) \( E_b > E_f \)
(d) \( E_b < E_f \)

13. Consider the reaction: \( \text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3 \) carried out at constant temperature and pressure. If \( \Delta H \) and \( \Delta U \) are the enthalpy and internal energy changes for the reaction, which of the following expressions is true? [2005]
(a) \( \Delta H > \Delta U \)
(b) \( \Delta H < \Delta U \)
(c) \( \Delta H = \Delta U \)
(d) \( \Delta H = 0 \)

14. If the bond dissociation energies of \( \text{XY} \), \( \text{X}_2 \) and \( \text{Y}_2 \) (all diatomic molecules) are in the ratio of \( 1:1:0.5 \) and \( \Delta H_f \) for the formation of \( \text{XY} \) is \( -200 \) kJ mole\(^{-1}\). The bond dissociation energy of \( \text{X}_2 \) will be [2005]
(a) 400 kJ mol\(^{-1}\)
(b) 300 kJ mol\(^{-1}\)
(c) 200 kJ mol\(^{-1}\)
(d) 100 kJ mol\(^{-1}\)
15. An ideal gas is allowed to expand both reversibly and irreversibly in an isolated system. If $T_i$ is the initial temperature and $T_f$ is the final temperature, which of the following statements is correct?  
(a) $T_{rev} = T_{irrev}$  
(b) $T_f = T_i$ for both reversible and irreversible processes  
(c) $T_{irrev} > T_{rev}$  
(d) $T_f > T_i$ for reversible process but $T_f = T_i$ for irreversible process  

16. The standard enthalpy of formation ($\Delta H^\circ$) at 298 K for methane, $\text{CH}_4(g)$ is $-74.8 \text{ kJ mol}^{-1}$. The additional information required to determine the average energy for $\text{C} - \text{H}$ bond formation would be  
(a) the first four ionization energies of carbon and electron gain enthalpy of hydrogen  
(b) the dissociation energy of hydrogen molecule, $\text{H}_2$  
(c) the dissociation energy of $\text{H}_2$ and enthalpy of sublimation of carbon  
(d) latent heat of vaporization of methane  

17. The enthalpy changes for the following processes are listed below.  

- $\text{Cl}_2(g) \rightarrow 2\text{Cl}(g)$, 242.3 kJ mol\(^{-1}\)  
- $\text{I}_2(g) \rightarrow 2\text{I}(g)$, 151.0 kJ mol\(^{-1}\)  
- $\text{ICl}(g) \rightarrow \text{I}(g) + \text{Cl}(g)$, 211.3 kJ mol\(^{-1}\)  
- $\text{I}_2(s) \rightarrow \text{I}_2(g)$, 62.76 kJ mol\(^{-1}\)  

Given that the standard states for iodine and chlorine are $\text{I}_2(s)$ and $\text{Cl}_2(g)$, the standard enthalpy of formation for $\text{ICl}(g)$ is:  
(a) $+16.8 \text{ kJ mol}^{-1}$  
(b) $+244.8 \text{ kJ mol}^{-1}$  
(c) $-14.6 \text{ kJ mol}^{-1}$  
(d) $-16.8 \text{ kJ mol}^{-1}$  

18. ($\Delta H - \Delta U$) for the formation of carbon monoxide (CO) from its elements at 298 K is  

\[ (R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \]  

(a) $-2477.571 \text{ J mol}^{-1}$  
(b) $2477.571 \text{ J mol}^{-1}$  
(c) $-1238.781 \text{ J mol}^{-1}$  
(d) $1238.781 \text{ J mol}^{-1}$  

19. In conversion of lime-stone to lime,  

$\text{CaCO}_3(s) \rightarrow \text{CaO(s)} + \text{CO}_2(g)$ the values the of $\Delta H^\circ$ and $\Delta S^\circ$ are $+179.1 \text{ kJ mol}^{-1}$ and 160.2 J/K respectively at 298 K and 1 bar. Assuming that $\Delta H^\circ$ and $\Delta S^\circ$ do not change with temperature, temperature above which conversion of limestone to lime will be spontaneous is  

(a) 1118 K  
(b) 1008 K  
(c) 1200 K  
(d) 845 K.  

20. Assuming that water vapour is an ideal gas, the internal energy change ($\Delta U$) when 1 mol of water is vapourised at 1 bar pressure and 100°C, given : molar enthalpy of vapourisation of water at 1 bar and 373 K = 41 kJ mol\(^{-1}\) and $R = 8.3 \text{ J mol}^{-1} \text{ K}^{-1}$ will be  

(a) 41.00 kJ mol\(^{-1}\)  
(b) 4.100 kJ mol\(^{-1}\)  
(c) 3.7904 kJ mol\(^{-1}\)  
(d) 37.904 kJ mol\(^{-1}\)  

21. Identify the correct statement regarding a spontaneous process:  
(a) Lowering of energy in the process is the only criterion for spontaneity.  
(b) For a spontaneous process in an isolated system, the change in entropy is positive.  
(c) Endothermic processes are never spontaneous.  
(d) Exothermic processes are always spontaneous.  

22. Oxidising power of chlorine in aqueous solution can be determined by the parameters indicated below:  

\[ \frac{1}{2}\text{Cl}_2(g) \rightarrow \frac{1}{2}\Delta\text{dissH}^\Theta \rightarrow \text{Cl}(g) \rightarrow \Delta\text{aqH}^\Theta \rightarrow \text{Cl}^-(g) \]  

\[ \Delta\text{HydH}^\Theta \rightarrow \text{Cl}^-(aq) \]  

(using the data,  
\[ \Delta\text{dissH}^\Theta \text{Cl}_2 = 240 \text{ kJ mol}^{-1}, \]  
\[ \Delta\text{aqH}^\Theta \text{Cl}^- = -349 \text{ kJ mol}^{-1}, \]  
\[ \Delta\text{hydH}^\Theta \text{Cl}^- = -381 \text{ kJ mol}^{-1} \]  

will be)  

(a) $+152 \text{ kJ mol}^{-1}$  
(b) $-610 \text{ kJ mol}^{-1}$  
(c) $-850 \text{ kJ mol}^{-1}$  
(d) $+120 \text{ kJ mol}^{-1}$  

23. Standard entropy of $X_2$, $Y_2$ and $XY_3$ are 60, 40 and 50 $\text{ JK}^{-1} \text{ mol}^{-1}$ respectively. For the reaction,  

\[ \frac{1}{2}X_2 + \frac{3}{2}Y_2 \rightarrow XY_3, \Delta H = -30 \text{ kJ} \]  

to be at equilibrium, the temperature will be  

(a) 1250 K  
(b) 500 K  
(c) 750 K  
(d) 1000 K  

24. On the basis of the following thermochemical data :  

\[ (\Delta G^\circ\text{H}_2O(aq) = 0) \]  

\[ \text{H}_2\text{O}(l) \rightarrow \text{H}^+(aq) + \text{OH}^-(aq); \Delta H = 57.32 \text{ kJ} \]  

\[ \text{H}_2(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{H}_2\text{O}(l); \Delta H = -286.20 \text{ kJ} \]  

The value of enthalpy of formation of $\text{OH}^-$ ion at 25°C C is:  

(a) $-228.88 \text{ kJ}$  
(b) +228.88 kJ  
(c) $-343.52 \text{ kJ}$  
(d) $-22.88 \text{ kJ}$  

25. The standard enthalpy of formation of $\text{NH}_3$ is $-46.0 \text{ kJ mol}^{-1}$. If the enthalpy of formation of $\text{H}_2$ from its atoms is $-436 \text{ kJ mol}^{-1}$ and that of $\text{N}_2$ is $-712 \text{ kJ mol}^{-1}$, the average bond enthalpy of $\text{N} - \text{H}$ bond in $\text{NH}_3$ is  

(a) $-964 \text{ kJ mol}^{-1}$  
(b) $+352 \text{ kJ mol}^{-1}$  
(c) $+1056 \text{ kJ mol}^{-1}$  
(d) $-1102 \text{ kJ mol}^{-1}$  

26. For a particular reversible reaction at temperature $T$, $\Delta H$ and $\Delta S$ were found to be both +ve. If $T_e$ is the temperature at equilibrium, the reaction would be spontaneous when  

(a) $T_e > T$  
(b) $T > T_e$  
(c) $T_e$ is 5 times $T$  
(d) $T = T_e$
27. The entropy change involved in the isothermal reversible expansion of 2 mole of an ideal gas from a volume of 10 dm$^3$ to a volume of 100 dm$^3$ at 27°C is:

- (a) 38.3 J mol$^{-1}$ K$^{-1}$
- (b) 35.8 J mol$^{-1}$ K$^{-1}$
- (c) 32.3 J mol$^{-1}$ K$^{-1}$
- (d) 42.3 J mol$^{-1}$ K$^{-1}$

28. The incorrect expression among the following is:

- (a) $\frac{\Delta G_{\text{system}}}{\Delta S_{\text{total}}} = -T$
- (b) In isothermal process, $w_{\text{reversible}} = -nRT \ln \frac{V_f}{V_i}$
- (c) $\ln K = \frac{\Delta H^o - T\Delta S^o}{RT}$
- (d) $K = e^{-\Delta G^o/RT}$

29. A piston filled with 0.04 mol of an ideal gas expands reversibly from 50.0 mL to 375 mL at a constant temperature of 37°C. As it does so, it absorbs 208 J of heat. The values of $q$ and $w$ for the process will be:

- (a) $q = +208$ J, $w = -208$ J
- (b) $q = -208$ J, $w = +208$ J
- (c) $q = -208$ J, $w = +208$ J
- (d) $q = +208$ J, $w = +208$ J

30. For complete combustion of ethanol, $\text{C}_2\text{H}_5\text{OH}(l) + 3\text{O}_2(g) \rightarrow 2\text{CO}_2(g) + 3\text{H}_2\text{O}(l)$, the amount of heat produced as measured in bomb calorimeter, is 1364.47 kJ mol$^{-1}$ at 25°C. Assuming ideality, the enthalpy of combustion, $\Delta_c^o\text{H}$, for the reaction will be:

- (a) $-1366.95$ kJ mol$^{-1}$
- (b) $-1361.95$ kJ mol$^{-1}$
- (c) $-1460.95$ kJ mol$^{-1}$
- (d) $-1350.50$ kJ mol$^{-1}$

31. The heats of combustion of carbon and carbon monoxide are $-393.5$ and $-283.5$ kJ mol$^{-1}$, respectively. The heat of formation (in kJ) of carbon monoxide per mole is:

- (a) $-676.5$
- (b) $-110.5$
- (c) $110.5$
- (d) $676.5$
CHAPTER 7

Equilibrium

Section-A

A Fill in the Blanks

1. The conjugate base of HSO₄⁻ in aqueous solution is .............. (1982 - 1 Mark)
2. An element which can exist as a positive ion in acidic solution and also as a negative ion in basic solution is said to be .................. (1984 - 1 Mark)
3. For a given reversible reaction at a fixed temperature, equilibrium constants K_p and K_c are related by........... (1994 - 1 Mark)
4. A ten-fold increase in pressure on the reaction, N₂(g) + 3H₂(g) ⇌ 2NH₃(g) at equilibrium results in .... in K_p (1996 - 1 Mark)
5. In the reaction I⁻ + I₂ → I₃⁻, the Lewis acid is ............. (1997 - 1 Mark)

B True / False

1. Aluminium chloride (AlCl₃) is a Lewis acid because it can donate electrons. (1982 - 1 Mark)
2. If equilibrium constant for the reaction A₂ + B₂ ⇌ 2AB, is K, then for the backward reaction AB ⇌ ½ A₂ + ½ B₂, the equilibrium constant is 1/K. (1984 - 1 Mark)
3. When a liquid and its vapour are at equilibrium and the pressure is suddenly decreased, cooling occurs. (1984 - 1 Mark)
4. Solubility of sodium hydroxide increases with increase in temperature. (1985 - ½ Mark)

C MCQs with One Correct Answer

1. Molten sodium chloride conducts electricity due to the presence of (1981 - 1 Mark)
   (a) free electrons (b) free ions (c) free molecules (d) atoms of sodium and chlorine
2. An acidic buffer solution can be prepared by mixing the solutions of (1981 - 1 Mark)
   (a) ammonium acetate and acetic acid (b) ammonium chloride and ammonium hydroxide (c) sulphuric acid and sodium sulphate (d) sodium chloride and sodium hydroxide.
3. The pH of a 10⁻⁸ molar solution of HCl in water is (1981 - 1 Mark)
   (a) 8 (b) -8 (c) between 7 and 8 (d) between 6 and 7
4. The oxidation of SO₂ by O₂ to SO₃ is an exothermic reaction. The yield of SO₃ will be maximum if (1981 - 1 Mark)
   (a) temperature is increased and pressure is kept constant (b) temperature is reduced and pressure is increased (c) both temperature and pressure are increased (d) both temperature and pressure are reduced
5. For the reaction: H₂(g) + I₂(g) ⇌ 2HI(g) the equilibrium constant K_p changes with (1981 - 1 Mark)
   (a) total pressure (b) catalyst (c) the amounts of H₂ and I₂ present (d) temperature
6. Of the given anions, the strongest Bronsted base is (1981 - 1 Mark)
   (a) ClO⁻ (b) ClO₂⁻ (c) ClO₃⁻ (d) ClO₄⁻
7. At 90°C, pure water has [H₃O⁺] 10⁻⁶ mole litre⁻¹. What is the value of K_w at 90°C? (1981 - 1 Mark)
   (a) 10⁻⁶ (b) 10⁻¹² (c) 10⁻¹⁴ (d) 10⁻⁸
8. The precipitate of CaF₂(K_w = 1.7 × 10⁻¹⁰) is obtained when equal volumes of the following are mixed (1982 - 1 Mark)
   (a) 10⁻⁴M Ca²⁺ + 10⁻⁴M F⁻ (b) 10⁻²M Ca²⁺ + 10⁻³M F⁻ (c) 10⁻⁵M Ca²⁺ + 10⁻³M F⁻ (d) 10⁻³M Ca²⁺ + 10⁻⁵M F⁻
9. A liquid is in equilibrium with its vapour at its boiling point. On the average, the molecules in the two phases have equal : (1984 - 1 Mark)
   (a) inter-molecular forces (b) potential energy (c) total energy (d) kinetic energy
10. Pure ammonia is placed in a vessel at a temperature where its dissociation constant \( K_p \) is appreciable. At equilibrium:

\[ \text{(1984 - 1 Mark)} \]

(a) \( K_p \) does not change significantly with pressure.
(b) does not change with pressure.
(c) concentration of \( \text{NH}_3 \) does not change with pressure.
(d) concentration of hydrogen is less than that of nitrogen.

11. A certain buffer solution contains equal concentration of \( X^- \) and \( \text{HX} \). The \( K_p \) for \( X^- \) is \( 10^{-10} \). The pH of the buffer is:

\[ \text{(1984 - 1 Mark)} \]

(a) 4 \hspace{1cm} (b) 7 \hspace{1cm} (c) 10 \hspace{1cm} (d) 14

12. A certain weak acid has a dissociation constant of \( 1.0 \times 10^{-4} \). The equilibrium constant for its reaction with a strong base is:

\[ \text{(1984 - 1 Mark)} \]

(a) \( 1.0 \times 10^{-4} \) \hspace{1cm} (b) \( 1.0 \times 10^{-10} \) \hspace{1cm} (c) \( 1.0 \times 10^{10} \) \hspace{1cm} (d) \( 1.0 \times 10^{14} \)

13. An example of a reversible reaction is:

\[ \text{(1985 - 1 Mark)} \]

(a) \( \text{Pb(NO}_3\text{)}_2\text{aq} + 2\text{NaCl} \rightarrow \text{PbCl}_2\text{(s)} + 2\text{NaNO}_3\text{aq} \)
(b) \( \text{AgNO}_3\text{aq} + \text{HCl} \rightarrow \text{AgCl(s)} + \text{NaNO}_3\text{aq} \)
(c) \( 2\text{Na}(s) + \text{H}_2\text{O(l)} \rightarrow 2\text{NaOH}(aq) + \text{H}_2(g) \)
(d) \( \text{KNO}_3\text{aq} + \text{NaCl}(aq) \rightarrow \text{KCl}(aq) + \text{NaNO}_3\text{aq} \)

14. The best indicator for detection of end point in titration of a weak acid and a strong base is:

\[ \text{(1985 - 1 Mark)} \]

(a) methyl orange \( (3 \text{ to } 4) \)
(b) methyl red \( (5 \text{ to } 6) \)
(c) bromothymol blue \( (6 \text{ to } 7.5) \)
(d) phenolphthalein \( (8 \text{ to } 9.6) \)

15. The conjugate acid of \( \text{NH}_2^- \) is:

\[ \text{(1985 - 1 Mark)} \]

(a) \( \text{NH}_3 \) \hspace{1cm} (b) \( \text{NH}_2\text{OH} \)
(c) \( \text{NH}_4^+ \) \hspace{1cm} (d) \( \text{N}_2\text{H}_4 \)

16. The compound that is not a Lewis acid is:

\[ \text{(1985 - 1 Mark)} \]

(a) \( \text{BF}_3 \) \hspace{1cm} (b) \( \text{AlCl}_3 \)
(c) \( \text{BeCl}_2 \) \hspace{1cm} (d) \( \text{SnCl}_4 \)

17. The compound insoluble in acetic acid is:

\[ \text{(1986 - 1 Mark)} \]

(a) calcium oxide \hspace{1cm} (b) calcium carbonate
(c) calcium oxalate \hspace{1cm} (d) calcium hydroxide

18. The compound whose 0.1 M solution is basic is:

\[ \text{(1986 - 1 Mark)} \]

(a) ammonium acetate \hspace{1cm} (b) ammonium chloride
(c) ammonium sulphate \hspace{1cm} (d) sodium acetate

19. When equal volumes of the following solutions are mixed, precipitation of \( \text{AgCl} \) \( (K_p = 1.8 \times 10^{-10}) \) will occur only with:

\[ \text{(1988 - 1 Mark)} \]

(a) \( 10^{-4} \text{M} \text{(Ag}^+\text{)} \) and \( 10^{-4} \text{M} \text{(Cl}^-\text{)} \)
(b) \( 10^{-5} \text{M} \text{(Ag}^+\text{)} \) and \( 10^{-5} \text{M} \text{(Cl}^-\text{)} \)
(c) \( 10^{-6} \text{M} \text{(Ag}^+\text{)} \) and \( 10^{-6} \text{M} \text{(Cl}^-\text{)} \)
(d) \( 10^{-10} \text{M} \text{(Ag}^+\text{)} \) and \( 10^{-10} \text{M} \text{(Cl}^-\text{)} \)

20. The \( pK_p \) of acetylsalicylic acid (aspirin) is 3.5. The pH of gastric juice in human stomach is about 2-3 and the pH in the small intestine is about 8. Aspirin will be:

\[ \text{(1988 - 1 Mark)} \]

(a) unionised in the small intestine and in the stomach
(b) completely ionised in the small intestine and in the stomach
(c) ionised in the stomach and almost unionised in the small intestine
(d) ionised in the small intestine and almost unionised in the stomach.

21. Which one of the following is the strongest acid?

\[ \text{(1989 - 1 Mark)} \]

(a) \( \text{ClO}_2\text{(OH)} \)
(b) \( \text{ClO}_2\text{(OH)} \)
(c) \( \text{SO}_3\text{(OH)}_2 \)
(d) \( \text{SO}_3\text{(OH)}_2 \)

22. Amongst the following hydroxides, the one which has the lowest value of \( K_p \) at ordinary temperature (about 25°C) is:

\[ \text{(1990 - 1 Mark)} \]

(a) \( \text{Mg(OH)}_2 \)
(b) \( \text{Ca(OH)}_2 \)
(c) \( \text{Ba(OH)}_2 \)
(d) \( \text{Be(OH)}_2 \)

23. The reaction which proceeds in the forward direction is:

\[ \text{(1991 - 1 Mark)} \]

(a) \( \text{Fe}_2\text{O}_3 + 6\text{HCl} \rightarrow 2\text{FeCl}_3 + 3\text{H}_2\text{O} \)
(b) \( \text{NH}_3 + \text{H}_2\text{O} + \text{NaCl} \rightarrow \text{NH}_4\text{Cl} + \text{NaOH} \)
(c) \( \text{SnCl}_4 + \text{H}_2\text{O} \rightarrow \text{SnCl}_2 + 2\text{H}_2\text{Cl}_2 \)
(d) \( 2\text{Cu} + \text{I}_2 + 4\text{K}^+ \rightarrow 2\text{Cu}^{2+} + 4\text{KI} \)

24. The following equilibrium in established when hydrogen chloride is dissolved in acetic acid.

\[ \text{HCl + CH}_3\text{COOH} \rightleftharpoons \text{Cl}^- + \text{CH}_3\text{COOH}_2^+ \]

The set that characterises the conjugate acid-base pairs is:

\[ \text{(1992 - 1 Mark)} \]

(a) \( \text{HCl, CH}_3\text{COOH}^+_2 \) and \( \text{Cl}^- \)
(b) \( \text{HCl, CH}_3\text{COOH}_2^+ \) and \( \text{CH}_3\text{COOH}^- \)
(c) \( \text{CH}_3\text{COOH}_2^+, \text{HCl} \) and \( \text{Cl}^-, \text{CH}_3\text{COOH} \)
(d) \( \text{HCl, Cl}^- \) and \( \text{CH}_3\text{COOH}_2^+, \text{CH}_3\text{COOH} \)

25. Which of the following solutions will have pH close to 1.0?

\[ \text{(1992 - 1 Mark)} \]

(a) 100 ml of (M/10) HCl + 100 ml of (M/10) NaOH
(b) 55 ml of (M/10) HCl + 45 ml of (M/10) NaOH
(c) 10 ml of (M/10) HCl + 90 ml of (M/10) NaOH
(d) 75 ml of (M/5) HCl + 25 ml of (M/5) NaOH

26. The degree of dissociation of water at 25°C is \( 1.9 \times 10^{-7}% \) and density is 1.0 g cm\(^{-3}\). The ionic constant for water is:

\[ \text{(1995S)} \]

(a) \( 1.0 \times 10^{-10} \)
(b) \( 1.0 \times 10^{-14} \)
(c) \( 1.0 \times 10^{-16} \)
(d) \( 1.0 \times 10^{-8} \)

27. Which one is more acidic in aqueous solution?

\[ \text{(1995S)} \]

(a) \( \text{NiCl}_2 \)
(b) \( \text{FeCl}_3 \)
(c) \( \text{AlCl}_3 \)
(d) \( \text{BeCl}_2 \)

28. The following acids have been arranged in the order of decreasing acid strength. Identify the correct order.

\[ \text{ClO}_2\text{(I)}, \text{BrO}_2\text{(II)}, \text{IO}_2\text{(III)} \]

\[ \text{(1996 - 1 Mark)} \]

(a) \( 1 > II > III \)
(b) \( II > I > III \)
(c) \( III > II > I \)
(d) \( I > III > II \)
29. The pH of 0.1 M solution of the following salts increases in the order. (1999 - 2 Marks)
   (a) NaCl < NH₄Cl < NaCN < HCl
   (b) HCl < NH₄Cl < NaCl < NaCN
   (c) NaCN < NH₄Cl < NaCl < HCl
   (d) HCl < NaCl < NaCN < NH₄Cl

30. For the chemical reaction $3X(g) + Y(g) \rightleftharpoons X_3Y(g)$, the amount of $X_3Y$ at equilibrium is affected by (1999 - 2 Marks)
   (a) temperature and pressure
   (b) temperature only
   (c) pressure only
   (d) temperature, pressure and catalyst

31. For the reversible reaction, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ at 500°C, the value of $K_p$ is $1.44 \times 10^{-5}$ when partial pressure is measured in atmospheres. The corresponding value of $K_c$, with concentration in molare-1, is (2000S)
   (a) $\frac{1.44 \times 10^{-5}}{(0.082 \times 500)^2}$
   (b) $\frac{1.44 \times 10^{-5}}{(8.314 \times 773)^2}$
   (c) $\frac{1.44 \times 10^{-5}}{(0.082 \times 773)^2}$
   (d) $\frac{1.44 \times 10^{-5}}{(0.082 \times 773)}$

32. When two reactants, $A$ & $B$, are mixed to give products $C$ & $D$, the reaction quotient $Q_c$ at the initial stages of the reaction (2000S)
   (a) is zero
   (b) decreases with time
   (c) is independent of time
   (d) increases with time

33. The set with correct order of acidity is (2001S)
   (a) HClO < HClO₂ < HClO₃ < HClO₄
   (b) HClO₂ < HClO₃ < HClO₄ < HClO
   (c) HClO < HClO₂ < HClO₃ < HClO₄
   (d) HClO₄ < HClO₂ < HClO₃ < HClO

34. For a sparingly soluble salt $A_pB_q$, the relationship of its solubility product ($L_s$) with its solubility ($S$) is (2001S)
   (a) $L_s = S^{p+q} \cdot P^p \cdot Q^q$
   (b) $L_s = S^{p+q} \cdot p^p \cdot q^q$
   (c) $L_s = S^{p+q} \cdot p^p \cdot q^q$
   (d) $L_s = S^{p+q} \cdot (pq)^{p+q}$

35. At constant temperature, the equilibrium constant ($K_p$) for the decomposition reaction $N_2O_4 \rightleftharpoons 2NO_2$ is expressed by $K_p = (4x^2P^2)(1-x^2)$, where $P$ = pressure, $x$ = extent of decomposition. Which one of the following statements is true? (2001S)
   (a) decreases with increase of $P$
   (b) $K_p$ increases with increase of $x$
   (c) $K_p$ increases with decrease of $x$
   (d) $K_p$ remains constant with change in $P$ and $x$

36. Consider the following equilibrium in a closed container (2002S)
   \[ N_2O_4(g) \rightleftharpoons 2NO_2(g) \]
   At a fixed temperature, the volume of the reaction container is halved. For this change, which of the following statements holds true regarding the equilibrium constant ($K_p$) and degree of dissociation ($\alpha$)? (a) neither $K_p$ nor $\alpha$ changes
   (b) both $K_p$ and $\alpha$ change
   (c) $K_p$ changes, but $\alpha$ does not change
   (d) $K_p$ does not change, but $\alpha$ changes

37. A weak acid HX has the dissociation constant $1 \times 10^{-5}$ M. It forms a salt NaX on reaction with alkali. The percentage hydrolysis of 0.1 M solution of NaX is (2004S)
   (a) 0.0001%  (b) 0.01%  (c) 0.1%  (d) 0.15%

38. A 0.004 M solution of Na₂SO₄ is isotonie with 0.010 M solution of glucose at same temperature. The percentage dissociation of Na₂SO₄ is (2004S)
   (a) 25%  (b) 50%  (c) 75%  (d) 85%

39. 0.1 mole of CH₃NH₂ ($K_b = 5 \times 10^{-4}$) is mixed with 0.08 mole of HCl and diluted to one litre. What will be the H⁺ concentration in the solution? (2005S)
   (a) $8 \times 10^{-2}$ M  (b) $8 \times 10^{-11}$ M  (c) $1.6 \times 10^{-11}$ M  (d) $8 \times 10^{-5}$ M

40. The Haber's process for the formation of NH₃ at 298K is
   \[ N_2 + 3H_2 \rightleftharpoons 2NH_3; \Delta H = -46.0 \text{ kJ} \]
   Which of the following is the correct statement (2006 - 3M, -1)
   (a) The condition for equilibrium is
   \[ G_{N_2} + 3G_{H_2} = 2G_{NH_3} \]
   where G is Gibb's free energy per mole of the gaseous species measured at that partial pressure.
   (b) On adding N₂, the equilibrium will shift to forward direction because according to II nd law of thermodynamics the entropy must increase in the direction of spontaneous reaction
   (c) The catalyst will increase the rate of forward reaction by 2 times and that of backward reaction by 1.5 times
   (d) None of these

41. 2.5 ml of (2/5) M weak monobasic acid ($K_a = 1 \times 10^{-12}$ at 25°C) is titrated (2/15) M HCl in water at 25°C. The concentration of H⁺ at equivalence point is ($K_w = 1 \times 10^{-14}$ at 25°C) (2008S)
   (a) $3.7 \times 10^{-14}$ M  (b) $3.2 \times 10^{-7}$ M  (c) $3.2 \times 10^{-2}$ M  (d) $2.7 \times 10^{-2}$ M

42. Solubility product constant ($K_{sp}$) of salts of types MX, MX₂ and MX₃ at temperature T are $4.0 \times 10^{-8}, 3.2 \times 10^{-14}$ & $2.7 \times 10^{-15}$, respectively. Solubilities (mol dm⁻³) of the salts at temperature T are in the order (2008S)
   (a) MX > MX₂ > MX₃  (b) M₃X > MX₂ > MX  (c) MX₂ > M₃X > MX  (d) MX > M₃X > MX₂
D MCQs with One or More Than One Correct

1. For the gas phase reaction: \( \text{C}_2\text{H}_4 + \text{H}_2 \rightleftharpoons \text{C}_2\text{H}_6 \) (\( \Delta H = -32.7 \text{ kcal} \)) carried out in a vessel, the equilibrium concentration of \( \text{C}_2\text{H}_4 \) can be increased by:
   (a) increasing the temperature
   (b) decreasing the pressure
   (c) removing some \( \text{H}_2 \)
   (d) adding some \( \text{C}_2\text{H}_6 \)

2. When \( \text{NaNO}_3 \) is heated in a closed vessel, oxygen is liberated and \( \text{NaNO}_2 \) is left behind. At equilibrium. (1986 - 1 Mark)
   (a) addition of \( \text{NaNO}_2 \) favours reverse reaction
   (b) addition of \( \text{NaNO}_3 \) favours forward reaction
   (c) increasing temperature favours forward reaction
   (d) increasing pressure favours reverse reaction

3. The equilibrium: \( \text{SO}_3\text{Cl}_2(g) \rightleftharpoons \text{SO}_2(g) + \text{Cl}_2(g) \)
   is attained at \( 25^\circ \text{C} \) in a closed container and an inert gas, helium is introduced. Which of the following statements are correct?
   (a) Concentration of \( \text{SO}_3\text{Cl}_2 \) and \( \text{SO}_2 \) do not change
   (b) More chlorine is formed
   (c) Concentration of \( \text{SO}_2 \) is reduced
   (d) More \( \text{SO}_2 \) is formed.

4. For the reaction: \( \text{PCl}_3(g) \rightarrow \text{PCl}_2(g) + \text{Cl}_2(g) \)
   The forward reaction at constant temperature is favoured by:
   (a) introducing an inert gas at constant volume
   (b) introducing chlorine gas at constant volume
   (c) introducing an inert gas at constant pressure
   (d) increasing the volume of the container
   (e) introducing \( \text{PCl}_3 \) at constant volume

5. For the reaction \( \text{CO}(g) + \text{H}_2\text{O}(g) \rightarrow \text{CO}_2(g) + \text{H}_2(g) \) at a given temperature the equilibrium amount of \( \text{CO}_2(g) \) can be increased by:
   (a) adding a suitable catalyst
   (b) adding an inert gas
   (c) decreasing the volume of the container
   (d) increasing the amount of \( \text{CO}(g) \).

6. Which of the following statements is (are) correct?
   (1998 - 2 Marks)
   (a) The pH of \( 1.0 \times 10^{-8} \text{ M} \) solution of \( \text{HCl} \) is 8
   (b) The conjugate base of \( \text{H}_2\text{PO}_4^- \) is \( \text{HPO}_4^{2-} \)
   (c) Autoprotolysis constant of water increases with temperature
   (d) When a solution of a weak monoprotic acid is titrated against a strong base, at half-neutralisation point pH = \((1/2) \cdot pK_a\).

7. A buffer solution can be prepared from a mixture of
   (1999 - 3 Marks)
   (a) sodium acetate and acetic acid in water
   (b) sodium acetate and hydrochloric acid in water
   (c) ammonia and ammonium chloride in water
   (d) ammonia and sodium hydroxide in water

8. Aqueous solutions of \( \text{HNO}_3 \), \( \text{KOH} \), \( \text{CH}_3\text{COOH} \) and \( \text{CH}_3\text{COONa} \) of identical concentrations are provided. The pair(s) of solutions which form a buffer upon mixing is(are)
   (a) \( \text{HNO}_3 \) and \( \text{CH}_3\text{COOH} \)
   (b) \( \text{KOH} \) and \( \text{CH}_3\text{COONa} \)
   (c) \( \text{HNO}_3 \) and \( \text{CH}_3\text{COONa} \)
   (d) \( \text{CH}_3\text{COOH} \) and \( \text{CH}_3\text{COONa} \)

9. The initial rate of hydrolysis of methyl acetate (1M) by a weak acid (\( \text{HA} \), 1M) is 1/100th of that of a strong acid (\( \text{HX} \), 1M), at 25°C. The \( K_a \) of HA is
   (2010)
   (a) \( 1 \times 10^{-4} \)
   (b) \( 1 \times 10^{-5} \)
   (c) \( 1 \times 10^{-6} \)
   (d) \( 1 \times 10^{-3} \)

10. The \( K_{sp} \) of \( \text{Ag}_2\text{CrO}_4 \) is \( 1.1 \times 10^{-12} \) at 298 K. The solubility (in mol/L) of \( \text{Ag}_2\text{CrO}_4 \) in a 0.1 M \( \text{AgNO}_3 \) solution is
   (JEE Adv. 2013)
   (a) \( 1.1 \times 10^{-11} \)
   (b) \( 1.1 \times 10^{-10} \)
   (c) \( 1.1 \times 10^{-12} \)
   (d) \( 1.1 \times 10^{-9} \)

11. The thermal dissociation equilibrium of \( \text{CaCO}_3(s) \) is studied under different conditions
   (JEE Adv. 2013)
   \( \text{CaCO}_3(s) \rightleftharpoons \text{CaO}(s) + \text{CO}_2(g) \). For this equilibrium, the correct statement(s) is(are)
   (a) \( \Delta H \) is dependent on \( T \)
   (b) \( K \) is independent of the initial amount of \( \text{CaCO}_3 \)
   (c) \( K \) is dependent on the pressure of \( \text{CO}_2 \) at a given \( T \)
   (d) \( \Delta H \) is independent of catalyst, if any

12. The %yield of ammonia as a function of time in the reaction \( \text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g) \), \( \Delta H < 0 \) at \((P, T_1)\) is given below

   ![Graph showing %yield vs. time](image)

   If this reaction is conducted at \((P, T_2)\), with \( T_2 > T_1 \), the %yield of ammonia as a function of time is represented by
   (JEE Adv. 2015)

   ![Graph showing %yield vs. time](image)

E Subjective Problems

1. A solution contains \( \text{Na}_2\text{CO}_3 \) and \( \text{NaHCO}_3 \). 10 ml of solution requires 2.5 ml of 0.1 \text{ M} \text{ H}_2\text{SO}_4 \) for neutralisation using phenolphthalein as an indicator. Methyl orange is then added when a further 2.5ml of 0.2 \text{ M} \text{ H}_2\text{SO}_4 \) was required. Calculate the amount of \( \text{Na}_2\text{CO}_3 \) and \( \text{NaHCO}_3 \) in one litre of the solution.
   (1979)
2. How many moles of sodium propionate should be added to one litre of an aqueous solution containing 0.02 mole of propionic acid to obtain a buffer solution of pH 4.75? What will be pH if 0.01 mole of hydrogen chloride is dissolved in the above buffer solution. Compare the last pH value with the pH of 0.01 molar HCl solution. Dissociation constant of propionic acid, $K_a$ at 25°C = $1.34 \times 10^{-5}$. 

*(1981 - 4 Marks)*

3. One mole of nitrogen is mixed with three moles of hydrogen in a 4 litre container. If 0.25 per cent of nitrogen is converted to ammonia by the following reaction  

$$ \text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g) $$

calculate the equilibrium constant ($K_e$) in concentration units. What will be the value of $K_e$ for the following equilibrium? 

$$ \frac{1}{2} \text{N}_2(g) + \frac{3}{2} \text{H}_2(g) \rightleftharpoons \text{NH}_3(\text{ag}) $$

*(1981 - 4 Marks)*

4. Twenty ml. of 0.2 M sodium hydroxide is added to 50 ml. of 0.2 M acetic acid to give 70 ml of the solution. What is the pH of this solution? Calculate the additional volume of 0.2 M NaOH required to make the pH of the solution 4.74. The ionization constant of acetic acid is 1.8 $\times$ 10$^{-5}$. 

*(1982 - 3 Marks)*

5. The dissociation constant of a weak acid HA is 4.9 $\times$ 10$^{-8}$. After making the necessary approximations, calculate (i) percentage ionization, (ii) pH and (iii) OH$^-$ concentration in a decimolar solution of the acid. Water has a pH of 7. 

*(1983 - 2 Marks)*

6. A solution contains a mixture of Ag (0.10 M) and H$_2$SO$_4$ (0.10 M) which are to be separated by selective precipitation. Calculate the maximum concentration of iodide ion at which one of them gets precipitated almost completely. What percentage of that metal ion is precipitated? 

$$ K_{sp} : \text{AgI} = 8.5 \times 10^{-17}; \text{Hg}_2\text{I}_2 = 2.5 \times 10^{-26} $$

*(1984 - 4 Marks)*

7. One mole of Cl$_2$ and 3 moles of PCl$_5$ are placed in a 100 litre vessel heated to 227°C. The equilibrium pressure is 2.05 atmosphere. Assuming ideal behaviour, calculate the degree of dissociation for PCl$_5$ and $K_p$ for the reaction: 

$$ \text{PCl}_5(g) \rightleftharpoons \text{PCl}_3(g) + \text{Cl}_2(g) $$

*(1984 - 6 Marks)*

8. Arrange the following in: 

(i) increasing bond length : F$_2$, N$_2$, Cl$_2$, O$_2$ 

*(1985 - 1 Mark)*

(ii) increasing acid strength : HClO$_3$, HClO$_4$, HClO$_2$, HClO 

*(1986 - 1 Mark)*

(iii) increasing basicity : H$_2$O, OH$^-$, CH$_3$OH, CH$_3$O$^-$ 

*(1992 - 1 Mark)*

(iv) Arrange the following oxides in the decreasing order of Bronsted basicity : 

BaO, SO$_3$, CO$_2$, Cl$_2$O, B$_2$O$_3$ 

*(2004 - 2 Marks)*

9. The [H$^+$] in 0.2 M solution of formic acid is 6.4 $\times$ 10$^{-3}$ mole litre$^{-1}$. To this solution sodium formate is added so as to adjust the concentration of sodium formate to one mole litre$^{-1}$. What will be pH of this solution? $K_p$ for HCOOH is 2.4 $\times$ 10$^{-4}$ and degree of dissociation of HCOONa is 0.75. 

*(1985 - 3 Marks)*

10. The equilibrium constant of the reaction 

$$ \text{A}_2(g) + \text{B}_2(g) \rightleftharpoons 2\text{AB}(g) $$

at 100°C is 50. If a one litre flask containing one mole of A$_2$, is connected to a two litre flask containing two mole of B$_2$, how many mole of AB will be formed at 373°C? 

*(1985 - 4 Marks)*

11. The solubility of Mg(OH)$_2$ in pure water is 9.57 $\times$ 10$^{-3}$ g/litre. Calculate its solubility (in g/litre) in 0.02 M Mg(NO$_3$)$_2$ solution. 

*(1986 - 5 Marks)*

12. What is the pH of the solution when 0.20 mole of hydrochloric acid is added to one litre of a solution containing: 

(i) 1 M each of acetic acid and acetic ion? 
(ii) 0.1 M each of acetic acid and acetic ion? 

Assume the total volume is one litre. $K_a$ for acetic acid = 1.8 $\times$ 10$^{-5}$. 

*(1987 - 5 Marks)*

13. At a certain temperature equilibrium constant ($K_e$) is 16 for the reaction: 

$$ \text{SO}_2(g) + \text{NO}_2(g) \rightleftharpoons \text{SO}_3(g) + \text{NO}(g) $$

If we take one mole each of all the four gases in one litre container, what would be the equilibrium concentrations of NO(g) and NO$_2$(g)? 

*(1988 - 5 Marks)*

14. N$_2$O$_4$ is 25% dissociated at 37°C and one atmosphere pressure. Calculate (i) $K_e$ and (ii) the percentage dissociation at 0.1 atmosphere and 37°C. 

*(1988 - 4 Marks)*

15. How many gram-mole of HCl will be required to prepare one litre of buffer solution (containing NaCN and HCI) of pH 8.5 using 0.01 gram formula weight of NaCN? $K$ dissociation (HCN) = 4.1 $\times$ 10$^{-10}$. 

*(1988 - 4 Marks)*

16. The equilibrium constant $K_p$ of the reaction: 

$$ \text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons \text{SO}_3(g) $$

is 900 atm. at 800 K. A mixture containing SO$_2$ and O$_2$ having initial partial pressure of 1 and 2 atm. respectively is heated at constant volume to equilibrate. Calculate the partial pressure of each gas at 800 K. 

*(1989 - 3 Marks)*

17. Freshly precipitated aluminium and magnesium hydroxides are stirred vigorously in a buffer solution containing 0.25 mole/l of ammonium chloride and 0.05 mole/l of ammonium hydroxide. Calculate the concentration of aluminium and magnesium ions in solution: 

$$ K_{p[NH_4OH]} = 1.80 \times 10^{-5} $$

$$ K_{p[Mg(OH)_2]} = 6.0 \times 10^{-10} $$

$$ K_{p[Al(OH)_3]} = 6.0 \times 10^{-32} $$

*(1989 - 3 Marks)*

18. For the reaction : 

$$ \text{CO}(g) + 2\text{H}_2(g) \rightleftharpoons \text{CH}_3\text{OH}(g) $$

hydrogen gas is introduced into a five litre flask at 327°C, containing 0.2 mole of CO(g) and a catalyst, until the pressure is 4.92 atm. At this point 0.1 mole of CH$_3$OH(g) is formed. Calculate the equilibrium constant, $K_p$ and $K_c$. 

*(1990 - 5 Marks)*

19. What is the pH of 1.0 M solution of acetic acid? To what volume must one liter of this solution be diluted so that the pH of the resulting solution will be twice the original value? 

Given : $K_a = 1.8 \times 10^{-5}$. 

*(1990 - 4 Marks)*

20. The solubility product of Ag$_2$C$_2$O$_4$ at 25°C is 1.29 $\times$ 10$^{-11}$ mol$^3$/l$^3$. A solution of K$_2$CO$_3$ containing 0.1520 mole in 500 ml water is shaken at 25°C with excess of Ag$_2$C$_2$O$_4$ till the following equilibrium is reached : 

$$ \text{Ag}_2\text{CO}_3 + K_2\text{CO}_3 \rightleftharpoons 2\text{AgC}_2\text{O}_4 + K_2\text{CO}_3 $$

At equilibrium the solution contains 0.0358 mole of K$_2$CO$_3$. Assuming the degree of dissociation of K$_2$CO$_3$ and K$_2$C$_2$O$_4$ to be equal, calculate the solubility product of Ag$_2$C$_2$O$_4$. 

*(1991 - 4 Marks)*
21. A 40.0 ml solution of weak base, BOH, is titrated with 0.1N HCl solution. The pH of the solution is found to be 10.04 and 9.14 after adding 5.0 ml and 20.0 ml of the acid respectively. Find out the dissociation constant of the base.  

\[(1991 - 6 \text{ Marks})\]

22. The solubility product \((K_{sp})\) of Ca(OH)\(_2\) at 25°C is 4.42 \times 10^{-5}. A 500 ml of saturated solution of Ca(OH)\(_2\) is mixed with equal volume of 0.4 M NaOH. How much Ca(OH)\(_2\) in milligrams is precipitated? \n
\[(1992 - 4 \text{ Marks})\]

23. 0.15 mole of CO taken in a 2.5 l flask is maintained at 750 K along with a catalyst so that the following reaction can take place:  

\[
\text{CO}(g) + 2\text{H}_2(g) \rightleftharpoons \text{CH}_3\text{OH}(g)
\]

Hydrogen is introduced until the total pressure of the system is 8.5 atmosphere at equilibrium and 0.08 mole of methanol is formed. Calculate (i) \(K_p\) and \(K_c\), and (ii) the final pressure if the same amount of CO and H\(_2\) as before are used, but with no catalyst so that the reaction does not take place.  

\[(1993 - 5 \text{ Marks})\]

24. The pH of blood stream is maintained by a proper balance of H\(_2\)CO\(_3\) and NaHCO\(_3\) concentrations. What volume of 5M NaHCO\(_3\) solution should be mixed with a 10 ml sample of blood which is 2M in H\(_2\)CO\(_3\) in order to maintain a pH of 7.4? \(K_a\) for H\(_2\)CO\(_3\) in blood is 7.8 \times 10^{-7}. \n
\[(1993 - 2 \text{ Marks})\]

25. An aqueous solution of a metal bromide MB\(_2\) (0.05M) is saturated with H\(_2\)S. What is the minimum pH at which MS will precipitate? \n
\[(1993 - 3 \text{ Marks})\]

\[K_{sp} \text{ for } \text{MS} = 6.0 \times 10^{-21}; \text{ concentration of saturated H}_2\text{S} = 0.1 \text{ M}\]

\[K_1 = 10^{-7} \text{ and } K_2 = 1.3 \times 10^{-13}, \text{ for H}_2\text{S.}\]

26. At temperature \(T\), a compound AB\(_2\) (g) dissociates according to the reaction  

\[
2\text{AB}_2(g) \rightleftharpoons 2\text{AB}(g) + \text{B}_2(g)
\]

with a degree of dissociation \(x\) which is small compared with unity. Deduce the expression for \(x\) in terms of the equilibrium constant \(K_p\) and the total pressure, \(P\).  

\[(1994 - 4 \text{ Marks})\]

27. For the reaction  

\[
[\text{Ag(CN)}_2^-] \rightleftharpoons \text{Ag}^+ + 2\text{CN}^-
\]

the equilibrium constant, at 25°C, is 4.0 \times 10^{-19}. Calculate the silver ion concentration in a solution which was originally 0.10 molar in KCN and 0.03 molar in AgNO\(_3\).  

\[(1994 - 3 \text{ Marks})\]

28. Calculate the pH of an aqueous solution of 1.0 M ammonium formate assuming complete dissociation. \(pK_a\) of formic acid = 3.8 and \(pK_b\) of ammonia = 4.8.  

\[(1995 - 2 \text{ Marks})\]

29. What is the pH of 0.5 M aqueous NaCN solution? \(pK_c\) of CN\(^-\) is 4.70.  

\[(1996 - 2 \text{ Marks})\]

30. A sample of AgCl was treated with 5.00 ml of 1.5 M Na\(_2\)CO\(_3\) solution to give Ag\(_2\)CO\(_3\). The remaining solution contained 0.0026 g of Cl\(^-\) per litre. Calculate the solubility product of AgCl \((K_{sp}(\text{Ag}_2\text{CO}_3) = 8.2 \times 10^{-12})\).  

\[(1997 - 5 \text{ Marks})\]

31. An acid type indicator, HIn differs in colour from its conjugate base (In\(^-\)). The human eye is sensitive to colour differences only when the ratio [In\(^-\)]/[HIn] is greater than 10 or smaller than 0.1. What should be the minimum change in the pH of the solution to observe a complete colour change \((K_a = 1.0 \times 10^{-5})\)?  

\[(1997 - 2 \text{ Marks})\]

32. Given: \(\text{Ag(NH}_3)_2^+ \rightleftharpoons \text{Ag}^+ + 2\text{NH}_3\), \(K_c = 6.2 \times 10^{-8}\) and \(K_{sp}\) of AgCl = 1.8 \times 10^{-10} at 298 K. If ammonia is added to a water solution containing excess of AgCl(s) only, calculate the concentration of the complex in 1.0 M aqueous ammonia.  

\[(1998 - 5 \text{ Marks})\]

33. What will be the resultant pH when 200 mL of an aqueous solution of HCl (pH = 2.0) is mixed with 300 mL of an aqueous solution of NaOH (pH = 12.0)?  

\[(1998 - 2 \text{ Marks})\]

34. When 3.06 g of solid NH\(_3\)H\(_2\)S is introduced into a two litre evacuated flask at 27°C, 30% of the solid decomposes into gaseous ammonia and hydrogen sulphide. (i) Calculate \(K_c\) and \(K_p\) for the reaction at 27°C. (ii) What would happen to the equilibrium when more solid NH\(_3\)H\(_2\)S is introduced into the flask?  

\[(1999 - 7 \text{ Marks})\]

35. The solubility of Pb(OH)\(_2\) in water is 6.7 \times 10^{-6} M. Calculate the solubility of Pb(OH)\(_2\) in a buffer solution of pH = 8.  

\[(1999 - 4 \text{ Marks})\]

36. The average concentration of SO\(_2\) in the atmosphere over a city on a certain day is 10 ppm, when the average temperature is 298 K. Given that the solubility of SO\(_2\) in water at 298 K is 1.3653 moles litre\(^{-1}\) and the \(pK_a\) of H\(_2\)SO\(_4\) is 1.92, estimate the pH of rain on that day.  

\[(2000 - 5 \text{ Marks})\]

37. 500 mL of 0.2 M aqueous solution of acetic acid is mixed with 500 mL of 0.2 M HCl at 25°C.  

(i) Calculate the degree of dissociation of acetic acid in the resulting solution and pH of the solution.  

(ii) If 6 g of NaOH is added to the above solution, determine the final pH. \[\text{[Assume there is no change in volume on mixing, } K_a \text{ of acetic acid is } 1.75 \times 10^{-5} \text{ mol L}^{-1}\].  

\[(2002 - 5 \text{ Marks})\]

38. Match the following if the molecular weights of X, Y and Z are same.  

\[(2003 - 2 \text{ Marks})\]

<table>
<thead>
<tr>
<th>Boiling Point</th>
<th>(K_p)</th>
</tr>
</thead>
<tbody>
<tr>
<td>x</td>
<td>100</td>
</tr>
<tr>
<td>y</td>
<td>27</td>
</tr>
<tr>
<td>z</td>
<td>253</td>
</tr>
</tbody>
</table>

G Comprehension Based Questions

PARAGRAPH 1

When 100 mL of 1.0 M HCl was mixed with 100 mL of 1.0 M NaOH in an insulated beaker at constant pressure, a temperature increase of 5.7 °C was measured for the beaker and its contents (Expt 1). Because the enthalpy of neutralization of a strong acid with a strong base is a constant (–57.0 kJ mol\(^{-1}\)), this experiment could be used to measure the calorimeter constant. In a second experiment (Expt 2), 100 mL of 2.0 M acetic acid (\(K_a = 2.0 \times 10^{-5}\)) was mixed with 100 mL of 1.0 M NaOH (under identical conditions to Expt 1) where a temperature rise of 5.6 °C was measured. (Consider heat capacity of all solutions as 4.2 J g\(^{-1}\) K\(^{-1}\) and density of all solutions as 1.0 g mL\(^{-1}\))  

\[(JEE \text{ Adv. 2015})\]
1. Enthalpy of dissociation (in kJ mol\(^{-1}\)) of acetic acid obtained from the Expt. 2 is
   (a) 1.0  (b) 10.0  (c) 24.5  (d) 51.4

2. The pH of the solution after Expt. 2 is
   (a) 2.8  (b) 4.7  (c) 5.0  (d) 7.0

**PARAGRAPH 2**

Thermal decomposition of gaseous X\(_2\) to gaseous X at 298 K takes place according to the following equation:

\[ X_2(g) \rightleftharpoons 2X(g) \]

The standard reaction Gibbs energy, \(\Delta G^\circ\), of this reaction is positive. At the start of the reaction, there is one mole of \(X_2\) and no X. As the reaction proceeds, the number of moles of X formed is given by \(\beta\). Thus, \(\beta_{\text{equilibrium}}\) is the number of moles of X formed at equilibrium. The reaction is carried out at a constant total pressure of 2 bar. Consider the gases to behave ideally. (Given R = 0.083 L bar K\(^{-1}\) mol\(^{-1}\)) \((\text{JEE Adv. 2016})\)

3. The equilibrium constant \(K_p\) for this reaction at 298 K, in terms of \(\beta_{\text{equilibrium}}\) is
   \[
   K_p = \frac{8\beta_{\text{equilibrium}}^2}{2 - 4\beta_{\text{equilibrium}}^2} \quad \text{or} \quad \frac{8\beta_{\text{equilibrium}}^2}{4 - 4\beta_{\text{equilibrium}}^2}
   \]
   (a) \(\frac{8\beta_{\text{equilibrium}}^2}{2 - 4\beta_{\text{equilibrium}}^2}\)  (b) \(\frac{8\beta_{\text{equilibrium}}^2}{4 - 4\beta_{\text{equilibrium}}^2}\)
   (c) \(\frac{4\beta_{\text{equilibrium}}^2}{2 - 4\beta_{\text{equilibrium}}^2}\)  (d) \(\frac{4\beta_{\text{equilibrium}}^2}{4 - 4\beta_{\text{equilibrium}}^2}\)

4. The INCORRECT statement among the following, for this reaction, is
   (a) Decrease in the total pressure will result in formation of more moles of gaseous X
   (b) At the start of the reaction, dissociation of gaseous \(X_2\) takes place spontaneously
   (c) \(\beta_{\text{equilibrium}} = 0.7\)
   (d) \(K_p < 1\)

**H Assertion & Reason Type Questions**

1. Each question contains STATEMENT-1 (Assertion) and STATEMENT-2 (Reason). Each question has 5 choices (a), (b), (c) and (d) out of which ONLY ONE is correct. Mark your answer as
   (a) If both Statement -1 and Statement -2 are correct, and Statement -2 is the correct explanation of the Statement -2.

2. Species acting as both Bronsted acid and base is
   (a) (HSO\(_4\))\(^{-1}\)  (b) Na\(_2\)CO\(_3\)  (c) NH\(_3\)  (d) OH\(^{-1}\) \([2002]\)

3. Let the solubility of an aqueous solution of Mg(OH)\(_2\) be \(x\) then its \(K_{sp}\) is
   (a) \(4x^3\)  (b) \(108x^5\)  (c) \(27x^4\)  (d) \(9x\) \([2002]\)

4. Change in volume of the system does not alter which of the following equilibria?
   (a) \(\text{JEE Main / AIEEE}\)

   (a) \(\text{HSO}_4^-\)  (b) Na\(_2\)CO\(_3\)  (c) NH\(_3\)  (d) OH\(^{-1}\) \([2002]\)
(a) \( \text{N}_2(g) + \text{O}_2(g) \leq \text{2NO(g)} \)
(b) \( \text{PCl}_5(g) \leq \text{PCl}_3(g) + \text{Cl}_2(g) \)
(c) \( \text{N}_2(g) + 3\text{H}_2(g) \leq \text{2NH}_3(g) \)
(d) \( \text{SO}_2\text{Cl}_2(g) \leq \text{SO}_3(g) + \text{Cl}_2(g) \).

5. For the reaction \( \text{CO(g)} + (1/2) \text{O}_2(g) = \text{CO}_2(g) \), \( K_p/K_c \) is
   (a) \( RT \)
   (b) \( (RT)^{-1} \) \[2002\]
   (c) \( (RT)^{-1/2} \)
   (d) \( (RT)^{1/2} \)

6. Which one of the following statements is not true? \[2003\]
   (a) \( \text{pH + pOH} = 14 \) for all aqueous solutions
   (b) The pH of 1 \( \times \) 10\(^{-6} \) M \( \text{HCl} \) is 8
   (c) 96,500 coulombs of electricity when passed through a CuSO\(_4\) solution deposits 1 gram equivalent of copper at the cathode
   (d) The conjugate base of \( \text{H}_2\text{PO}_4^- \) is \( \text{HPO}_3^- \)

7. The solubility in water of a sparingly soluble salt \( \text{AB}_2 \) is \( 1.0 \times 10^{-7} \) mol L\(^{-1}\). Its solubility product number will be
   (a) \( 4 \times 10^{-10} \)
   (b) \( 1 \times 10^{-15} \) \[2003\]
   (c) \( 1 \times 10^{-10} \)
   (d) \( 4 \times 10^{-15} \)

8. For the reaction equilibrium \( \text{N}_2\text{O}_4(g) \leq \text{2 NO}_2(g) \)
   the concentrations of \( \text{N}_2\text{O}_4 \) and \( \text{NO}_2 \) at equilibrium are \( 4.8 \times 10^{-2} \) and \( 1.2 \times 10^{-2} \) mol L\(^{-1}\) respectively. The value of \( K_c \) for the reaction is
   (a) \( 3 \times 10^{-4} \) mol L\(^{-1}\)
   (b) \( 3 \times 10^{-3} \) mol L\(^{-1}\)
   (c) \( 3 \times 10^3 \) mol L\(^{-1}\)
   (d) \( 3.3 \times 10^2 \) mol L\(^{-1}\)

9. Consider the reaction equilibrium
   \( 2 \text{SO}_2(g) + \text{O}_2(g) \leq 2 \text{SO}_3(g) \), \( \Delta H = -198 \) kJ
   On the basis of Le Chatelier’s principle, the condition favourable for the forward reaction is
   (a) increasing temperature as well as pressure
   (b) lowering the temperature and increasing the pressure
   (c) any value of temperature and pressure
   (d) lowering of temperature as well as pressure

10. When rain is accompanied by a thunderstorm, the collected rain water will have a pH value
    (a) slightly higher than that when the thunderstorm is not there
    (b) uninfluenced by occurrence of thunderstorm
    (c) which depends on the amount of dust in air
    (d) slightly lower than that of rain water without thunderstorm

11. The conjugate base of \( \text{H}_2\text{PO}_4^- \) is
    (a) \( \text{H}_3\text{PO}_4 \)
    (b) \( \text{P}_2\text{O}_5 \)
    (c) \( \text{PO}_4^{3-} \)
    (d) \( \text{HPO}_3^{2-} \)

12. What is the equilibrium expression for the reaction \( \text{P}_4(s) + \text{SO}_2(g) \leq \text{P}_4\text{O}_10(s) \) ?
    (a) \( K_c = [\text{O}_2]^5 \)
    (b) \( K_c = [\text{P}_4\text{O}_{10}] / [\text{P}_4][\text{O}_2] \)
    (c) \( K_c = [\text{P}_4\text{O}_{10}] / [\text{P}_4][\text{O}_2]^5 \)
    (d) \( K_c = 1/[\text{O}_2]^5 \)

13. For the reaction \( \text{CO(g)} + \text{Cl}_2(g) \leq \text{COCl}_2(g) \) the
    \( K_p/K_c \) is equal to \[2004\]
    (a) \( \sqrt{RT} \)
    (b) \( RT \)
    (c) \( 1/RT \)
    (d) \( 1.0 \)

14. The equilibrium constant for the reaction \( \text{N}_2(g) + \text{O}_2(g) \leq 2 \text{NO}_2(g) \) at temperature \( T \) is \( 4 \times 10^{-4} \). The value of \( K_c \) for the reaction
    \( \text{NO}_2(g) \leq \frac{1}{2} \text{N}_2(g) + \frac{1}{2} \text{O}_2(g) \) at the same temperature is
    (a) \( 4 \times 10^{-4} \)
    (b) \( 50 \) \[2004\]
    (c) \( 2.5 \times 10^2 \)
    (d) \( 0.02 \)

15. The molar solubility (in mol L\(^{-1}\)) of a sparingly soluble salt \( \text{MX}_2 \) is ‘s’. The corresponding solubility product is \( K_{sp} \) ‘s’ is
given in term of \( K_{sp} \) by the relation \[2004\]
    (a) \( \text{s} = (256 K_{sp})^{1/4} \)
    (b) \( s = (128 K_{sp})^{1/4} \)
    (c) \( \text{s} = (K_{sp}/128)^{1/4} \)
    (d) \( s = (K_{sp} / 256)^{1/5} \)

16. If \( \alpha \) is the degree of dissociation of Na\(_2\)SO\(_4\), the Vant Hoff’s factor (i) used for calculating the molecular mass is
    (a) \( 1 - 2 \alpha \)
    (b) \( 1 + 2 \alpha \)
    (c) \( 1 \alpha \)
    (d) \( 1 + \alpha \)

17. The solubility product of a salt having general formula \( \text{MX}_2 \), in water is \( 4 \times 10^{-12} \). The concentration of M\(^{2+}\) ions in the aqueous solution of the salt is \[2005\]
    (a) \( 4.0 \times 10^{-10} \) M
    (b) \( 1.6 \times 10^{-4} \) M
    (c) \( 1.0 \times 10^{-4} \) M
    (d) \( 2.0 \times 10^{-6} \) M

18. The exothermic formation of CIF\(_3\) is represented by the equation:
    \( \text{Cl}_2(g) + 3\text{F}_2(g) \leq \text{2CIF}_3(g) \), \( \Delta H = -329 \) kJ
    Which of the following will increase the quantity of CIF\(_3\) in an equilibrium mixture of Cl\(_2\), F\(_2\) and CIF\(_3\)? \[2005\]
    (a) Adding F\(_2\)
    (b) Increasing the volume of the container
    (c) Removing Cl\(_2\)
    (d) Increasing the temperature

19. For the reaction \( \text{2NO}_2(g) \leq \text{2NO(g)} + \text{O}_2(g) \),
    \( K_c = 1.8 \times 10^{-6} \) at 184°C (R = 0.0831 kJ/(mol K))
When \( K_p \) and \( K_c \) are compared at 184°C, it is found that \( K_p \) depends upon the total gas pressure.

(a) Whether \( K_p \) is greater than, less than or equal to \( K_c \)
(b) \( K_p = K_c \)
(c) \( K_p \) is less than \( K_c \)
(d) \( K_p \) is greater than \( K_c \)

20. Hydrogen ion concentration in mol/L in a solution of pH = 5.4 will be:

(a) \( 3.98 \times 10^{-6} \) (b) \( 3.68 \times 10^{-6} \)
(c) \( 3.88 \times 10^{6} \) (d) \( 3.98 \times 10^{8} \)

21. What is the conjugate base of \( \text{OH}^- \)?

(a) \( \text{O}^2^- \) (b) \( \text{O}^- \)
(c) \( \text{H}_2\text{O} \) (d) \( \text{O}_2 \)

22. An amount of solid \( \text{NH}_4\text{HS} \) is placed in a flask already containing ammonia gas at a certain temperature and 0.50 atm pressure. Ammonium hydrogen sulphide decomposes to yield \( \text{NH}_3 \) and \( \text{H}_2\text{S} \) gases in the flask. When the decomposition reaction reaches equilibrium, the total pressure in the flask rises to 0.84 atm. The equilibrium constant for \( \text{NH}_4\text{HS} \) decomposition at this temperature is:

(a) 0.11 (b) 0.17
(c) 0.18 (d) 0.30

23. Phosphorus pentachloride dissociates as follows, in a closed reaction vessel:

\[
\text{PCl}_5(g) \rightleftharpoons \text{PCl}_3(g) + \text{Cl}_2(g)
\]

If total pressure at equilibrium of the reaction mixture is \( P \) and degree of dissociation of \( \text{PCl}_3 \) is \( x \), the partial pressure of \( \text{PCl}_3 \) will be:

(a) \( \left( \frac{x}{1-x} \right) P \) (b) \( \left( \frac{x}{1-x} \right) P \)
(c) \( \left( \frac{x}{x+1} \right) P \) (d) \( \left( \frac{2x}{1-x} \right) P \)

24. The equilibrium constant for the reaction:

\[
\text{SO}_3(g) \rightleftharpoons \text{SO}_2(g) + \frac{1}{2} \text{O}_2(g)
\]

is \( K_c = 4.9 \times 10^{-2} \). The value of \( K_c \) for the reaction:

\[
2\text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{SO}_3(g)
\]

will be:

(a) \( 9.8 \times 10^{-2} \) (b) \( 4.9 \times 10^{-2} \)
(c) 416 (d) \( 2.40 \times 10^{-3} \)

25. The data at 25°C:

\[
\begin{align*}
\text{Ag} + \text{I}^- & \rightarrow \text{AgI} + e^- \quad E^e = 0.152 \text{ V} \\
\text{Ag} & \rightarrow \text{Ag}^+ + e^- \quad E^e = -0.800 \text{ V}
\end{align*}
\]

What is the value of log \( K_{sp} \) for AgI? (2.303 \( RT/F = 0.059 \text{ V} \))

(a) -37.83 (b) -16.13
(c) -8.12 (d) +8.612

26. The first and second dissociation constants of an acid \( \text{H}_2\text{A} \) are \( 1.0 \times 10^{-5} \) and \( 5.0 \times 10^{-10} \) respectively. The overall dissociation constant of the acid will be:

(a) \( 0.2 \times 10^{5} \) (b) \( 5.0 \times 10^{-5} \)
(c) \( 5.0 \times 10^{15} \) (d) \( 5.0 \times 10^{-15} \)

27. The \( pK_a \) of a weak acid (HA) is 4.5. The pOH of an aqueous buffer solution of HA in which 50% of the acid is ionized is:

(a) 7.0 (b) 4.5
(c) 2.5 (d) 9.5

28. In a saturated solution of the sparingly soluble strong electrolyte \( \text{AgI}_3\text{O}_3 \) (molar mass = 283) the equilibrium which sets in is \( \text{AgI}_3\text{O}_3 \rightleftharpoons \text{Ag}^+ + \text{IO}_3^- \). If the solubility product constant \( K_{sp} \) of AgI_3O_3 at a given temperature is \( 1.0 \times 10^{-48} \), what is the mass of AgI_3O_3 contained in 100 ml of its saturated solution?

(a) \( 1.0 \times 10^{-4} \text{ g} \) (b) \( 28.3 \times 10^{-2} \text{ g} \)
(c) \( 2.83 \times 10^{-2} \text{ g} \) (d) \( 1.0 \times 10^{-2} \text{ g} \)

29. The equilibrium constants \( K_{P_1} \) and \( K_{P_2} \) for the reactions:

\[
X \rightleftharpoons 2Y \text{ and } Z \rightleftharpoons P + Q,
\]

respectively, are in the ratio of 1 : 9. If the degree of dissociation of X and Z are equal then the ratio of total pressures at these equilibria is:

(a) \( 1:36 \) (b) \( 1:1 \)
(c) \( 1:3 \) (d) \( 1:9 \)

30. For the following three reactions a, b and c, equilibrium constants are given:

(i) \( \text{CO}(g) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CO}_2(g) + \text{H}_2(g); K_1 \)
(ii) \( \text{CH}_4(g) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CO}(g) + 3\text{H}_2(g); K_2 \)
(iii) \( \text{CH}_4(g) + 2\text{H}_2\text{O}(g) \rightleftharpoons \text{CO}_2(g) + 4\text{H}_2(g); K_3 \)

(a) \( K_1 \sqrt{K_2} = K_3 \) (b) \( K_2 K_3 = K_1 \)
(c) \( K_3 = K_1 K_2 \) (d) \( K_3 K_2^3 = K_1^2 \)

31. Four species are listed below:

i. \( \text{HCO}_3^- \) ii. \( \text{H}_3\text{O}^+ \)
iii. \( \text{HSO}_4^- \) iv. \( \text{HSO}_3^- \)

Which one of the following is the correct sequence of their acid strength?

(a) \( iv < ii < iii < i \) (b) \( ii < iii < i < iv \)
(c) \( i < ii < iv < iii \) (v) \( iii < i < iv < ii \)

32. The \( pK_a \) of a weak acid, HA, is 4.80. The \( pK_a \) of a weak base, BOH, is 4.78. The pH of an aqueous solution of the corresponding salt, BA, will be:

(a) 9.58 (b) 4.79
(c) 7.01 (d) 9.22
33. Solid Ba(NO₃)₂ is gradually dissolved in a 1.0 × 10⁻⁴ M Na₂CO₃ solution. At what concentration of Ba²⁺ will a precipitate begin to form? (Ksp for for BaCO₃ = 5.1 × 10⁻⁹) [2009]

(a) 5.1 × 10⁻⁵ M  (b) 8.1 × 10⁻⁸ M  
(c) 8.1 × 10⁻⁷ M  (d) 4.1 × 10⁻⁵ M

34. Three reactions involving H₂PO₄⁻ are given below:
(i) H₃PO₄ + H₂O → H₂PO₄⁻ + H₃O⁺
(ii) H₂PO₄⁻ + H₂O → HPO₄²⁻ + H₃O⁺
(iii) H₂PO₄⁻ + OH⁻ → H₃PO₄ + O²⁻

In which of the above does H₂PO₄⁻ act as an acid? [2010]

(a) (ii) only  (b) (i) and (ii)  
(c) (iii) only  (d) (i) only

35. In aqueous solution the ionization constants for carbonic acid are
K₁ = 4.2 × 10⁻⁷ and K₂ = 4.8 × 10⁻¹¹.

Select the correct statement for a saturated 0.034 M solution of the carbonic acid. [2010]

(a) The concentration of CO₃²⁻ is 0.034 M.
(b) The concentration of CO₃²⁻ is greater than that of HCO₃⁻.
(c) The concentrations of H⁺ and HCO₃⁻ are approximately equal.
(d) The concentration of H⁺ is double that of CO₃²⁻.

36. Solubility product of silver bromide is 5.0 × 10⁻¹⁰. The quantity of potassium bromide (molar mass taken as 120 g mol⁻¹) to be added to 1 litre of 0.05 M solution of silver nitrate to start the precipitation of AgBr is [2010]

(a) 1.2 × 10⁻¹⁰ g  (b) 1.2 × 10⁻⁹ g  
(c) 6.2 × 10⁻⁵ g  (d) 5.0 × 10⁻⁸ g

37. At 25°C, the solubility product of Mg(OH)₂ is 1.0 × 10⁻¹². At which pH, will Mg²⁺ ions start precipitating in the form of Mg(OH)₂ from a solution of 0.001 M Mg²⁺ ions? [2010]

(a) 9 
(b) 10 
(c) 11 
(d) 8

38. A vessel at 1000 K contains CO₂ with a pressure of 0.5 atm. Some of the CO₂ is converted into CO on the addition of graphite. If the total pressure at equilibrium is 0.8 atm, the value of K is: [2011]

(a) 1.8 atm  (b) 3 atm  
(c) 0.3 atm  (d) 0.18 atm

39. The equilibrium constant (Kₑ) for the reaction N₂(g) + O₂(g) → 2NO(g) at temperature T is 4.0 × 10⁻⁴. The value of Kₑ for the reaction NO(g) → \( \frac{1}{2} N₂(g) + \frac{1}{2} O₂(g) \) at the same temperature is:

(a) 0.2  (b) 2.5 × 10²  
(c) 4 × 10⁻⁴  (d) 50.0

40. The pH of a 0.1 molar solution of the acid HQ is 3. The value of the ionization constant, Kₐ of the acid is: [2012]

(a) 3 × 10⁻¹  (b) 1 × 10⁻³  
(c) 1 × 10⁻⁵  (d) 1 × 10⁻⁷

41. How many litres of water must be added to 1 litre an aqueous solution of HCl with a pH of 1 to create an aqueous solution with pH of 2? [JEE M 2013]

(a) 0.1 L  (b) 0.9 L  
(c) 2.0 L  (d) 9.0 L

42. For the reaction \( \text{SO}_2(g) + \frac{1}{2} \text{O}_2(g) \longrightarrow \text{SO}_3(g) \), if \( K_P = K_C (RT)^x \) where the symbols have usual meaning then the value of x is (assuming ideality): [JEE M 2014]

(a) −1  (b) \( \frac{1}{2} \)  
(c) \( \frac{1}{2} \)  (d) 1

43. The standard Gibbs energy change at 300 K for the reaction 2A \( \longrightarrow \) B + C is 2494.2 J. At a given time, the composition of the reaction mixture is [A] = \( \frac{1}{2} \), [B] = 2 and [C] = \( \frac{1}{2} \). The reaction proceeds in the : [R = 8.314 J/K/mol, e = 2.718] [JEE M 2015]

(a) forward direction because Q < K_c  
(b) reverse direction because Q < K_c  
(c) forward direction because Q > K_c  
(d) reverse direction because Q > K_c

44. The following reaction is performed at 298 K.

\[ 2\text{NO}(g) + \text{O}_2(g) \longrightarrow 2\text{NO}_2(g) \]

The standard free energy of formation of NO(g) is 86.6 kJ/mol at 298 K. What is the standard free energy of formation of NO₂(g) at 298 K? (\( K_p = 1.6 \times 10^{12} \)) [JEE M 2015]

(a) 86600 − \( \frac{\ln(1.6 \times 10^{12})}{R(298)} \)  
(b) 0.5[2 × 86600 − R(298) \ln(1.6 \times 10^{12})]  
(c) R(298) \ln(1.6 \times 10^{12})− 86600  
(d) 86600 + R(298) \ln(1.6 \times 10^{12})

45. The equilibrium constant at 298 K for a reaction A + B \( \rightleftharpoons \) C + D is 100. If the initial concentration of all the four species were 1 M each, then equilibrium concentration of D (in mol L⁻¹) will be: [JEE M 2016]

(a) 1.818  (b) 1.182  
(c) 0.182  (d) 0.818
1. Anhydrous MgCl₂ is obtained by heating hydrated salt with .......... (1980)
2. The absorption of hydrogen by palladium is commonly known as .......... . (1983 - 1 Mark)
5. Ca²⁺ has a smaller ionic radius than K⁺ because it has .......... . (1993 - 1 Mark)

B  True / False
1. MgCl₂·6H₂O on heating give anhydrous MgCl₂. (1982 - 1 Mark)
2. The softness of group I-A metals increases down the group with increasing atomic number. (1986 - 1 Mark)
3. Sodium when burnt in excess of oxygen gives sodium oxide. (1987 - 1 Mark)

C  MCQs with One Correct Answer
1. A substance absorbs CO₂ and violently reacts with water. The substance is (1978)
   (a) CaCO₃ (b) CaO (c) H₂SO₄ (d) ZnO
2. H₂O₂ is added to following oxides. Which one would give H₂O₂? (1980)
   (a) MnO₂ (b) PbO₂ (c) BaO₂8H₂O (d) NO₂
3. Calcium is obtained by (1980)
   (a) electrolysis of molten CaCl₂. (b) electrolysis of solution of CaCl₂ in water.
   (c) Reduction of CaCl₂ with carbon. (d) roasting of limestone.
4. A solution of sodium metal in liquid ammonia is strongly reducing due to the presence of (1981 - 1 Mark)
   (a) sodium atoms (b) sodium hydride (c) sodium amide (d) solvated electrons
5. Heavy water is (1983 - 1 Mark)
   (a) H₂¹⁸O (b) water obtained by repeated distillation (c) D₂O (d) water at 4°C
6. The hydration energy of Mg²⁺ is larger than that of: (1984 - 1 Mark)
   (a) Al³⁺ (b) Na⁺ (c) Be⁺⁺ (d) Mg³⁺
7. The oxide that gives hydrogen peroxide on treatment with a dilute acid is: (1985 - 1 Mark)
   (a) PbO₂ (b) Na₂O₂ (c) MnO₂ (d) TiO₂
8. Molecular formula of Glauber’s salt is: (1985 - 1 Mark)
   (a) MgSO₄·7H₂O (b) CuSO₄·5H₂O (c) FeSO₄·7H₂O (d) Na₂SO₄·10H₂O
9. Hydrogen gas will not reduce: (1985 - 1 Mark)
   (a) heated cupric oxide (b) heated ferric oxide (c) heated stannic oxide (d) heated aluminium oxide
10. The pair of compounds which cannot exist together in solution is: (1986 - 1 Mark)
    (a) NaHCO₃ and NaOH (b) Na₂CO₃ and NaHCO₃ (c) Na₂CO₃ and NaOH (d) NaHCO₃ and NaCl
11. The metallic lustre exhibited by sodium is explained by (1987 - 1 Mark)
    (a) diffusion of sodium ions (b) oscillation of loose electrons
    (c) excitation of free protons (d) existence of body centered cubic lattice
12. The volume strength of 1.5 N H₂O₂ solution is (1991 - 1 Mark)
    (a) 4.8 (b) 8.4 (c) 3.0 (d) 8.0
13. The following compounds have been arranged in order of their increasing thermal stabilities. Identify the correct order. (1996 - 1 Mark)
    K₂CO₃ (I) MgCO₃ (II) CaCO₃ (III) BeCO₃ (IV)
    (a) I < II < III < IV (b) IV < II < III < I (c) IV < II < I < III (d) II < IV < I < III
14. The set representing the correct order of first ionization potential is (2001S)
    (a) K > Na > Li (b) Be > Mg > Ca (c) B > C > N (d) Ge > Si > C
15. A sodium salt on treatment with MgCl₂ gives white precipitate only on heating. The anion of the sodium salt is
(a) HCO₃⁻ (b) CO₃²⁻ (c) NO₃⁻ (d) SO₄²⁻ (2004 S)

16. Hydrogen peroxide in its reaction with KIO₄ and NH₃OH respectively, is acting as a (JEE Adv. 2014)
(a) Reducing agent, oxidising agent
(b) Reducing agent, reducing agent
(c) Oxidising agent, oxidising agent
(d) Oxidising agent, reducing agent

**MCQs with One or More Than One Correct**

1. When zeolite, which is hydrated sodium aluminium silicate, is treated with hard water the sodium ions are exchanged with (1990 - 1 Mark)
(a) H⁺ ions (b) Ca²⁺ ions (c) SO₄²⁻ ions (d) Mg²⁺ ions (e) OH⁻ ions

2. The species that do not contain peroxide ions are (1992 - 1 Mark)
(a) PbO₂ (b) H₂O₂ (c) SrO₂ (d) BaO₂

3. Highly pure dilute solution of sodium in liquid ammonia (1998 - 2 Marks)
(a) shows blue colour (b) exhibits electrical conductivity
(c) produces sodium amide (d) produces hydrogen gas.

4. The species present in solution when CO₂ is dissolved in water are (2006 - 5M, -1)
(a) CO₂, H₂CO₃, HCO₃⁻, CO₃²⁻ (b) H₂CO₃, CO₃²⁻
(c) CO₃²⁻, HCO₃⁻ (d) CO₂, H₂O

5. MgSO₄ on reaction with NH₄OH and Na₃HPO₄ forms a white crystalline precipitate. What is its formula? (2006 - 5M, -1)
(a) Mg(NH₄)PO₄ (b) Mg₃(PO₄)₂
(c) MgCl₂·MgSO₄ (d) MgSO₄

6. The compound(s) formed upon combustion of sodium metal in excess air is (are) (2009 - 5M, -1)
(a) Na₂O₂ (b) Na₂O (c) NaO₂ (d) NaOH

7. The reagent(s) used for softening the temporary hardness of water is (are) (2010)
(a) Ca₃(PO₄)₂ (b) Ca(OH)₂ (c) Na₂CO₃ (d) NaCl

**Subjective Problems**

1. Give reasons for the following:
(i) Sodium carbonate is made by Solvay process but the same process is not extended to the manufacture of potassium carbonate. (1981 - 1 Mark)
(ii) Hydrogen peroxide is a better oxidising agent than water. (1986 - 1 Mark)
(iii) Magnesium oxide is used for the lining of steel making furnace. (1987 - 1 Mark)
(iv) Why is sodium chloride added during electrolysis of fused anhydrous magnesium chloride? (1987 - 1 Mark)
(v) Hydrogen peroxide acts as an oxidising as well as a reducing agent. (1992 - 1 Mark)
(vi) The crystalline salts of alkaline earth metals contain more water of crystallisation than the corresponding alkali metal salts. (1997 - 2 Marks)
(vii) BeCl₂ can be easily hydrolysed. (1999 - 2 Marks)

2. How will you prepare bleaching powder from slaked lime (1982 - 1 Mark)

3. Write down the balanced equations for the reactions when:
(i) Calcium phosphate is heated with a mixture of sand and carbon; (1985 - 1 Mark)
(ii) An alkaline solution of potassium ferricyanide is reacted with hydrogen peroxide. (1982 - 1 Mark)
(iii) Carbon dioxide is passed through a concentrated aqueous solution of sodium chloride saturated with ammonia. (1988 - 1 Mark)
(iv) Potassium ferricyanide reacts with hydrogen peroxide in basic solution. (1989 - 1 Mark)
(v) Carbon dioxide is passed through a suspension of lime stone in water. (1991 - 1 Mark)

4. Give briefly the isolation of magnesium from sea water by the Dow process. Give equations for the steps involved. (1993 - 3 Marks)

5. Complete and balance the following reactions:
Ca₅(PO₄)₃F + H₂SO₄ + H₂O → \[\text{Heat} \rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O} + \ldots\ldots\ldots\ldots\ldots\] (1994 - 1 Mark)

6. A 5.0 cm³ solution of H₂O₂ liberates 0.508 g of iodine from an acidified KI solution. Calculate the strength of H₂O₂ solution in terms of volume strength at STP (1995 - 2 Marks)

7. Explain the difference in the nature of bonding in LiF and Lil (1996 - 2 Marks)

8. To a 25ml H₂O₂ solution, excess of acidified solution of potassium iodide was added. The iodine liberated required 20 ml of 0.3 N sodium thiosulphate solution. Calculate the volume strength of H₂O₂ solution. (1997 - 5 Marks)


11. Arrange the following sulphates of alkaline earth metals in order of decreasing thermal stability: BeSO₄, MgSO₄, CaSO₄, SrSO₄. (1997 - 1 Mark)

12. Work out the following using chemical equation: Chlorination of calcium hydroxide produces bleaching powder. (1998 - 2 Marks)

13. Hydrogen peroxide acts both as an oxidising and as a reducing agent in alkaline solution towards certain first row transition metal ions. Illustrate both these properties of H₂O₂ using chemical equations. (1998 - 4 Marks)

**Assertion & Reason Type Questions**

1. Read the following statement and explanation and answer as per the options given below:

   **Statement:** The alkali metals can form ionic hydrides which contain the hydride ion H⁻.

   **Explanation:** The alkali metals have low electronegativity; their hydrides conduct electricity when fused and liberate hydrogen at the anode. (1994 - 2 Marks)

   (a) Both S and E are true and E is the correct explanation of S.
   (b) Both S and E are true but E is not the correct explanation of S.
   (c) С is true but E is false.
   (d) С is false but E is true.

   This question contains STATEMENT-1 (Assertion) and STATEMENT-2 (Reason) and has 4 choices (a), (b), (c) and (d) out of which ONLY ONE is correct. (2007)

   **STATEMENT-1:** Alkali metals dissolve in liquid ammonia to give blue solutions. because

   **STATEMENT-2:** Alkali metals is liquid ammonia give solvated species of the type [M(NH₃)₅]⁺ (M = alkali metals).

   (a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1
   (b) Statement-1 is True, Statement-2 is True; Statement-2 is not correct explanation for Statement-1
   (c) Statement-1 is True, Statement-2 is False
   (d) Statement-1 is False, Statement-2 is True.

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**Section-B**

1. KO₂ (potassium super oxide) is used in oxygen cylinders in space and submarines because it [2002]
   (a) absorbs CO₂ and increases O₂ content
   (b) eliminates moisture
   (c) absorbs CO₂
   (d) produces ozone.

2. The metallic sodium dissolves in liquid ammonia to form a deep blue coloured solution. The deep blue colour is due to formation of: [2002]
   (a) solvated electron, e(NH₃)ₓ⁻
   (b) solvated atomic sodium, Na(NH₃)ₓ⁻
   (c) Na⁺ + Na⁻
   (d) NaNHₓ + H₂

3. A metal M readily forms its sulphate MSO₄ which is water-soluble. It forms its oxide MO which becomes inert on heating. It forms an insoluble hyroxide M(OH)₂ which is soluble in NaOH solution. Then M is [2002]
   (a) Mg
   (b) Ba
   (c) Ca
   (d) Be.

4. In curing cement plasters water is sprinkled from time to time. This helps in [2003]
   (a) developing interlocking needle-like crystals of hydrated silicates
   (b) hydrating sand and gravel mixed with cement
   (c) converting sand into silicic acid
   (d) keeping it cool

5. The substance not likely to contain CaCO₃ is [2003]
   (a) calcined gypsum
   (b) sea shells
   (c) dolomite
   (d) a marble statue

6. The solubilities of carbonates decrease down the magnesium group due to a decrease in [2003]
   (a) hydration energies of cations
   (b) inter-ionic attraction
   (c) entropy of solution formation
   (d) lattice energies of solids

7. Which one of the following processes will produce hard water? [2003]
   (a) Saturation of water with MgCO₃
   (b) Saturation of water with CaSO₄
   (c) Addition of Na₂SO₄ to water
   (d) Saturation of water with CaCO₃

8. One mole of magnesium nitride on the reaction with an excess of water gives: [2004]
   (a) two moles of ammonia
   (b) one mole of nitric acid
   (c) one mole of ammonia
   (d) two moles of nitric acid

9. Which of the following species is diamagnetic in nature? [2005]
   (a) H₂⁻
   (b) H₂⁺
   (c) H₂
   (d) He₂⁺
10. Based on lattice energy and other considerations which one of the following alkali metal chlorides is expected to have the highest melting point? [2005]
(a) RbCl
(b) KCl
(c) NaCl
(d) LiCl

11. Which of the following statements in relation to the hydrogen atom is correct? [2005]
(a) 3s, 3p and 3d orbitals all have the same energy
(b) 3s and 3p orbitals are of lower energy than 3d orbital
(c) 3p orbital is lower in energy than 3d orbital
(d) 3s orbital is lower in energy than 3p orbital

12. The ionic mobility of alkali metal ions in aqueous solution is maximum for [2006]
(a) Li⁺
(b) Na⁺
(c) K⁺
(d) Rb⁺

13. In context with the industrial preparation of hydrogen from water gas $(\text{CO} + \text{H}_2)$, which of the following is the correct statement? [2008]
(a) CO and H₂ are fractionally separated using differences in their densities
(b) CO is removed by absorption in aqueous Cu₂Cl₂ solution
(c) H₂ is removed through occlusion with pd
(d) CO is oxidised to CO₂ with steam in the presence of a catalyst followed by absorption of of CO₂ in alkali

14. Which of the following on thermal decomposition yields a basic as well as acidic oxide? [2012]
(a) NaNO₃
(b) KClO₃
(c) CaCO₃
(d) NH₄NO₃

15. Very pure hydrogen (99.9) can be made by which of the following processes? [2012]
(a) Reaction of methane with steam
(b) Mixing natural hydrocarbons of high molecular weight
(c) Electrolysis of water
(d) Reaction of salts like hydrides with water

16. In which of the following reactions H₂O₂ acts as a reducing agent? [JEE M 2014]
(a) $\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow 2\text{H}_2\text{O}$
(b) $\text{H}_2\text{O}_2 + 2\text{e}^- \rightarrow \text{O}_2 + 2\text{H}^+$
(c) $\text{H}_2\text{O}_2 + 2\text{e}^- \rightarrow 2\text{OH}^-$
(d) $\text{H}_2\text{O}_2 + 2\text{OH}^- + 2\text{e}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O}$

17. Which one of the following alkaline earth metal sulphates has its hydration enthalpy greater than its lattice enthalpy? [JEE M 2015]
(a) BaSO₄
(b) SrSO₄
(c) CaSO₄
(d) BeSO₄

18. The molecular formula of a commercial resin used for exchanging ions in water softening is $\text{C}_8\text{H}_{12}\text{SO}_3^- \text{Na}^+$ (Mol. wt. 206). What would be the maximum uptake of Ca²⁺ ions by the resin when expressed in mole per gram resin? [JEE M 2015]
(a) $\frac{2}{309}$
(b) $\frac{1}{412}$
(c) $\frac{1}{103}$
(d) $\frac{1}{206}$

19. From the following statements regarding $\text{H}_2\text{O}_2$, choose the incorrect statement: [JEE M 2015]
(a) It has to be stored in plastic or wax lined glass bottles in dark
(b) It has to be kept away from dust
(c) It can act only as an oxidizing agent
(d) It decomposes on exposure to light

20. Which one of the following statements about water is FALSE? [JEE M 2016]
(a) There is extensive intramolecular hydrogen bonding in the condensed phase.
(b) Ice formed by heavy water sinks in normal water.
(c) Water is oxidized to oxygen during photosynthesis.
(d) Water can act both as an acid and as a base.

21. Which of the following atoms has the highest first ionization energy? [JEE M 2016]
(a) K
(b) Sc
(c) Rb
(d) Na

22. The main oxides formed on combustion of Li, Na and K in excess of air are, respectively: [JEE M 2016]
(a) Li₂O₂, Na₂O₂ and KO₂
(b) Li₂O, Na₂O₂ and KO₂
(c) Li₂O, Na₂O and KO₂
(d) LiO₂, Na₂O₂ and K₂O
CHAPTER 9

Organic Chemistry — Some Basic Principles and Techniques

Section-A

JEE Advanced/ IIT-JEE

A  Fill in the Blanks

1. Among the given cations, ............... is most stable. (1981)
   (sec-butyl carbocation ion; tert-butyl carbocation ion; n-butyl
   carbocation ion)
2. The compound having both sp and sp² hybridized carbon
   atoms is ............... (1981)
   (propene, propane, propadiene)
3. ............... ring is most strained. (1981)
   (Cyclopropane, Cyclobutane, Cyclopentane)
4. The terminal carbon atom in butane is ............... hybridised. (1985)
5. A ............... diol has two hydroxyl groups on ............... carbon
   atoms. (1986)
6. Isomers which are ............... mirror images are known as
   ............... . (1988)
   (superimposable, non-superimposable, enantiomers,
   diastereomers, epimers)
7. The valence atomic orbitals on carbon in silver acetylde is
   ............... hybridized. (1990)
8. The kind of delocalization involving sigma bond orbitals is
called ............... . (1994)
9. The IUPAC name of succinic acid is ............... . (1994)

B  True / False

1. Iodide is a better nucleophile than bromide. (1985 - ½ Mark)
2. An electron donating substituent in benzene orients the
   incoming electrophilic group to the meta position. (1987)
3. 2, 3, 4-Trichloropentane has three asymmetric carbon atoms.
   (1990)
4. During S_N_1 reaction, the leaving group leaves the molecule
   before the incoming group is attached to the molecule. (1990)

C  MCQs with One Correct Answer

1. The bond order of individual carbon-carbon bonds in
   benzene is ............... (1981)
   (a) one        (b) two
   (c) between one and two  (d) one and two, alternately
2. Molecule in which the distance between the two adjacent
   carbon atoms is largest is ............... (1981)
   (a) Ethane   (b) Ethene
   (c) Ethyne   (d) Benzene
3. The compound which is not isomeric with diethyl ether is
   ............... (1981)
   (a) n-propyl methyl ether    (b) butan-1-ol
   (c) 2-methylpropan-2-ol      (d) butanone
4. Among the following, the compound that can be most readily
   sulphonated is ............... (1982)
   (a) benzene    (b) nitrobenzene
   (c) toluene    (d) chlorobenzene
5. The compound 1, 2-butadiene has ............... (1983)
   (a) only sp hybridized carbon atoms
   (b) only sp² hybridized carbon atoms
   (c) both sp and sp² hybridized carbon atoms
   (d) sp, sp² and sp³ hybridized carbon atoms
6. Which of the following compounds will exhibit cis-trans
   (geometrical) isomerism? ............... (1983)
   (a) 2-butene      (b) 2-butyne
   (c) 2-butanol     (d) butanal
7. The IUPAC name of the compound having the formula
   \[
   \begin{align*}
   &\text{CH}_3 \\
   &\text{H}_3\text{C} - \text{C} - \text{CH} = \text{CH}_2 \\
   &\text{CH}_3
   \end{align*}
   \]
   is ............... (1984)
   (a) 3, 3, 3-Trimethyl-1-propene
   (b) 1, 1, 1-Trimethyl-2-propene
   (c) 3, 3-Dimethyl-1-butene
   (d) 2, 2-Dimethyl-3-butene
8. An isomer of ethanol is ............... (1986)
   (a) methanol    (b) diethyl ether
   (c) acetone    (d) dimethyl ether
9. Out of the following compounds, which will have a zero
   dipole moment? ............... (1987)
   (a) 1, 1-dichloroethylene
   (b) cis-1, 2-dichloroethylene
   (c) trans-1, 2-dichloroethylene
   (d) None of these compounds
10. The bond between carbon atom (1) and carbon atom (2) in compound $\text{N} = \text{C} - \text{CH} = \text{CH}_2$ involves the hybrids as $sp^2$ and $sp^2$.

11. The IUPAC name of the compound $\text{CH}_2 = \text{CH} - \text{CH} - \text{CH}_2$ is
   (a) 1,1-dimethyl-2-propene  (b) 3-methyl 1-butene
   (c) 2-vinylpropane  (d) 1-isopropylenylene

12. The number of isomers of $\text{C}_6\text{H}_4$ is
   (a) 4  (b) 5  (c) 6  (d) 7

13. The Cl—C—Cl angle in 1,1,2,2-tetrachloroethene and tetrachloromethane respectively will be about
   (a) $120^\circ$ and $109.5^\circ$  (b) $90^\circ$ and $109.5^\circ$
   (c) $109.5^\circ$ and $90^\circ$  (d) $109.5^\circ$ and $120^\circ$

14. In $\text{CH}_3\text{CH}_2\text{OH}$, the bond that undergoes heterolytic cleavage most readily is
   (a) C—C  (b) C—O  (c) C—H  (d) O—H

15. The compound which has one isopropyl group is:
   (a) 2,2,3,3-tetramethylpentane  (b) 2,2-dimethylpentane
   (c) 2,2,3-trimethylpentane  (d) 2-methylpentane

16. The C—H bond distance is the longest in:
   (a) $\text{C}_2\text{H}_2$  (b) $\text{C}_2\text{H}_4$  (c) $\text{C}_2\text{H}_5$  (d) $\text{C}_2\text{H}_4\text{Br}_2$

17. The number of sigma and pi-bonds in 1-butene-3-yne are:
   (a) 5 sigma and 5 pi  (b) 7 sigma and 3 pi  (c) 8 sigma and 2 pi  (d) 5 sigma and 4 pi

18. The compound which gives the most stable carbonium ion on dehydration is:
   (a) $\text{CH}_3 - \text{CH} - \text{CH}_2\text{OH}$  (b) $\text{CH}_3 - \text{C} - \text{OH}$
   (c) $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2\text{OH}$  (d) $\text{CH}_3 - \text{CH} - \text{CH}_2 - \text{CH}_3$

19. The hybridization of carbon atoms in C—C single bond of $\text{HC} \equiv \text{C} - \text{CH} = \text{CH}_2$ is
   (a) $sp^3 - sp^3$  (b) $sp^2 - sp^3$
   (c) $sp - sp^2$  (d) $sp^3 - sp$

20. The products of combustion of an aliphatic thiol (RSH) at 298 K are
   (a) $\text{CO}_2(g)$, $\text{H}_2\text{O}(g)$ and $\text{SO}_2(g)$  (b) $\text{CO}_2(g)$, $\text{H}_2\text{O}(l)$ and $\text{SO}_2(g)$
   (c) $\text{CO}_2(l)$, $\text{H}_2\text{O}(l)$ and $\text{SO}_2(g)$  (d) $\text{CO}_2(g)$, $\text{H}_2\text{O}(l)$ and $\text{SO}_2(l)$

21. Isomers which can be interconverted through rotation around a single bond are
   (a) Conformers  (b) Diastereomers
   (c) Enantiomers  (d) Positional isomers

22. The structure shows:
   (a) geometrical isomerism  (b) optical isomerism
   (c) geometrical & optical isomerism  (d) tautomerism

23. Allyl isocyanide has:
   (a) 9$\pi$ and 4$\pi$ bonds  (b) 8$\pi$ and 5$\pi$ bonds
   (c) 9$\sigma$, 3$\pi$ and 2 non-bonded electrons  (d) 8$\sigma$, 3$\pi$ and 4 non-bonded electrons

24. Arrange in order of decreasing trend towards $S_E$ Reactions:
   Chlorobenzene, benzene, anilinium chloride, toluene
   (a) II > I > III > IV  (b) III > I > II > IV
   (c) IV > II > I > III  (d) I > II > III > IV

25. Most stable carbonium ion is:
   (a) $p-$NO$_2$—C$_6$H$_4$—CH$_2^+$  (b) C$_6$H$_5$CH$_3^+$
   (c) $p-$Cl—C$_6$H$_4$—CH$_2^+$  (d) p-$CH_3$O—C$_6$H$_4$—CH$_2^+$

26. In the following compounds,
   (a) $\text{HO}$  (b) $\text{CH}_3$
   (c) $\text{NO}_2$  (d) $\text{ND}_2$

   The order of acidity is:
   (a) III > IV > I > II  (b) I > IV > III > II
   (c) II > I > III > IV  (d) IV > III > I > II

27. Arrange the following compounds in order of increasing dipole moment.
   Toluene (I)  $m$-dichlorobenzene (II)  o-dichlorobenzene (III)  $p$-dichlorobenzene (IV)
   (a) I < IV < II < III  (b) IV < I < II < III
   (c) IV < I < III < II  (d) IV < III < I < II

28. How many optically active stereoisomers are possible for butane-2, 3-diol?
   (a) 1  (b) 2  (c) 3  (d) 4
29. In the compound $\text{CH}_2 = \text{CH} - \text{CH}_2 - \text{CH}_2 - \text{C} = \text{CH}$, the $\text{C}_2 - \text{C}_3$ bond is of the type, $\text{(1999)}$ (a) $sp - sp^2$  
(b) $sp^3 - sp^3$  
(c) $sp - sp^3$  
(d) $sp^3 - sp^3$  

30. The optically active tartaric acid is named as D-$(+)$-tartaric acid because it has a positive $\text{(1999)}$ (a) optical rotation and is derived from D-glucose  
(b) pH in organic solvent  
(c) optical rotation and is derived from D-$(+)$-glyceraldehyde  
(d) optical rotation only when substituted by deuterium

31. Which of the following compounds will exhibit geometrical isomerism? $\text{(2000S)}$ (a) 1-Phenyl-2-butene  
(b) 3-Phenyl-1-butene  
(c) 2-Phenyl-1-butene  
(d) 1,1-Diphenyl-1-propene

32. Which of the following has the highest nucleophilicity? $\text{(2000S)}$ (a) $\text{F}^-$  
(b) $\text{OH}^-$  
(c) $\text{CH}_3^-$  
(d) $\text{NH}_2^-$

33. The order of reactivities of the following alkyl halides for an $\text{S}_\text{N} 2$ reaction is $\text{(2000S)}$ (a) $\text{RF} > \text{RCl} > \text{RBr} > \text{RI}$  
(b) $\text{RF} > \text{RBr} > \text{RCl} > \text{RI}$  
(c) $\text{RCl} > \text{RBr} > \text{RF} > \text{RI}$  
(d) $\text{RI} > \text{RBr} > \text{RCl} > \text{RF}$

34. Which of the following has the most acidic hydrogen? $\text{(2000S)}$ (a) 3-Hexanone  
(b) 2,4-Hexanediene  
(c) 2,5-Hexanediene  
(d) 2,3-Hexanediene

35. The number of isomers for the compound with molecular formula $\text{C}_2\text{H}_3\text{BrClIF}$ is $\text{(2001S)}$ (a) 3  
(b) 4  
(c) 5  
(d) 6

36. An $\text{S}_\text{N} 2$ reaction at an asymmetric carbon of a compound always gives $\text{(2001S)}$ (a) an enantiomer of the substrate  
(b) a product with opposite optical rotation  
(c) a mixture of diastereomers  
(d) a single stereoisomer

37. Which of the following compounds exhibit stereoisomerism? $\text{(2002S)}$ (a) 2-methylbutene-$1$  
(b) 3-methylbutene-$1$  
(c) 3-methylbutanoic acid  
(d) 2-methylbutanoic acid

38. Which of the following acids has the smallest dissociation constant? $\text{(2002S)}$ (a) $\text{CH}_3\text{CH}_{\text{F}}\text{COOH}$  
(b) $\text{FCH}_2\text{CH}_2\text{COOH}$  
(c) $\text{BrCH}_2\text{CH}_2\text{COOH}$  
(d) $\text{CH}_2\text{CHBrCOOH}$

39. Identify the correct order of boiling points of the following compounds; $\text{(2002S)}$ (a) $1 > 2 > 3$  
(b) $3 > 1 > 2$  
(c) $1 > 3 > 2$  
(d) $3 > 2 > 1$

40. Identify the correct order of reactivity in electrophilic substitution reactions of the following compounds $\text{(2002S)}$

41. Which of the following hydrocarbons has the lowest dipole moment? $\text{(2002S)}$ (a) $1 > 2 > 3 > 4$  
(b) $4 > 3 > 2 > 1$  
(c) $2 > 1 > 3 > 4$  
(d) $2 > 3 > 1 > 4$

42. Which of the following represents the given mode of hybridisation $sp^2 - sp^2 - sp - sp$ from left to right? $\text{(2003S)}$ (a) $\text{H}_2\text{C} = \text{CH} - \text{C} = \text{N}$  
(b) $\text{HC} = \text{C} = \text{C} = \text{CH}$  
(c) $\text{H}_2\text{C} = \text{C} = \text{C} = \text{CH}_2$  
(d) $\text{H}_2\text{C} = \text{C} = \text{C} = \text{CH}_2$

43. Among the following, the molecule with the highest dipole moment is: $\text{(2003S)}$ (a) $\text{CH}_3\text{Cl}$  
(b) $\text{CH}_2\text{Cl}_2$  
(c) $\text{CHCl}_3$  
(d) $\text{CCl}_4$

44. In the given conformation, if $\text{C}_2$ is rotated about $\text{C}_2 - \text{C}_3$ bond anticlockwise by an angle of $120^\circ$ then the conformation obtained is $\text{(2004S)}$ (a) fully eclipsed conformation  
(b) partially eclipsed conformation  
(c) gauche conformation  
(d) staggered conformation

45. Which of the following resonating structures of 1-methoxy-1,3-butadiene is least stable? $\text{(2005S)}$ (a) $\text{CH}_2 - \text{CH} = \text{CH} = \text{O} - \text{CH}_3$  
(b) $\text{CH}_2 = \text{CH} - \text{CH} = \text{O} - \text{CH}_3$  
(c) $\text{CH}_2 = \text{CH} - \text{CH} = \text{O} - \text{CH}_3$  
(d) $\text{CH}_2 = \text{CH} - \text{CH} - \text{O} - \text{CH}_3$
46. Compound on hydrolysis in aqueous acetone will give 

\[ \text{(2005S)} \]

(i) \( \text{CH}_3O-\text{O} \) \( \text{H} \) \( \text{Cl} \) \( \text{CH}_3 \) \( \text{CH}_3 \) \( \text{NO}_2 \)

(ii) \( \text{CH}_3O-\text{O} \) \( \text{H} \) \( \text{OH} \) \( \text{CH}_3 \) \( \text{CH}_3 \) \( \text{CH}_3 \) \( \text{NO}_2 \)

(iii) \( \text{CH}_3O-\text{O} \) \( \text{OH} \) \( \text{H} \) \( \text{CH}_3 \) \( \text{OH} \) \( \text{CH}_3 \) \( \text{CH}_3 \) \( \text{NO}_2 \)

(a) Mixture of (i) and (ii) (b) Mixture of (i) and (iii)
(c) Only (iii) (d) Only (i)

47. The IUPAC name of \( \text{C}_6\text{H}_5\text{COCl} \) is 

\[ \text{(2006 - 3M, -I)} \]

(a) Benzene chloro ketone (b) Benzoyl chloride
(c) Chloro phenyl ketone (d) Benzene carbonyl chloride

48. In the following reaction,

\[ \text{Conc. HNO}_3 \]

the structure of the major product 'X' is 

(a) \( \text{O} \) \( \text{O} \) \( \text{N} \) \( \text{O} \) \( \text{H} \)

(b) \( \text{O}_2\text{N} \) \( \text{N} \) \( \text{O} \) \( \text{H} \) \( \text{H} \)

(c) \( \text{O} \) \( \text{O} \) \( \text{N} \) \( \text{O} \) \( \text{H} \)

49. Among the following, the least stable resonance structure is 

\[ \text{(2007)} \]

(a) \( \text{CH}_3 \) \( \text{O} \) \( \text{N} \) \( \text{O} \) \( \text{H} \)

(b) \( \text{CH}_3 \) \( \text{O} \) \( \text{N} \) \( \text{O} \) \( \text{H} \)

(c) \( \text{CH}_3 \) \( \text{O} \) \( \text{N} \) \( \text{O} \) \( \text{H} \)

(d) \( \text{O}_2\text{N} \) \( \text{N} \) \( \text{O} \) \( \text{H} \) \( \text{H} \)

50. The number of stereoisomers obtained by bromination of \( \text{trans-2-butene} \) is 

\[ \text{(2007)} \]

(a) 1 (b) 2 (c) 3 (d) 4

51. Hyperconjugation involves overlap of the following orbitals 

\[ \text{(2008)} \]

(a) \( \sigma-\pi \) (b) \( \sigma-\sigma \) (c) \( p-p \) (d) \( \pi-\pi \)

52. The correct stability order for the following species is 

\[ \text{(2008)} \]

(i) \( \text{O} \) \( \text{O} \) \( \text{O} \) \( \text{O} \) \( \text{O} \) (ii) \( \text{O} \) \( \text{O} \) \( \text{O} \) \( \text{O} \) \( \text{O} \) (iii) \( \text{O} \) \( \text{O} \) \( \text{O} \) \( \text{O} \) \( \text{O} \) (iv) \( \text{O} \) \( \text{O} \) \( \text{O} \) \( \text{O} \) \( \text{O} \)

(a) \( \text{II} > \text{IV} > \text{I} > \text{III} \) (b) \( \text{I} > \text{II} > \text{III} > \text{IV} \)

(c) \( \text{II} > \text{I} > \text{IV} > \text{III} \) (d) \( \text{I} > \text{II} > \text{III} > \text{IV} \)

53. The IUPAC name of the following compound is 

\[ \text{(2009)} \]

(a) 4-Bromo-3-cyanophenol (b) 2-Bromo-5-hydroxybenzonitrile
(c) 2-Cyano-4-hydroxybromobenzene (d) 6-Bromo-3-hydroxybenzonitrile
54. In the following carbocation, H/CH\(_3\) that is most likely to migrate to the positively charged carbon is \(\text{(2009)}\)

\[
\begin{array}{c}
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\end{array}
\]

(a) CH\(_3\) at C-4
(b) H at C-4
(c) CH\(_3\) at C-2
(d) H at C-2

55. Among the following compounds, the most acidic is \(\text{(2011)}\)

(a) p-nitrophenol
(b) p-hydroxybenzoic acid
(c) o-hydroxybenzoic acid
(d) p-toluic acid

56. KI in acetone, undergoes \(S\text{N}_2\) reaction with each of P, Q, R and S. The rates of the reaction vary as \(J\text{EE Adv. 2013}\)

\[
\begin{array}{c}
\text{H} \\
\text{C} \\
\text{Cl} \\
\end{array}
\]

P Q R S

(a) \(P > Q > R > S\)
(b) \(S > P > R > Q\)
(c) \(P > R > Q > S\)
(d) \(R > P > S > Q\)

D MCQs with One or More Than One Correct

1. Resonance structures of a molecule should have:
   (a) identical arrangement of atoms \(\text{(1984)}\)
   (b) nearly the same energy content
   (c) the same number of paired electrons
   (d) identical bonding

2. Phenol is less acidic than:
   (a) acetic acid \(\text{(1986)}\)
   (b) \(p\)-methoxyphenol
   (c) \(p\)-nitrophenol
   (d) ethanol

3. Dipole moment is shown by:
   (a) 1,4-dichlorobenzene \(\text{(1986)}\)
   (b) cis-1,2-dichloroethane
   (c) trans-1,2-dichloroethene
   (d) trans-1,2-dichloro-2-pentene

4. Only two isomeric monochloro derivatives are possible for:
   (a) \(n\)-butane \(\text{(1986)}\)
   (b) 2,4-dimethylpentane
   (c) benzene
   (d) 2-methylpropane

5. Which of the following have asymmetric carbon atom? \(\text{(1989)}\)

\[
\begin{array}{c}
\text{Cl} \\
\text{Br} \\
\end{array}
\]

(a) H–C–C–H
(b) H–C–C–Cl
(c) H–C–C–CH\(_2\)Cl
(d) H–C–C–CH\(_3\)

6. What is the decreasing order of strength of the bases OH\(^-\), NH\(_2\), H-C≡C- and CH\(_3\)CH\(_2\)? \(\text{(1993)}\)

(a) CH\(_3\)–CH\(_2\) > NH\(_2\) > H–C≡C- > OH\(^-\)
(b) H–C≡C- > CH\(_3\)–CH\(_2\) > NH\(_2\) > OH\(^-\)
(c) OH\(^-\) > NH\(_2\) > H–C≡C- > CH\(_3\)–CH\(_2\)
(d) NH\(_2\) > H–C≡C- > OH\(^-\) > CH\(_3\)–CH\(_2\)

7. Which of the following compounds will show geometrical isomerism? \(\text{(1998)}\)

(a) 2-butene
(b) propene
(c) 1-phenylpropene
(d) 2-methyl-2-butene

8. Among the following compounds, the strongest acid is \(\text{(1998)}\)

(a) HC≡CH
(b) C\(_6\)H\(_5\)
(c) C\(_2\)H\(_6\)
(d) CH\(_3\)OH

9. Tautomerism is exhibited by \(\text{(1998)}\)

(a) \(\begin{array}{c}
\text{O} \\
\text{O} \\
\end{array}\)

(b) \(\begin{array}{c}
\text{O} \\
\text{O} \\
\end{array}\)

(c) \(\begin{array}{c}
\text{O} \\
\text{O} \\
\end{array}\)

(d) \(\begin{array}{c}
\text{O} \\
\text{O} \\
\end{array}\)

10. An aromatic molecule will:
    (a) have 4n \(\pi\) electrons \(\text{(1999)}\)
    (b) have \((4n+2)\) \(\pi\) electrons
    (c) be planar
    (d) be cyclic

11. The correct statements(s) concerning the structures E,F and G is (are)— \(\text{(2008)}\)

\[
\begin{array}{c}
\text{H} \\
\text{C} \\
\text{C} \\
\text{H} \\
\text{C} \\
\end{array}
\]

(a) E,F, and G are resonance structures
(b) E, F and G are tautomers
(c) F and G are geometrical isomers
(d) F and G are diastereomers

12. The correct statement(s) about the compound given below is (are) \(\text{(2008)}\)

\[
\begin{array}{c}
\text{C} \\
\text{C} \\
\text{C} \\
\text{H} \\
\text{H} \\
\text{Cl} \\
\text{Cl} \\
\text{H} \\
\end{array}
\]

(a) The compound is optically active
(b) The compound possesses centre of symmetry
(c) The compound possesses plane of symmetry
(d) The compound possesses axis of symmetry
13. The correct statement(s) about the compound $\text{H}_2\text{C(HO)}\text{HC}^=\text{CH}^=\text{CH(OH)}\text{CH}_3(X)$ is (are) 
(a) The total number of stereoisomers possible for $X$ is 6 
(b) The total number of diastereomers possible for $X$ is 3 
(c) If the stereochemistry about the double bond in $X$ is trans, the number of enantiomers possible for $X$ is 4 
(d) If the stereochemistry about the double bond in $X$ is cis, the number of enantiomers possible for $X$ is 2

14. In the Newman projection for 2,2-dimethylbutane

X and Y can respectively be 
(a) H and H 
(b) H and C$_2$H$_5$ 
(c) C$_2$H$_5$ and H 
(d) CH$_3$ and CH$_3$

15. Amongst the given options, the compound(s) in which all the atoms are in one plane in all the possible conformations (if any), is (are) 

(a) \[ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \] 
(b) \[ \text{H} \quad \equiv \quad \equiv \quad \equiv \quad \text{H} \] 
(c) H$_2$C$\equiv$C$\equiv$O 
(d) H$_2$C$\equiv$C=CH$_2$

16. Which of the following molecules, in pure form, is (are) unstable at room temperature? 
(a) \[ \text{\includegraphics[width=1cm]{benzene}} \] 
(b) \[ \text{\includegraphics[width=1cm]{benzaldehyde}} \] 
(c) \[ \text{\includegraphics[width=1cm]{oxoacetic_acid}} \] 
(d) \[ \text{\includegraphics[width=1cm]{pyrrole}} \]

17. Which of the given statement(s) about N, O, P and Q with respect to M is (are) correct? 

(a) M and N are non-mirror image stereoisomers 
(b) M and O are identical 
(c) M and P are enantiomers 
(d) M and Q are identical

18. The hyperconjugative stabilities of tert-butyl cation and 2-butene, respectively, are due to 
(a) $\sigma \rightarrow \pi$ (empty) and $\sigma \rightarrow \pi^*$ electron delocalisations 
(b) $\sigma \rightarrow \sigma^*$ and $\sigma \rightarrow \pi$ electron delocalisations 
(c) $\sigma \rightarrow \pi$ (filled) and $\sigma \rightarrow \pi$ electron delocalisations 
(d) $\pi$ (filled) $\rightarrow \sigma^*$ and $\sigma \rightarrow \pi^*$ electron delocalisations

**Subjective Problems**

1. Arrange the following in: 
   (i) Increasing reactivity towards HCN 
   \[ \text{H}_2\text{CHCHO}, \text{CH}_2\text{CHOH}, \text{HCHO}, \text{C}_2\text{H}_5\text{COCH}_3 \] 
   (ii) n-butane, n-butanol, n-butyl chloride, isobutane in increasing order of boiling point. 
   (1988) 
   (iii) benzene, toluene, methoxybenzene, chlorobenzene in increasing order of reactivity towards sulphonation with fuming sulphuric acid. 
   (1988) 
   (iv) Increasing order of acid strength: 
   \[ \text{ClCH}_2\text{COOH(I)}, \text{CH}_2\text{CH}_2\text{COOH(II)}, \text{ClCH}_3\text{CH}_2\text{COOH(III)}, \text{CH}_3\text{CH}_2\text{CH}_2\text{COOH(IV)}, \text{CH}_3\text{COOH(V)} \] 
   (1991) 
   (v) Increasing reactivity in nucleophilic substitution reactions 
   \[ \text{CH}_3\text{F}, \text{CH}_3\text{I}, \text{CH}_3\text{Br}, \text{CH}_3\text{Cl} \] 
   (1992)

2. (i) Write the IUPAC name of: 
   \[ \text{CH}_3\text{CH}_2\text{CH}=\text{CHOH} \] 
   (1986) 
   (ii) Give the IUPAC name of the following compound: 
   \[ \text{Me} = \text{Methyl} \] 
   \[ \text{Me} \quad \text{Me} \quad \text{Me} \quad \text{Me} \quad \text{Me} \quad \text{Me} \quad \text{Me} \] 
   (1990) 
   (iii) Write the IUPAC name for the following:
3. For nitromethane molecule, write structure(s).
   (i) showing significant resonance stabilisation. (1986)
   (ii) indicating tautomerism. (1986)

4. Give reasons for the following:
   (i) Carbon oxygen bond lengths in formic acid are 1.23 Å
       and 1.36 Å and both the carbon oxygen bonds in
       sodium formate have the same value i.e. 1.27 Å. (1988)
   (ii) Phenyl group is known to exert negative inductive
       effect. But each phenyl ring in biphenyl (C₆H₅-C₆H₅)
       is more reactive than benzene towards electrophilic
       substitution. (1992)
   (iii) Aryl halides are less reactive than alkylic halides towards
       nucleophilic reagents. (1994)
   (iv) CH₂=CH⁻ is more basic than HC⁻ = C⁻.
   (v) Normally, benzene gives electrophilic substitution
       reaction rather than electrophilic addition reaction
       although it has double bonds.

5. Write the structural formula of 4-chloro-2-pentene. (1988)


7. Write down the structures of the stereoisomers formed when
   cis-2-butene is reacted with bromine. (1995)

8. Discuss the hybridisation of carbon atoms in allene (C₃H₄)
   and show the π-orbital overlaps. (1999)

9. Identify the pairs of enantiomers and diastereomers from
   the following compounds I, II and III. (2000)

10. Which one is more soluble in diethyl ether – anhydrous
    AlCl₃ or hydrous AlCl₃? Explain in terms of bonding. (2003)

11. Match the \( K_a \) values (2003)

   (a) Benzoic acid
       \[ 6.4 \times 10^{-5} \]

   (b) O₂N
       \[ 30.6 \times 10^{-5} \]

   (c) Cl
       \[ 10.2 \times 10^{-5} \]

   (d) H₃CO
       \[ 3.3 \times 10^{-5} \]

   (e) H₃C
       \[ 4.2 \times 10^{-5} \]


13. Which of the following is more acidic and why? (2004)

\[ \text{H}_3\text{N} \quad \text{H}_3\text{N} \quad \text{H}_3\text{N} \]

14. (i) \( \mu_{obs} = \sum_i \mu_i x_i \), where \( \mu_i \) is the dipole moment of a
    stable conformer of the molecule, \( Z - CH_2 - CH_2 - Z \)
    and \( x_i \) is the mole fraction of the stable conformer.
    Given : \( \mu_{obs} = 1.0 \text{ D} \) and \( x_{(Anti)} = 0.82 \)
    Draw all the stable conformers of \( Z - CH_2 - CH_2 - Z \)
    and calculate the value of \( \mu_{(Gaucho)} \)

(ii) Draw the stable conformer of \( Y - CHD - CHD - Y \)
    (meso form), when \( Y = CH_3 \) (rotation about \( C_2 - C_3 \))
    and \( Y = OH \) (rotation about \( C_1 - C_2 \)) in Newmann
    projection. (2005)
Match the Following

Each question contains statements given in two columns, which have to be matched. The statements in Column-I are labelled A, B, C and D, while the statements in Column-II are labelled p, q, r, s and t. Any given statement in Column-I can have correct matching with ONE OR MORE statement(s) in Column-II. The appropriate bubbles corresponding to the answers to these questions have to be darkened as illustrated in the following example:
If the correct matches are A-p, s and t; B-q and r; C-p and q; and D-s then the correct darkening of bubbles will look like the given.

1. Given below are certain matching type questions, where two columns (each having 4 items) are given. Immediately after the columns the matching grid is given, where each item of Column I has to be matched with the items of Column II, by encircling the correct match(es). Note that an item of Column I can match with more than one item of Column II. All the items of Column II must be matched. Match the following:
   **(2006 - 6M)**

   \[
   \begin{array}{ccc}
   \text{Column I} & \text{Column II} \\
   \text{(A)} C_6H_5H_2CH_2CD_2Br on reaction with C_2H_5O^- & (p) \text{ E1 reaction} \\
   \text{(B)} PhCHBrCH_3 and PhCHBrCD_3, both react with the same rate & (q) \text{ E2 reaction} \\
   \text{(C)} C_6H_5H_2CH_2Br on treatment with C_2H_5O^- and C_2H_5OD gives C_6H_5CD=CH_2 & (r) \text{ E1cB reaction} \\
   \text{(D)} C_6H_5H_2CH_2CH_2Br reacts faster than C_6H_5CD_2CH_2Br on reaction with C_2H_5O^- in ethanol & (s) \text{ First order reaction} \\
   \end{array}
   \]

2. Match the compounds/ions in Column I with their properties/reactions in Column II. Indicate your answer by darkening the appropriate bubbles of the 4 \times 4 matrix given in the ORS.
   **(2007)**

   \[
   \begin{array}{ccc}
   \text{Column I} & \text{Column II} \\
   \text{(A)} C_6H_5CHO & (p) \text{ gives precipitate with 2, 4-dinitrophenylhydrazine} \\
   \text{(B)} CH_3C=CH & (q) \text{ gives precipitate with AgNO}_3 \\
   \text{(C)} CN^- & (r) \text{ is a nucleophile} \\
   \text{(D)} I^- & (s) \text{ is involved in cyanohydrin formation} \\
   \end{array}
   \]

3. Match each of the compounds given in Column-I with the reaction(s), that they can undergo, given in Column-II. **(2009)**

   \[
   \begin{array}{ccc}
   \text{Column-I} & \text{Column-II} \\
   \text{(A)} & (p) \text{ Nucleophilic substitution} \\
   \text{(B)} & (q) \text{ Elimination} \\
   \text{(C)} & (r) \text{ Nucleophilic addition} \\
   \text{(D)} & (s) \text{ Esterification with acetic anhydride} \\
   \end{array}
   \]

   \[
   \begin{array}{ccc}
   & \text{(t) Dehydrogenation} \\
   \end{array}
   \]
4. Match the reactions in Column I with appropriate types of steps/ reactive intermediate involved in these reactions as given in Column II.

Column I

(A) \[ \text{H}_{3}	ext{C} \quad \text{O} \quad \text{C} \quad \text{H}_{3} \quad \text{C} \quad \text{O} \]

\[ \text{aq. NaOH} \rightarrow \]

\[ \text{H}_{2}\text{C} \quad \text{C} \quad \text{H}_{3} \quad \text{C} \quad \text{O} \]

(B) \[ \text{O} \quad \text{CH}_{2}\text{C}_{2}\text{H}_{5}\text{CH}_{2}\text{Cl} \]

\[ \text{CH}_{3}\text{MgI} \rightarrow \]

\[ \text{CH}_{3} \quad \text{CH}_{3} \]

(C) \[ \text{O} \quad \text{CH}_{2}\text{C}_{2}\text{H}_{5}\text{CH}_{2}\text{OH} \]

\[ \text{H}_{2}\text{SO}_{4} \rightarrow \]

\[ \text{H}_{2}\text{C} \quad \text{O} \quad \text{C} \quad \text{H}_{3} \]

(D) \[ \text{CH}_{2}\text{C}_{2}\text{H}_{5}\text{C(CH}_{3})_{2} \]

\[ \text{H}_{2}\text{SO}_{4} \rightarrow \]

\[ \text{H}_{3}\text{C} \quad \text{CH}_{3} \]

 Column II

(p) Nucleophilic substitution

(q) Electrophilic substitution

(r) Dehydration

(s) Nucleophilic addition

(t) Carbanion

---

**H Assertion & Reason Type Questions**

Read the following Statement-1 (Assertion) and Statement -2 (Reason) and answer as per the options given below:

(a) If both Statement -1 and Statement -2 are correct, and Statement -2 is the correct explanation of the Statement -1.

(b) If both Statement -1 and Statement -2 are correct, but Statement -2 is not the correct explanation of the Statement -1.

(c) If Statement -1 is correct but Statement -2 is incorrect.

(d) If Statement -1 is incorrect but Statement -2 is correct.

1. **Statement -1:** Aryl halides undergo nucleophilic substitution with ease.

   **Statement -2:** The carbon-halogen bond in aryl halides has partial double bond character. (1991)

2. **Statement -1:** Phenol is more reactive than benzene towards electrophilic substitution reactions.

   **Statement -2:** In the case of phenol, the intermediate carboxication is more resonance stabilized. (2000)

3. **Statement -1:** Molecules that are not superimposable on their mirror images are chiral.

   **Statement -2:** All chiral molecules have chiral centres. (2007)

---

**I Integer Value Correct Type**

1. The total number of cyclic structural as well as stereo isomers possible for a compound with the molecular formula \( C_{4}H_{10} \) is (2009)

2. The total number of cyclic isomers possible for a hydrocarbon with the molecular formula \( C_{4}H_{8} \) is 5. (2010)

3. The maximum number of isomers (including stereoisomers) that are possible on monochlorination of the following compound is (2011)

\[
\begin{array}{c}
\text{CH}_{3} \\
\text{CH}_{3} \text{CH}_{2} \\
\text{CH}_{2}\text{CH}_{3} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\end{array}
\]

4. The total number of contributing structures showing hyperconjugation (involving C–H bonds) for the following carbocation is (2011)

\[
\begin{array}{c}
\text{H} \\
\text{C} \\
\text{+} \\
\text{CH}_{3} \text{CH}_{3} \\
\end{array}
\]
5. The total number(s) of **stable** conformers with **non-zero** dipole moment for the following compound is (are) 

\[(CH_3)_2C--<(CH_3)_2CH--<CH_3--CH_2--\]

(JEE Adv. 2014)

6. The total number of stereoisomers that can exist for M is 

\[(CH_3)_2C--<(CH_3)_2CH--<CH_3--CH_2--\] \[\rightarrow\] 2-methyl-3-pentanone

(JEE Adv. 2015)

---

**Section-B**

### JEE Main / AIEEE

1. Arrangement of \((CH_3)_2C--<(CH_3)_2CH--<CH_3--CH_2--\) when attached to benzyl or an unsaturated group in increasing order of inductive effect is [2002]

(a) \((CH_3)_2C--<(CH_3)_2CH--<CH_3--CH_2--\)

(b) \(CH_3--CH--<CH_2--<CH_3--C--\)

(c) \((CH_3)_2CH--<CH_3--C--<CH_3--\)

(d) \((CH_3)_2C--<CH_3--CH_2--(CH_3)_2CH--\)

2. A similarity between optical and geometrical isomerism is that [2002]

(a) each forms equal number of isomers for a given compound

(b) if in a compound one is present then so is the other

(c) both are included in stereoisomerism

(d) they have no similarity.

3. Which of the following does not show geometrical isomerism? [2002]

(a) 1,2-dichloro-1-pentene

(b) 1,3-dichloro-2-pentene

(c) 1,1-dichloro-1-pentene

(d) 1,4-dichloro-2-pentene

4. The functional group, which is found in amino acid is [2002]

(a) –COOH group

(b) –NH\(_2\) group

(c) –\(CH_3\) group

(d) both (a) and (b).

5. Which of the following compounds has wrong IUPAC name? [2002]

(a) \(CH_3--CH_2--CH_2--COO--CH_2--CH_3\) \[\rightarrow\] ethyl butanoate

(b) \(CH_3--CH--CH_2--CHO\) \[\rightarrow\] 3-methyl-butanal

(c) \(CH_3--CH--CH--CH_3\) \[\rightarrow\] 2-methyl-3-butanol

(d) \(CH_3--CH--CH--CH_3\) \[\rightarrow\] 2-methyl-3-butanol

6. The IUPAC name of \(CH_3COCH(CH_3)_2\) is [2003]

(a) 2-methyl-3-butanone

(b) 4-methylisopropyl ketone

(c) 3-methyl-2-butanone

(d) Isopropylmethyl ketone

7. In which of the following species is the underlined carbon having \(sp^3\) hybridisation? [2002]

(a) \(CH_3COOH\)

(b) \(CH_3CH_2OH\)

(c) \(CH_3COCH_3\)

(d) \(CH_2=CH--CH_3\)

8. Racemic mixture is formed by mixing two [2002]

(a) isomeric compounds

(b) chiral compounds

(c) meso compounds

(d) enantiomers with chiral carbon.

9. Following types of compounds (as I, II) are studied in terms of isomerism in: [2002]

\(CH_3CH=CHCH_3\)

II

CH\(_3\)CHOH

are studied in terms of isomerism in:

(a) chain isomerism

(b) position isomerism

(c) conformers

(d) stereoisomerism

10. The reaction: [2002]

\((CH_3)_2C--Br\) \[\rightarrow\] \((CH_3)_2C--OH\)

(a) elimination reaction

(b) substitution reaction

(c) free radical reaction

(d) displacement reaction.
11. In the anion HCOO⁻ the two carbon-oxygen bonds are found to be of equal length. What is the reason for it? [2003]
   (a) The C = O bond is weaker than the C — O bond
   (b) The anion HCOO⁻ has two resonating structures
   (c) The anion is obtained by removal of a proton from the acid molecule
   (d) Electronic orbitals of carbon atom are hybridised

12. The general formula CₙH₂ₙO₂ could be for open chain (a) carboxylic acids (b) diols [2003]
    (c) dialdehydes (d) diketones

13. Among the following four structures I to IV, [2003]
    \[ \text{CH}_3 \quad \text{CH}_3 \]
    \[ \text{C}_2\text{H}_5 - \text{CH} - \text{C}_3\text{H}_7, \quad \text{CH}_3 - \text{C} - \text{CH} - \text{C}_2\text{H}_5, \]
    (I) (II)
    \[ \text{H} \quad \text{C}_2\text{H}_5 - \text{CH} - \text{C}_2\text{H}_5 \]
    \[ \text{H}, \quad \text{CH}_3 \]
    (III) (IV)

    It is true that
    (a) only I and II are chiral compounds
    (b) only III is a chiral compound
    (c) only II and IV are chiral compounds
    (d) all four are chiral compounds

14. Which one of the following has the minimum boiling point? [2004]
    (a) 1 - Butene (b) 1 - Butyne
    (c) n-Butane (d) isobutane

15. The IUPAC name of the compound is [2004]
    (a) 3, 3-dimethyl - 1 - cyclohexanol
    (b) 1, 1-dimethyl-3-hydroxy cyclohexane
    (c) 3, 3-dimethyl-1-hydroxy cyclohexane
    (d) 1, 1-dimethyl-3-cyclohexanol

16. Which one of the following does not have sp² hybridized carbon? [2004]
    (a) Acetonitrile (b) Acetic acid
    (c) Acetone (d) Acetamide

17. Which of the following will have a mesoisomer also? [2004]
    (a) 2, 3- Dichloropentane
    (b) 2, 3-Dichlorobutane
    (c) 2-Chlorobutane
    (d) 2-Hydroxypropanoic acid

18. Rate of the reaction [2004]
    \[ R - \overset{O}{\text{Z}} + \overset{\text{Nu}}{\text{Z}} \rightarrow R - \overset{O}{\text{Z}} + \overset{\text{Nu}}{\text{Z}} \]

19. Amongst the following compounds, the optically active alkane having lowest molecular mass is [2004]
    \[ \text{H} \quad \text{C}_2\text{H}_5 \]
    \[ \text{CH}_3 \quad \text{CH}_3 \]
    (a) \[ \text{CH}_3 - \text{CH} - \text{CH}_3 \]
    (b) \[ \text{CH}_3 - \text{CH} - \text{CH}_3 \]
    (c) \[ \text{CH}_3 - \text{CH} - \text{CH}_3 \]
    (d) \[ \text{CH}_3 - \text{CH} - \text{CH}_3 \]

20. Consider the acidity of the carboxylic acids:
    (a) PhCOOH (b) o-NO₂C₆H₄COOH
    (c) p-NO₂C₆H₄COOH (d) m-NO₂C₆H₄COOH

    Which of the following order is correct? [2004]
    (a) 2 > 4 > 1 > 3 (b) 2 > 4 > 3 > 1
    (c) 1 > 2 > 3 > 4 (d) 2 > 3 > 4 > 1

21. Which of the following is the strongest base? [2004]
    (a) \[ \text{H}_3\text{C} = \text{NHF}_2 \]
    (b) \[ \text{H}_3\text{C} = \text{NHCH}_3 \]
    (c) \[ \text{H}_3\text{C} = \text{NHF}_2 \]
    (d) \[ \text{H}_3\text{C} = \text{NH}_2 \]

22. Which of the following compounds is not chiral? [2004]
    (a) 1-chloro-2-methyl pentane
    (b) 2-chloropentane
    (c) 1-chloropentane
    (d) 3-chloro-2-methyl pentane

23. Due to the presence of an unpaired electron, free radicals are: [2005]
    (a) cations (b) anions
    (c) chemically inactive (d) chemically reactive

24. The decreasing order of nucleophilicity among the nucleophiles [2005]
    \[ \text{CH}_3\text{C} - \overset{\text{O}}{\text{O}} \quad (B) \quad \text{CH}_2\text{O}^- \]
    \[ \overset{\text{O}}{\text{O}} \]
    \[ \text{CN}^- \quad (D) \quad \text{H}_3\text{C} - \overset{\text{O}}{\text{O}}^- \]

    (a) (C), (B), (A), (D) (b) (B), (C), (A), (D)
    (c) (D), (C), (B), (A) (d) (A), (B), (C), (D)
25. The reaction
\[ R - C \xrightarrow{\text{O}} X + \text{Nu} \rightarrow R - C \xrightarrow{\text{O}} X + \text{Nu}^{+} \]
is fastest when X is
(a) \( \text{OCOR} \) (b) \( \text{OC}_{2}\text{H}_{5} \)
(c) \( \text{NH}_{2} \) (d) \( \text{Cl} \)

26. The IUPAC name of the compound shown below is:

(a) 3-bromo-1-chlorocyclohexene (b) 1-bromo-3-chlorocyclohexene
(c) 2-bromo-6-chlorocyclohex-1-ene (d) 6-bromo-2-chlorocyclohexene

27. The increasing order of stability of the following free radicals is

(a) \( (\text{C}_6\text{H}_5)_2\text{CH}<\text{C}(\text{C}_6\text{H}_5)_3\text{C} < (\text{CH}_3)_3\text{C} < (\text{CH}_3)_2\text{CH} \)
(b) \( \text{CH}_3\text{C} < (\text{CH}_3)_2\text{CH} < \text{C}(\text{C}_6\text{H}_5)_2\text{C} < (\text{C}_6\text{H}_5)_3\text{C} \)
(c) \( \text{CH}_3\text{C} < (\text{CH}_3)_2\text{CH} < (\text{CH}_3)_2\text{CH} < (\text{C}_6\text{H}_5)_3\text{C} \)
(d) \( (\text{C}_6\text{H}_5)_2\text{CH} < \text{C}(\text{C}_6\text{H}_5)_2\text{CH} < (\text{CH}_3)_2\text{CH} \)

28. \( \text{CH}_3\text{Br} + \text{Nu}^- \rightarrow \text{CH}_3^- + \text{Nu} + \text{Br}^- \) The decreasing order of the rate of the above reaction with nucleophiles \( \text{(Nu}^-) \text{A to D is} \)
\[ \text{Nu}^- = (\text{A) PhO}^-, (\text{B) AcO}^-, (\text{C) HO}^-, (\text{D) CH}_3\text{O}^-) \]
(a) \( A > B > C > D \) (b) \( B > D > C > A \)
(c) \( D > C > A > B \) (d) \( D > C > B > A \)

29. The alkene formed as a major product in the above elimination reaction is

(a) (b) (c) Me

30. Increasing order of stability among the three main conformations (i.e. Eclipse, Anti, Gauche) of 2-fluoroethanol is

(a) Eclipse, Anti, Gauche (b) Anti, Gauche, Eclipse
(c) Eclipse, Gauche, Anti (d) Gauche, Eclipse, Anti

31. The IUPAC name of

(a) 3-ethyl-4,4-dimethylheptane (b) 1, 1-diethyl-2,2-dimethylpentane
(c) 4, 4-dimethyl-5,5-diethylpentane (d) 5, 5-diethyl-4,4-dimethylpentane.

32. Which of the following molecules is expected to rotate the plane of plane-polarised light?

(a) (b) (c) (d)

33. Presence of a nitro group in a benzene ring
(a) deactivates the ring towards electrophilic substitution
(b) activates the ring towards electrophilic substitution
(c) renders the ring basic
(d) deactivates the ring towards nucleophilic substitution.

34. Which one of the following conformations of cyclohexane is chiral?

(a) Boat (b) Twist boat (c) Rigid (d) Chair.

35. The absolute configuration of

(a) \( S, S \) (b) \( R, R \) (c) \( R, S \) (d) \( S, R \)

36. The electrophile, \( E^+ \) attacks the benzene ring to generate the intermediate \( \sigma^- \)-complex. Of the following, which \( \sigma^- \)-complex is lowest energy?

(a) (b) (c) (d)
37. The correct decreasing order of priority for the functional groups of organic compounds in the IUPAC system of nomenclature is [2008]
(a) −COOH, −SO₂H, −CONH₂, −CHO
(b) −SO₂H, −COOH, −CONH₂, −CHO
(c) −CHO, −COOH, −SO₂H, −CONH₂
(d) −CONH₂, −CHO, −SO₂H, −COOH

38. The IUPAC name of neopentane is [2009]
(a) 2,2 dimethylpropane
(b) 2 methylpropane
(c) 2,2 dimethylbutane
(d) 2-methylbutane

39. Arrange the carbanions, [2009]
(CH₃)₂Cc(Cl)Cl₂, (CH₃)₂CH, C₆H₅CH₂ in order of decreasing stability:
(a) (CH₃)₂C ≈ Cl > C₆H₅CH₂ > (CH₃)₂C
(b) C₆H₅CH₂ > (CH₃)₂CH > (CH₃)₂C
(c) (CH₃)₂C ≈ Cl > (CH₃)₂CH > C₆H₅CH₂
(d) C₆H₅CH₂ > Cl > (CH₃)₂C > (CH₃)₂CH

40. The alkene that exhibits geometrical isomerism is:
(a) 2- methyl propene [2009]
(b) 2-butenes
(c) 2- methyl-2-butenes
(d) propene

41. The number of stereoisomers possible for a compound of the molecular formula
CH₃–CH = CH–CH(OH)–Me is:
(a) 6 [2009]
(b) 2
(c) 4
(d) 6

42. The correct order of increasing basicity of the given conjugate bases (R = CH₃) is [2010]
(a) RCOO⁻ < HC ≈ CN ≈ R < NH₂
(b) R ≈ CN ≈ RCOO⁻ < NH₂
(c) RCOO⁻ < NH₂ < HC ≈ CN < R
(d) RCOO⁻ < HC = CN < NH₂ < R

43. Out of the following, the alkene that exhibits optical isomerism is [2010]
(a) 3-methyl-2-pentene (b) 4-methyl-1-pentene
(c) 3-methyl-1-pentene (d) 2-methyl-2-pentene

44. Identify the compound that exhibits tautomerism: [2011]
(a) 2-Butene (b) Lactic acid
(c) 2-Pentanone (d) Phenol

45. A solution of (−) – 1 – chloro – 1 – phenylethane in toluene racemises slowly in the presence of a small amount of SnCl₃ due to the formation of: [JEE M 2013]
(a) carbanion (b) carbene
(c) carboxcation (d) free radical

46. The order of stability of the following carbocations:

CH₂ ≈ CH ─ CH₂ ; CH₃ ≈ CH₂ ─ CH₂ ; CH₂ ≈ CH ─ CH₂

(a) III > II > I (b) II > III > I
(c) I > II > III (d) III > I > II

47. For the estimation of nitrogen, 1.4 g of an organic compound was digested by Kjeldahl method and the evolved ammonia was absorbed in 60 mL of \( \frac{M}{10} \) sulphuric acid. The unreacted acid required 20 mL of \( \frac{M}{10} \) sodium hydroxide for complete neutralization. The percentage of nitrogen in the compound is: [JEE M 2014]
(a) 6% (b) 10%
(c) 3% (d) 5%

48. Which of the following compounds will exhibit geometrical isomerism? [JEE M 2015]
(a) 2 - Phenyl - 1 - butene
(b) 1,1 - Diphenyl - 1 - propene
(c) 1 - Phenyl - 2 - butene
(d) 3 - Phenyl - 1 - butene

49. In Carius method of estimation of halogens, 250 mg of an organic compound gave 141 mg of AgBr. The percentage of bromine in the compound is: [JEE M 2015]
(at. mass Ag =108; Br = 80)
(a) 48 (b) 60
(c) 24 (d) 36
50. The absolute configuration of

\[
\begin{array}{c}
\text{CO}_2\text{H} \\
\text{H} \quad \text{OH} \\
\text{H} \quad \text{Cl} \\
\text{CH}_3
\end{array}
\]

is:
(a) (2S, 3S)  
(b) (2R, 3R)  
(c) (2R, 3S)  
(d) (2S, 3R)

51. The distillation technique most suited for separating glycerol from spent-lye in the soap industry is:

(a) Steam distillation.  
(b) Distillation under reduced pressure.  
(c) Simple distillation  
(d) Fractional distillation
CHAPTER

10

Hydrocarbons

Section-A

Fill in the Blanks

1. ................. is most acidic. (Ethane, Ethene, Ethyne) (1981 - 1 Mark)

2. Acetylene is treated with excess sodium in liquid ammonia. The product is reacted with excess methyl iodide. The final product is ................. . (1983 - 1 Mark)

3. The starting material for the manufacture of polyvinyl chloride is obtained by reacting HCl with ................. . (1983 - 1 Mark)


5. Addition of water to acetylenic compounds is catalyzed by...........and........... . (1993 - 1 Mark)

6. The bond dissociation energy needed to form the benzyl radical from toluene is...........than the formation of the methyl radical from methane. (1994 - 1 Mark)

7. 1, 3-Butadiene with bromine in molar ratio generates predominantly ................. . (1997 - 1 Mark)

True / False

1. Moist ethylene can be dried by passing it through concentrated sulphuric acid. (1982 - 1 Mark)


MCQs with One Correct Answer

   (a) C₂H₂   (b) CH₄   (c) H₂S   (d) CO

2. Which of the following decolourises alkaline KMnO₄ solution (1980)
   (a) C₃H₈   (b) C₂H₄   (c) CH₄   (d) CCl₄

3. The compound with the highest boiling point is (1982 - 1 Mark)
   (a) n-hexane   (b) n-pentane   (c) 2,2-dimethylpropane   (d) 2-methylbutane

4. The maximum number of isomers for an alkene with the molecular formula C₄H₈ is (1982 - 1 Mark)
   (a) 2   (b) 3   (c) 4   (d) 5

5. When propyne is treated with aqueous H₂SO₄ in presence of HgSO₄ the major product is (1983 - 1 Mark)
   (a) propanal   (b) propyl hydrogensulphate   (c) acetone   (d) propanol

6. Which of the following compounds does not dissolve in conc. H₂SO₄ even on warming? (1983 - 1 Mark)
   (a) ethylene   (b) benzene   (c) hexane   (d) aniline

7. Baeyer’s reagent is : (1984 - 1 Mark)
   (a) alkaline permanganate solution   (b) acidified permanganate solution   (c) neutral permanganate solution   (d) aqueous bromine solution

8. Acidic hydrogen is present in : (1985 - 1 Mark)
   (a) ethyne   (b) ethene   (c) benzene   (d) ethane

9. Anti-Markovnikoff addition of HBr is not observed in : (1985 - 1 Mark)
   (a) propene   (b) 1-butene   (c) but-2-ene   (d) pent-2-ene

10. The highest boiling point is expected for : (1986 - 1 Mark)
    (a) iso-octane   (b) n-octane   (c) 2,2,3,3-tetramethylbutane   (d) n-butane

11. Which of the following will have least hindered rotation about carbon-carbon bond? (1987 - 1 Mark)
    (a) Ethane   (b) Ethylene   (c) Acetylene   (d) Hexachloroethane
12. When cyclohexane is poured on water, it floats, because:
(a) cyclohexane is in 'boat' form  \( (1997 - 1 \text{ Mark}) \)
(b) cyclohexane is in 'chair' form
(c) cyclohexane is in 'crown' form
(d) cyclohexane is less dense than water.

13. The product(s) obtained via oxymercuration \( (\text{HgSO}_4 + \text{H}_2\text{SO}_4) \) of 1-butyne would be \( (1999 - 2 \text{ Marks}) \)

(a) \( \text{CH}_3 - \text{CH}_2 - \text{C} - \text{CH}_3 \)
(b) \( \text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CHO} \)
(c) \( \text{CH}_3 - \text{CH}_2 - \text{CHO} + \text{HCHO} \)
(d) \( \text{CH}_3\text{CH}_2\text{COOH} + \text{HCOOH} \)

14. Propyne and propene can be distinguished by \( (2000S) \)
(a) conc. \( \text{H}_2\text{SO}_4 \)
(b) \( \text{Br}_2 \) in \( \text{CCl}_4 \)
(c) dil. \( \text{KMnO}_4 \)
(d) \( \text{AgNO}_3 \) in ammonia

15. Which one of the following will react fastest with \( \text{H}_2 \) under catalytic hydrogenation condition? \( (2000S) \)

(a) \[ \text{R} = \text{R} \]  
(b) \[ \text{H} = \text{H} \]  
(c) \[ \text{R} = \text{R} \]  
(d) \[ \text{R} = \text{R} \]

16. In the presence of peroxide, hydrogen chloride and hydrogen iodide do not give anti-Markovnikov addition to alkenes because \( (2001S) \)
(a) both are highly ionic
(b) one is oxidizing and the other is reducing
(c) one of the steps is endothermic in both the cases
(d) all the steps are exothermic in both the cases

17. Hydrogenation of the above compound in the presence of poisoned palladium catalyst gives \( (2001S) \)
(a) an optically active compound
(b) an optically inactive compound
(c) a racemic mixture
(d) a diastereomeric mixture

18. The reaction of propene with \( \text{HOCI} \) proceeds via the addition of \( (2001S) \)
(a) \( \text{H}^+ \) in the first step
(b) \( \text{Cl}^+ \) in the first step
(c) \( \text{OH}^- \) in the first step
(d) \( \text{Cl}^+ \) and \( \text{OH}^- \) in a single step

19. The nodal plane in the \( \pi \)-bond of ethene is located in \( (2002S) \)
(a) the molecular plane
(b) a plane parallel to the molecular plane
(c) a plane perpendicular to the molecular plane which bisects the carbon - carbon \( \sigma \)-bond at right angle
(d) a plane perpendicular to the molecular plane which contains the carbon - carbon \( \sigma \)-bond.

20. Consider the following reaction \( (2002S) \)
\[
\text{H}_3\text{C} - \text{CH} = \text{CH} - \text{CH}_3 + \text{Br} \rightarrow 'X' + \text{HBr}
\]
Identify the structure of the major product 'X'

(a) \( \text{H}_3\text{C} - \text{CH} - \text{CH}_2 \)
(b) \( \text{H}_3\text{C} - \text{C} = \text{CH}_2 \)
(c) \( \text{H}_3\text{C} - \text{C} - \text{CH}_3 \)
(d) \( \text{H}_3\text{C} - \text{CH} - \text{CH}_3 \)

21. Identify the reagent from the following list which can easily distinguish between 1-butyne and 2-butyne \( (2002S) \)
(a) bromine, \( \text{CCl}_4 \)
(b) \( \text{H}_2\text{Pd/Lindlar catalyst} \)
(c) dilute \( \text{H}_2\text{SO}_4, \text{HgSO}_4 \)
(d) ammonical \( \text{CuCl}_2 \) solution

22. Ph\( \text{C} = \text{C} - \text{CH}_3 \text{Hg}^{2+}/\text{H}^+ \rightarrow A \). A is: \( (2003S) \)

(a) \[ \text{Ph} \overbrace{\text{C}}^{\text{O}} \text{H}_3\text{C} \]
(b) \[ \text{Ph} \overbrace{\text{C}}^{\text{O}} \text{H}_3\text{C} \]
(c) \[ \text{Ph} \overbrace{\text{C}}^{\text{OH}} \text{H}_3\text{C} \]
(d) \[ \text{Ph} \overbrace{\text{C}}^{\text{OH}} \text{H}_3\text{C} \]

23. Which of the following is used for the conversion of 2-hexyne into \( \text{trans}-2\)-hexene? \( (2004S) \)
(a) \( \text{H}_2/\text{Pd}/\text{BaSO}_4 \)
(b) \( \text{H}_2\text{PdCl}_2 \)
(c) \( \text{NaBH}_4 \)
(d) \( \text{Li}-\text{NH}_{3}/\text{C}_2\text{H}_5\text{OH} \)

24. On monochlorination of 2-methylbutane, the total number of chiral compounds formed is \( (2004S) \)

(a) 2  (b) 4  (c) 6  (d) 8

25. Identify the product, \( P \) in the following reaction:
\[
\text{CH}_3 - \text{CH} = \text{CH}_2 + \text{NOCI} \rightarrow P \quad (2006 - 3M - 1)
\]

(a) \[ \text{CH}_3 - \text{CH} - \text{CH}_2 \]
(b) \[ \text{CH}_3 - \text{CH} - \text{CH}_2 \]
(c) \[ \text{CH}_2 - \text{CH}_2 - \text{CH}_2 \]
(d) \[ \text{CH}_3 - \text{CH}_2 - \text{CH} \]

(a) \[ \overbrace{\text{NO}}^{\text{Cl}} \text{Cl} \]
(b) \[ \overbrace{\text{Cl}}^{\text{NO}} \text{Cl} \]
(c) \[ \overbrace{\text{NO}}^{\text{Cl}} \text{Cl} \]
(d) \[ \overbrace{\text{Cl}}^{\text{NO}} \text{Cl} \]
26. Cyclohexene on ozonolysis followed by reaction with zinc dust and water gives compound E. Compound E on further treatment with aqueous KOH yields compound F. Compound F is (2007)
   (a) CHO (b) COOH (c) COOH (d) COOH

27. The synthesis of 3-octyne is achieved by adding a bromoalkane into a mixture of sodium amide and an alkyne. The bromoalkane and alkyne respectively are (2010)
   (a) BrCH₂CH₂CH₂CH₂CH₂CH₂C≡CH
   (b) BrCH₂CH₂CH₂CH₂CH₂C≡CH
   (c) BrCH₂CH₂CH₂CH₂CH₂C≡CH
   (d) BrCH₂CH₂CH₂CH₂CH₂C≡CH

28. The bond energy (in kcal mol⁻¹) of a C–C single bond is approximately (2010)
   (a) 1 (b) 10 (c) 100 (d) 1000

29. In allene (C₃H₄), the type(s) of hybridisation of the carbon atoms is (are) : (2012)
   (a) sp and sp³ (b) sp and sp²
   (c) only sp³ (d) sp² and sp³

30. The number of optically active products obtained from the complete ozonolysis of the given compound is : (2012)
   [CH₃]
   \[\text{CH₃–CH=CH–CH=CH–CH}_3\]
   (a) 0 (b) 1 (c) 2 (d) 4

31. Isomers of hexane, based on their branching, can be divided into three distinct classes as shown in the figure. (JEE Adv. 2014)
   (I) and (II)
   (III)

   The correct order of their boiling point is
   (a) I > II > III (b) III > II > I
   (c) II > III > I (d) III > I > II

D. MCQs with One or More Than One Correct

1. Which one of the following has the smallest heat of hydrogenation per mole? (1993 - 1 Mark)
   (a) 1-butene (b) trans-2-butene (c) cis-2-butene (d) 1,3-butadiene

2. Toluene, when treated with Br₂/Fe, gives p-bromotoluene as the major product because CH₃ group (1999 - 3 Marks)
   (a) is para-directing (b) is meta-directing
   (c) activates the ring by hyperconjugation (d) deactivates the ring

3. \[
\begin{align*}
\text{Cl}_2, \text{hv} & \rightarrow \text{N (isomeric products)}; \\
\text{C}_3\text{H}_7\text{Cl} & \rightarrow \text{M (isomeric products)} \ rac{\text{fractional distillation}}{}
\end{align*}
\]
   Identify N and M (2006 - 5M, -1)
   (a) 6, 4 (b) 6, 6 (c) 4, 4 (d) 3, 3

4. Among P, Q, R and S, the aromatic compound(s) is/are (JEE Advanced 2013-I)
   \[
   \begin{align*}
   \text{Cl} & \rightarrow \text{AlCl₃} \rightarrow \text{P, } \text{Q} & \rightarrow \text{NaH} \rightarrow \text{Q} \\
   \end{align*}
   \[
   \text{O O} \rightarrow (\text{NH}_4\text{CO}_3) \rightarrow \text{R} & \rightarrow \text{S} & \rightarrow \text{HCl} \rightarrow \text{S}
   \]
   (a) P (b) R (c) Q (d) S

5. In the following reaction, the major product is (JEE Adv. 2015)
   \[
   \begin{align*}
   \text{H}_2\text{C} & \rightarrow \text{CH}_3 \rightarrow \text{HBr} \\
   \end{align*}
   \[
   \text{H}_2\text{C} \rightarrow \text{CH}_3 \rightarrow \text{HBr} \rightarrow \text{HBr}
   \]
   (a) H₂C (b) H₂C (c) H₂C (d) H₂C

6. Compound(s) that on hydrogenation produce(s) optically inactive compound(s) is (are) (JEE Adv. 2015)
   (a) (b) (c) (d)
7. Among the following, reaction(s) which gives(give) tert-butyl benzene as the major product is(are) \( \text{(JEE Adv. 2016)} \)

(a) \( \text{Br} \xrightarrow{\text{NaOC}_{2}H_{5}} \)

(b) \( \text{Cl} \xrightarrow{\text{AlCl}_{3}} \)

(c) \( \text{H}_{2}SO_{4} \xrightarrow{} \)

(d) \( \text{OH} \xrightarrow{\text{BF}_{3}OEt_{2}} \)

---

E \hspace{1cm} \text{Subjective Problems}

1. Give one characteristic test which would distinguish \( \text{CH}_{4} \) from \( \text{C}_{2}H_{2} \) \( \text{(1979)} \)

2. Write the structural formula of the major product in each of the following cases:
   (i) the compound obtained by the hydration of ethyne is treated with dilute alkali \( \text{(1981 - 1/2 Mark)} \)
   (ii) ethene mixed with air is passed under pressure over a silver catalyst at 250°C. \( \text{(1981 - 1/2 Mark)} \)
   (iii) \( \text{O} \xrightarrow{\text{(CH}_{3})_{2}CHCH_{2}Cl, \text{AlCl}_{3}} (1992 - 1 \text{ Mark}) \)
   (iv) \( \text{C}_{6}H_{6} + \text{(CH}_{3})_{2}CHCH_{2}OH \xrightarrow{\text{H}_{2}SO_{4}} (1994 - 1 \text{ Mark}) \)
   (v) \( \text{C}_{6}H}_{5}C_{2}H_{5} \xrightarrow{\text{1. Br}_{2}, \text{Heat, Light, 2. NaCN}} (1994 - 1 \text{ Mark}) \)
   (vi) \( \text{Me} \xrightarrow{} + \text{CH}_{3} \xrightarrow{} \text{H} \xrightarrow{} \text{CH}_{2}Br \xrightarrow{} \text{Anhyd. AlCl}_{3} \xrightarrow{} \text{C} \xrightarrow{} (1997 - 1 \text{ Mark}) \)
   (vii) \( \text{O} \xrightarrow{} + \text{CHBr}_{3} + \text{t-BuOK} \xrightarrow{} (1997 - 1 \text{ Mark}) \)
   (viii) \( \text{O} \xrightarrow{} \text{H}_{3} \xrightarrow{} \text{Lindlar catalyst} \xrightarrow{} (2000 - 1 \text{ Mark}) \)

3. Outline the reaction sequence for the conversion of ethene to ethyne (the number of steps should not be more than two). \( \text{(1981 - 1 Mark)} \)

4. State with balanced equations, what happens when propene is bubbled through a hot aqueous solution of potassium permanganate. \( \text{(1982 - 1 Mark)} \)

5. Give reasons for the following:
   (i) Methane does not react with chlorine in the dark. \( \text{(1983 - 1 Mark)} \)
   (ii) Propene reacts with HBr to give isopropyl bromide but does not give n-propyl bromide. \( \text{(1983 - 1 Mark)} \)
   (iii) Although benzene is highly unsaturated, normally it does not undergo addition reaction. \( \text{(1983 - 1 Mark)} \)

6. (i) 2-Methylpropene can be converted into isobutyl bromide by hydrogen bromide, is true under what conditions? \( \text{(1984 - 1 Mark)} \)
   (ii) 'Ethyne and its derivatives will give white precipitate with ammonical silver nitrate solution', is true under what conditions. \( \text{(1984 - 1 Mark)} \)

7. Write down the reactions involved in the preparation of the following, using the reagents indicated against it in parenthesis.
   Ethylbenzene from benzene \( \text{[C}_{2}H}_{3}OH, \text{PCI}_{5}, \text{anhydrous AlCl}_{3} \). \( \text{(1984 - 2 Marks)} \)

8. A certain hydrocarbon A was found to contain 85.7 percent carbon and 14.3 per cent hydrogen. This compound consumes 1 molar equivalent of hydrogen to give a saturated hydrocarbon B. 1.00 g of hydrocarbon A just decolourized 38.05 g of a 5 per cent solution (by weight) of Br\textsubscript{2} in CCl\textsubscript{4}. Compound A, on oxidation with concentrated KMnO\textsubscript{4}, gave compound C (molecular formula \text{C}_{4}H_{8}O) and acetic acid. Compound C could easily be prepared by the action of acidic aqueous mercuric sulphate on 2- butyne. Determine the molecular formula of A and deduce the structure of A, B and C. \( \text{(1984 - 6 Marks)} \)

9. How would you distinguish between
   (i) 2-butyne and 1-butyne. \( \text{(1985 - 1 Mark)} \)
   (ii) cyclohexane and cyclohexene. \( \text{(1988 - 1 Mark)} \)
10. \( n \)-Butane is produced by the monobromination of ethane followed by the Wurtz reaction. Calculate the volume of ethane at NTP required to produce 55 g \( n \)-butane, if the bromination takes place with 90 per cent yield and the Wurtz reaction with 85 per cent yield. \( (1989 - 3 \text{ Marks}) \)

11. Identify, B(C\(_6\)H\(_5\)Br) which adds on HBr in the presence and in the absence of peroxide to give the same product, C\(_6\)H\(_5\)HBr. \( (1993 - 1 \text{ Mark}) \)

12. Identify, D(C\(_6\)H\(_5\)I\(_2\)) an optically active hydrocarbon which on catalytic hydrogenation gives an optically inactive compound, C\(_6\)H\(_{14}\). \( (1993 - 1 \text{ Mark}) \)

13. Draw the stereochemical structures of the products in the following reactions: \( (1994 - 4 \text{ Marks}) \)

\[
R - C \equiv C - R \xrightarrow{\text{H}_2 / \text{Lindlar catalyst}}
\]

14. 1, 4-Pentadiene reacts with excess of HCl in the presence of benzoyl peroxide to give compound X which upon reaction with excess of Mg in dry ether forms Y. Compound Y on treatment with ethyl acetate followed by dilute acid yields Z. Identify the structures of compounds X, Y and Z. \( (1995 - 4 \text{ Marks}) \)

15. An organic compound E(C\(_6\)H\(_6\)) on hydrogenation gives compound F(C\(_6\)H\(_{12}\)). Compound E on ozonolysis gives formaldehyde and 2-ketopropanal. Deduce the structure of compound E. \( (1995 - 2 \text{ Marks}) \)

16. Optically active 2-iodobutane on treatment with NaI in acetone gives a product which does not show optical activity. Explain briefly. \( (1995 - 2 \text{ Marks}) \)

17. A hydrocarbon A, of the formula C\(_8\)H\(_{10}\), on ozonolysis gives compound B(C\(_2\)H\(_4\)O\(_2\)) only. The compound B can also be obtained from the alkyl bromide, C(C\(_3\)H\(_3\)Br) upon treatment with magnesium in dry ether, followed by carbon dioxide and acidification. Identify A, B and C and give equations for the reactions. \( (1996 - 3 \text{ Marks}) \)

18. Give the structures of the major organic products from 3-ethyl-2-pentene under each of the following reaction conditions. \( (1996 - 3 \text{ Marks}) \)

(a) HBr in the presence of peroxide  
(b) Br\(_2\)/H\(_2\)O  
(c) Hg(OAc)\(_2\)/H\(_2\)O, NaBH\(_4\)

19. The hydrocarbon A, adds one mole of hydrogen in the presence of a platinum catalyst to form n-hexane. When A is oxidized vigorously with K\(_2\)MnO\(_4\), a single carboxylic acid, containing three carbon atoms, is isolated. Give the structure of A and explain. \( (1997 - 2 \text{ Marks}) \)

20. Show the steps to carry out the following transformations. 
   (i) Ethylbenzene → benzene \( (1998 - 2 \text{ Marks}) \)  
   (ii) Ethylbenzene → 2-phenylpropanoic acid. \( (1998 - 3 \text{ Marks}) \)

21. Complete the following reactions with appropriate structures of products/reagents. 
   (i) C\(_6\)H\(_5\)CH\(_2\) = CH\(_2\) \( \xrightarrow{\text{Bn}} \) [A] \( (i) \text{NaNH}_2 (3.0 \text{ equiv.}) \) \( (ii) \text{CH}_3\text{I} \rightarrow [B] (1998 - 2 + 2 \text{ Marks}) \)

   \[
   (ii) \xrightarrow{1.} \xrightarrow{2.} \xrightarrow{3.} \]

   \( (1999 - 3 \text{ Marks}) \)

22. An alkene (A) C\(_{16}\)H\(_{16}\) on ozonolysis gives only one product (B) C\(_8\)H\(_8\)O. Compound (B) on reaction with NaOH/H\(_2\)O yields sodium benzoate. Compound (B) reacts with KOH/NH\(_2\)NH\(_2\) yielding a hydrocarbon (C) C\(_6\)H\(_{10}\). Write the structures of compounds (B) and (C). Based on this information, two isomeric structures can be proposed for alkene (A). Write their structures and identify the isomer which on catalytic hydrogenation (H\(_2\)/Pd – C) gives a racemic mixture. \( (2001 - 5 \text{ Marks}) \)

23. Write down the heterogeneous catalyst involved in the polymerisation of ethylene. \( (2003 - 2 \text{ Marks}) \)

24. A(C\(_6\)H\(_{12}\)) \( \xrightarrow{\text{HCl}} \) B + C \( (C_6\text{H}_3\text{Cl}) \) \( (2003 - 4 \text{ Marks}) \)

   B \( \xrightarrow{\text{alc KOH}} \) D (isomer of A)

   D-glycosylation \( \xrightarrow{\text{E (it gives negative test with Fehling solution but responds to iodooform test)}} \)

   A \( \xrightarrow{\text{Ozonolysis}} \) F + G (both gives positive Tollens’s test but do not give iodooform test).  

   F + G \( \xrightarrow{\text{conc. NaOH}} \) HCOONa + A primary alcohol.  

   Identify from A to G. \( (2004 - 2 \text{ Marks}) \)

25. Draw Newmann projection of relatively less stable staggered form of n-butane. The reason of low stability of this form is van der Waal’s repulsion, torsional strain, or both. \( (2004 - 2 \text{ Marks}) \)

\[ \text{G Comprehension Based Questions} \]

**PASSAGE-I**

An acyclic hydrocarbon P, having molecular formula C\(_6\)H\(_{10}\), gave acetone as the only organic product through the following sequence of reactions, in which Q is an intermediate organic compound.

\[
P (C_6\text{H}_{10}) \xrightarrow{(i) \text{dil. H}_2\text{SO}_4 / \text{HgSO}_4} Q \xrightarrow{(i) \text{conc. H}_2\text{SO}_4 \text{ (catalytic amount)}} \xrightarrow{(ii) \text{O}_3 \text{ (iii) Zn/H}_2\text{O}} 2
\]

\[ \text{H}_3\text{C} \xrightarrow{\text{C}} \text{CH}_3 \]

\( (2011 - I) \)

1. The structure of compound P is
   (a) CH\(_3\)CH\(_2\)CH\(_2\)CH\(_2\)C≡CH
   (b) CH\(_3\)CH\(_2\)C≡CCH\(_2\)CH\(_3\)
2. The structure of the compound Q is

(a) \[
\begin{align*}
\text{H}_3\text{C} & \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{C} \\
\text{H}_3\text{C} & \quad \text{H} \quad \text{H} \\
\text{H}_3\text{C} & \quad \text{OH} \\
\text{H}_3\text{C} & \quad \text{C} \quad \text{CH}_2\text{CH}_3
\end{align*}
\]

(b) \[
\begin{align*}
\text{H}_3\text{C} & \quad \text{C} \quad \text{C} \\
\text{H}_3\text{C} & \quad \text{H} \\
\text{H}_3\text{C} & \quad \text{OH} \\
\text{H}_3\text{C} & \quad \text{C} \quad \text{CH}_3
\end{align*}
\]

(c) \[
\begin{align*}
\text{H}_3\text{C} & \quad \text{C} \quad \text{C} \\
\text{H}_3\text{C} & \quad \text{H} \\
\text{H}_3\text{C} & \quad \text{OH} \\
\text{H}_3\text{C} & \quad \text{C} \quad \text{CH}_2\text{CH}_3
\end{align*}
\]

(d) \[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 & \\
\text{H}_3\text{C} & \quad \text{OH}
\end{align*}
\]

3. The product \(X\) is

(a) \[
\begin{align*}
\text{H}_3\text{C} & \quad \text{C} \quad \text{H} \\
\text{H}_3\text{C} & \quad \text{H} \\
\text{H}_3\text{C} & \quad \text{OH} \\
\text{H}_3\text{C} & \quad \text{C} \quad \text{H}_3\text{C}
\end{align*}
\]

(b) \[
\begin{align*}
\text{H}_3\text{C} & \quad \text{C} \quad \text{H} \\
\text{H}_3\text{C} & \quad \text{H} \\
\text{H}_3\text{C} & \quad \text{OH} \\
\text{H}_3\text{C} & \quad \text{C} \quad \text{H}_3\text{C}
\end{align*}
\]

(c) \[
\begin{align*}
\text{H}_3\text{C} & \quad \text{C} \quad \text{H} \\
\text{H}_3\text{C} & \quad \text{H} \\
\text{H}_3\text{C} & \quad \text{OH} \\
\text{H}_3\text{C} & \quad \text{C} \quad \text{H}_3\text{C}
\end{align*}
\]

(d) \[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 & \\
\text{H}_3\text{C} & \quad \text{OH}
\end{align*}
\]

4. The correct statement with respect to product \(Y\) is

(a) It gives a positive Tollens test and is a functional isomer of \(X\)

(b) It gives a positive Tollens test and is a geometrical isomer of \(X\)

(c) It gives a positive iodoform test and is a functional isomer of \(X\)

(d) It gives a positive iodoform test and is a geometrical isomer of \(X\)

**H. Assertion & Reason Type Questions**

Read the following statement (Assertion) and explanation (Reason) and answer each question as per the options given below:

(a) If both assertion and reason are correct, and reason is the correct explanation of the assertion.

(b) If both assertion and reason are correct, but reason is not the correct explanation of the assertion.

(c) If assertion is correct but reason is incorrect.

(d) If assertion is incorrect but reason is correct.

1. **Assertion**: Addition of \(\text{Br}_2\) to 1-butene gives two optical isomers.
   **Reason**: The product contains one asymmetric carbon.

2. **Assertion**: 1-Butene on reaction with \(\text{HBr}\) in the presence of a peroxide produces 1-bromobutane.
   **Reason**: It involves the formation of a primary radical.

3. **Assertion**: Addition of bromine to \(\text{trans}-2\)-butene yields \(\text{meso}-2,3\)-dibromobutane.
   **Reason**: Bromine addition to an alkene is an electrophilic addition.
Section-B

1. Which of these will not react with acetylene? \[2002\]
   (a) NaOH  (b) ammonical AgNO₃
   (c) Na    (d) HCl.

2. What is the product when acetylene reacts with hypochlorous acid? \[2002\]
   (a) CH₃COCl  (b) CICH₃CHO
   (c) Cl₂CHCHO  (d) CICH₃COOH.

3. On mixing a certain alkane with chlorine and irradiating it with ultraviolet light, it forms only one monochloroalkane. This alkane could be \[2003\]
   (a) pentane  (b) isopentane
   (c) neopentane  (d) propane.

4. 2-Methylbutane on reacting with bromine in the presence of sunlight gives mainly \[2005\]
   (a) 1-bromo-3-methylbutane
   (b) 2-bromo-3-methylbutane
   (c) 2-bromo-2-methylbutane
   (d) 1-bromo-2-methylbutane.

5. Butene-1 may be converted to butane by reaction with \[2003\]
   (a) Sn–HCl  (b) Zn–Hg
   (c) Pd/H₂  (d) Zn–HCl.

6. Reaction of one molecule of HBr with one molecule of 1,3-butadiene at 40°C gives predominantly \[2005\]
   (a) 1-bromo-2-butene under kinetically controlled conditions
   (b) 3-bromobutene under thermodynamically controlled conditions
   (c) 1-bromo-2-butene under thermodynamically controlled conditions
   (d) 3-bromobutene under kinetically controlled conditions.

7. Of the five isomeric hexanes, the isomer which can give two monochlorinated compounds is \[2005\]
   (a) 2-methylpentane  (b) 2,2-dimethylbutane
   (c) 2,3-dimethylbutane  (d) n-hexane.

8. Acid catalyzed hydration of alkenes except ethene leads to the formation of \[2005\]
   (a) mixture of secondary and tertiary alcohols
   (b) mixture of primary and secondary alcohols
   (c) secondary or tertiary alcohol
   (d) primary alcohol.

9. Which types of isomerism is shown by 2,3-dichlorobutane? \[2005\]
   (a) Structural  (b) Geometric
   (c) Optical  (d) Diastereos.

10. The compound formed as a result of oxidation of ethyl benzene by KMnO₄ is \[2007\]
    (a) benzyl alcohol  (b) benzophenone
    (c) acetophenone  (d) benzoic acid.

11. Which of the following reactions will yield 2,2-dibromopropane? \[2007\]
    (a) CH₃−CH=CH₂ + HBr →
    (b) CH₃−C≡CH + 2HBr →
    (c) CH₃CH=CHBr + HBr →
    (d) CH≡CH + 2HBr →

12. The reaction of toluene with Cl₂ in presence of FeCl₃ gives predominantly \[2007\]
    (a) m-chlorobenzene
    (b) benzoyl chloride
    (c) benzyl chloride
    (d) o- and p-chlorotoluene.

13. Toluene is nitrated and the resulting product is reduced with tin and hydrochloric acid. The product so obtained is diazotised and then heated with cuprous bromide. The reaction mixture so formed contains \[2008\]
    (a) mixture of o- and p-bromotoluenes
    (b) mixture of o- and p-dibromobenzenes
    (c) mixture of o- and p-bromoanilines
    (d) mixture of o- and m-bromotoluenes.

14. In the following sequence of reactions, the alkene affords the compound 'B'
    CH₃ − CH = CH − CH₃ \( \xrightarrow{O_3} \xrightarrow{H_2O/Zn} \)
    The compound B is \[2008\]
    (a) CH₂CH₂CHO  (b) CH₃COCH₃
    (c) CH₃CH₂COCH₃  (d) CH₅CHO.

15. The hydrocarbon which can react with sodium in liquid ammonia is \[2008\]
    (a) CH₃CH₂CH₂C≡CCH₂CH₃
    (b) CH₃CH₂C≡CH
    (c) CH₃CH = CHCH₃
    (d) CH₃CH₂C=CCH₂CH₃.

16. The treatment of CH₃MgX with CH₃C≡C−H produces \[2008\]
    (a) CH₃ − CH = CH₂
    (b) CH₃C≡C = CH₃
    (c) CH₃ − C = C−CH₃
    (d) CH₄.

17. One mole of a symmetrical alkene on ozonolysis gives two moles of an aldehyde having a molecular mass of 44 u. The alkene is \[2010\]
    (a) propene  (b) 1-butene
    (c) 2-butene  (d) ethene.
18. Ozonolysis of an organic compound gives formaldehyde as one of the products. This confirms the presence of:

(a) two ethylenic double bonds
(b) a vinyl group
(c) an isopropyl group
(d) an acetylenic triple bond

19. Which branched chain isomer of the hydrocarbon with molecular mass 72u gives only one isomer of mono substituted alkyl halide?

(a) Tertiary butyl chloride  (b) Neopentane
(c) Isohexane       (d) Neohexane

20. 2-Hexyne gives trans-2-Hexene on treatment with:

(a) Pt/H₂  (b) Li/NH₃
(c) Pd/BaSO₄   (d) LiAlH₄

21. Which compound would give 5-keto-2-methylhexanal upon ozonolysis?

(a) \[ \text{CH}_3 \]
(b) \[ \text{CH}_3 \]
(c) \[ \text{CH}_3 \]
(d) \[ \text{CH}_3 \]

22. The hottest region of Bunsen flame shown in the figure below is:

(a) region 3  (b) region 4
(c) region 1   (d) region 2

23. At 300 K and 1 atm, 15 mL of a gaseous hydrocarbon requires 375 mL air containing 20% O₂ by volume for complete combustion. After combustion the gases occupy 330 mL. Assuming that the water formed is in liquid form and the volumes were measured at the same temperature and pressure, the formula of the hydrocarbon is:

(a) \[ \text{C}_8\text{H}_8 \]  (b) \[ \text{C}_6\text{H}_{10} \]
(c) \[ \text{C}_7\text{H}_6 \]   (d) \[ \text{C}_5\text{H}_8 \]

24. The reaction of propene with HOCl (Cl₂ + H₂O) proceeds through the intermediate:

(a) \[ \text{CH}_3 - \text{CH} (=\text{OH}) - \text{CH}_2^+ \]
(b) \[ \text{CH}_3 - \text{CHCl} - \text{CH}_2^+ \]
(c) \[ \text{CH}_3 - \text{CH}^+ - \text{CH}_2 - \text{OH} \]
(d) \[ \text{CH}_3 - \text{CH}^+ - \text{CH}_2 - \text{Cl} \]
CHAPTER 11

The Solid State & Surface Chemistry

Section-A

JEE Advanced/ IIT-JEE

MCQs with One Correct Answer

1. CsBr has bcc structure with edge length 4.3. The shortest interionic distance in between Cs⁺ and Br⁻ is: (1995 S)
   (a) 3.72 (b) 1.86 (c) 7.44 (d) 4.3

2. The coordination number of a metal crystallizing in a hexagonal close-packed structure is (1999 - 2 Marks)
   (a) 12 (b) 4 (c) 8 (d) 6

3. In a solid ‘AB’ having the NaCl structure, ‘A’ atoms occupy the corners of the cubic unit cell. If all the face-centered atoms along one of the axes are removed, then the resultant stoichiometry of the solid is (2001S)
   (a) AB₂ (b) A₂B (c) A₄B₃ (d) A₃B₄

4. A substance A₂B₃ crystallizes in a face centred cubic (FCC) lattice in which atoms ‘A’ occupy each corner of the cube and atoms ‘B’ occupy the centres of each face of the cube. Identify the correct composition of the substance A₂B₃ (2002S)
   (a) AB₂ (b) A₂B₃ (c) A₂B (d) Composition cannot be specified

5. Rate of physisorption increases with (2003S)
   (a) decrease in temperature (b) increase in temperature (c) decrease in pressure (d) decrease in surface area

6. Adsorption of gases on solid surface is generally exothermic because (2004S)
   (a) enthalpy is positive (b) entropy decreases (c) entropy increases (d) free energy increases

7. In which of the following crystals alternate tetrahedral voids are occupied? (2005S)
   (a) NaCl (b) ZnS (c) CaF₂ (d) Na₂O

8. Lyophobic sols are (2005S)
   (a) Irreversible sols (b) They are prepared from inorganic compound (c) Coagulated by adding electrolytes (d) Self-stabilizing

9. Among the following, the surfactant that will form micelles in aqueous solution at the lowest molar concentration at ambient condition is: (2008S)
   (a) CH₃(CH₂)₁₄N⁺(CH₃)₃Br⁻
   (b) CH₃(CH₂)₁₁OSO₃⁻Na⁺
   (c) CH₃(CH₂)₆COO⁻Na⁺
   (d) CH₃(CH₂)₁₄N⁺(CH₃)₃Br⁻

10. Among the electrolytes Na₂SO₄, CaCl₂, Al₂(SO₄)₃ and NH₄Cl, the most effective coagulating agent for Sb₂S₃ sol is (2009S)
    (a) Na₂SO₄ (b) CaCl₂ (c) Al₂(SO₄)₃ (d) NH₄Cl

11. The packing efficiency of the two-dimensional square unit cell shown below is: (2010)

   ![Square unit cell diagram]

   (a) 39.27% (b) 68.02% (c) 74.05% (d) 78.54%

12. A compound M₅X₉ has cubic close packing (ccp) arrangement of X. Its unit cell structure is shown below. The empirical formula of the compound is (2012 - I)

   ![Unit cell diagram]

   (a) MX (b) MX₂ (c) M₂X (d) M₃X₁₄
13. The arrangement of $X^-$ ions around $A^+$ ion in solid $AX$ is given in the figure (not drawn to scale). If the radius of $X^-$ is 250 pm, the radius of $A^+$ is

JEE Adv. 2013)

(a) 104 pm  (c) 183 pm  (b) 125 pm  (d) 57 pm

14. Methylene blue, from its aqueous solution, is adsorbed on activated charcoal at 25°C. For this process, the correct statement is

JEE Adv. 2013)

(a) The adsorption requires activation at 25°C
(b) The adsorption is accompanied by a decrease in enthalpy
(c) The adsorption increases with increase of temperature
(d) The adsorption is irreversible

D MCQs with One or More Than One Correct

1. Which of the following statement(s) is (are) correct?

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(a) The coordination number of each type of ion in CsCl crystal is 8.
(b) A metal that crystallizes in bcc structure has a coordination number of 12.
(c) A unit cell of an ionic crystal shares some of its ions with other unit cells.
(d) The length of the unit cell in NaCl is 552 pm. ($r_{Na^+} = 95$ pm; $r_{Cl^-} = 181$ pm)

2. The correct statement(s) regarding defects in solids is (are)

JEE Adv. 2013)

(a) Frenkel defect is usually favoured by a very small difference in the sizes of cation and anion
(b) Frenkel defect is a dislocation defect
(c) Trapping of an electron in the lattice leads to the formation of F-centre
(d) Schottky defects have no effect on the physical properties of solids

3. The correct statement(s) pertaining to the adsorption of a gas on a solid surface is (are)

JEE Adv. 2013)

(a) Adsorption is always exothermic
(b) Physisorption may transform into chemisorption at high temperature
(c) Physisorption increases with increasing temperature but chemisorption decreases with increasing temperature
(d) Chemisorption is more exothermic than physisorption, however it is very slow due to higher energy of activation

4. Choose the correct reason(s) for the stability of the lyophobic colloidal particles.

JEE Adv. 2013)

(a) Preferential adsorption of ions on their surface from the solution.
(b) Preferential adsorption of solvent on their surface from the solution.
(c) Attraction between different particles having opposite charges on their surface.

5. The given graphs/data I, II, III and IV represent general trends observed for different physisorption and chemisorption processes under mild conditions of temperature and pressure. Which of the following choice(s) about I, II, III and IV is (are) correct?

JEE Adv. 2013)

(a) I is physisorption and II is chemisorption
(b) I is physisorption and III is chemisorption
(c) IV is chemisorption and II is chemisorption
(d) IV is chemisorption and III is chemisorption

6. If the unit cell of a mineral has cubic close packed (ccp) array of oxygen atoms with $m$ fraction of octahedral holes occupied by aluminium ions and $n$ fraction of tetrahedral holes occupied by magnesium ions, $m$ and $n$, respectively, are

JEE Adv. 2013)

(a) $\frac{1}{2}$  (b) $\frac{1}{4}$  (c) $\frac{1}{2}$  (d) $\frac{1}{4}$

7. When $O_2$ is adsorbed on a metallic surface, electron transfer occurs from the metal to $O_2$. The true statement(s) regarding this adsorption is (are)

JEE Adv. 2013)

(a) $O_2$ is physisorbed
(b) Heat is released
(c) Occupancy of $\Delta E_{O_2}$ of $O_2$ is increased
(d) Bond length of $O_2$ is increased
8. The CORRECT statement(s) for cubic close packed (ccp) three dimensional structure is (are)  
   (JEE Adv. 2016)  
   (a) The number of the nearest neighbours of an atom present in the topmost layer is 12  
   (b) The efficiency of atom packing is 74%  
   (c) The number of octahedral and tetrahedral voids per atom are 1 and 2, respectively  
   (d) The unit cell edge length is $2\sqrt{2}$ times the radius of the atom  

E  Subjective Problems

1. The density of mercury is 13.6 g/ml. Calculate approximately the diameter of an atom of mercury assuming that each atom is occupying a cube of edge length equal to the diameter of the mercury atom.  
   (1983 - 3 Marks)

2. Sodium metal crystallizes in body centred cubic lattice with the cell edge, $a = 4.29\text{Å}$. What is the radius of sodium atom?  
   (1994-2 Marks)

3. A metallic element crystallizes into a lattice containing a sequence of layers of ABABAB.... Any packing of spheres leaves out voids in the lattice. What percentage by volume of this lattice is empty space?  
   (1996 - 3 Marks)

4. Chromium metal crystallizes with a body centred cubic lattice. The length of the unit cell edge is found to be 287 pm. Calculate the atomic radius. What would be the density of chromium in g/cm$^3$?  
   (1997 - 3 Marks)

5. A metal crystallises into two cubic phases, face centered cubic (FCC) and body centred cubic (BCC), whose unit cell lengths are 3.5 and 3.0 Å, respectively. Calculate the ratio of densities of FCC and BCC.  
   (1999 - 3 Marks)

6. The figures given below show the location of atoms in three crystallographic planes in a FCC lattice. Draw the unit cell for the corresponding structure and identify these planes in your diagram.  
   (2000 - 3 Marks)

7. You are given marbles of diameter 10 mm. They are to be placed such that their centres are lying in a square bound by four lines each of length 40 mm. What will be the arrangements of marbles in a plane so that maximum number of marbles can be placed inside the area? Sketch the diagram and derive expression for the number of molecules per unit area.  
   (2003 - 2 Marks)

8. 1 gm of charcoal adsorbs 100 ml 0.5 M CH$_3$COOH to form a monolayer, and thereby the molarity of CH$_3$COOH reduces to 0.49. Calculate the surface area of the charcoal adsorbed by each molecule of acetic acid. Surface area of charcoal = $3.01 \times 10^3$ m$^2$/gm.  
   (2003 - 2 Marks)

9. A compound AB has rock salt type structure. The formula weight of AB is 6.023 Y amu, and the closest A-B distance is $1.35$ nm, where Y is an arbitrary number.  
   (2004 - 2 Marks)
   (a) Find the density of lattice  
   (b) If the density of lattice is found to be 20 kg m$^{-3}$, then predict the type of defect.

10. In face centred cubic (fcc) crystal lattice, edge length is 400 pm. Find the diameter of greatest sphere which can be fit into the interstitial void without distortion of lattice.  
   (2005 - 2 Marks)

11. 20% of surface sites are occupied by N$_2$ molecules. The density of surface site is $6.023 \times 10^{14}$ cm$^{-2}$ and total surface area is 1000 cm$^2$. The catalyst is heated to 300 K while N$_2$ is completely desorbed into a pressure of 0.001 atm and volume of 2.46 cm$^3$. Find the number of active sites occupied by each N$_2$ molecule.  
   (2005 - 4 Marks)

12. The edge length of unit cell of a metal having molecular weight 75 g/mol is 5Å which crystallizes in cubic lattice. If the density is 2 g/cc then find the radius of metal atom (N$_A$ = $6 \times 10^{23}$). Give the answer in pm.  
   (2006 - 6 M)

F  Match the Following

Each question contains statements given in two columns, which have to be matched. The statements in Column-I are labelled A, B, C and D, while the statements in Column-II are labelled p, q, r, s and t. Any given statement in Column-I can have correct matching with ONE OR MORE statement(s) in Column-II. The appropriate bubbles corresponding to the answers to these questions have to be darkened as illustrated in the following example:  

If the correct matches are A-p, s and t; B-q and r; C-p and q; and D-s then the correct darkening of bubbles will look like the given.

1. Match the crystal system/unit cells mentioned in Column I with their characteristic features mentioned in Column II. Indicate your answer by darkening the appropriate bubbles of the 4 × 4 matrix given in the ORS.  
   (2007)

<table>
<thead>
<tr>
<th>Column I</th>
<th>Column II</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A) Simple cubic and face-centered cubic parameters</td>
<td>(p) have these parameters, a = b = c and $\alpha = \beta = \gamma$</td>
</tr>
<tr>
<td>(B) cubic and rhombohedral</td>
<td>(q) are two crystal systems</td>
</tr>
<tr>
<td>(C) cubic and tetragonal</td>
<td>(r) have only two crystallo-graphic angles of 90°</td>
</tr>
<tr>
<td>(D) hexagonal and monoclinic</td>
<td>(s) belong to same crystal system</td>
</tr>
</tbody>
</table>
**Comprehension Based Questions**

**PASSAGE**

In hexagonal systems of crystals, a frequently encountered arrangement of atoms is described as a hexagonal prism. Here, the top and bottom of the cell are regular hexagons and three atoms are sandwiched in between them. A space-filling model of this structure, called hexagonal close-packed (HCP), is constituted of a sphere on a flat surface surrounded in the same plane by six identical spheres as closely as possible. There spheres are then placed over the first layer so that they touch each other and represent the second layer. Each one of these three spheres touches three spheres of the bottom layer. Finally, the second layer is covered with third layer that is identical to the bottom layer in relative position. Assume radius of every sphere to be ‘r’.

**Answer the following questions** -

1. The number of atoms in the HCP unit cell is
   - (a) 4
   - (b) 6
   - (c) 12
   - (d) 17

2. The volume of this HCP unit cell is
   - (a) $24\sqrt{2}r^3$
   - (b) $16\sqrt{2}r^3$
   - (c) $12\sqrt{2}r^3$
   - (d) $\frac{64}{3\sqrt{3}}r^3$

---

**Assertion & Reason Type Questions**

Read the following statement (Assertion) and explanation (Reason) and answer each question as per the options given below:

(a) If both assertion and reason are correct, and reason is the correct explanation of the assertion.
(b) If both assertion and reason are correct, but reason is not the correct explanation of the assertion.
(c) If assertion is correct but reason is incorrect.
(d) If assertion is incorrect but reason is correct.

1. **Assertion**: In any ionic solid [MX] with Schottky defects, the number of positive and negative ions are same.
   - **Reason**: Equal number of cation and anion vacancies are present.

2. **Assertion**: Micelles are formed by surfactant molecules above the critical micellar concentration (CMC).
   - **Reason**: The conductivity of a solution having surfactant molecules decreases sharply at the CMC.

---

**Integer Value Correct Type**

1. The number of hexagonal faces that are present in a truncated octahedron is

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**Section-B**

1. The formation of gas at the surface of tungsten due to adsorption is the reaction of order
   - (a) 0
   - (b) 1
   - (c) 2
   - (d) insufficient data.

2. Na and Mg crystallize in BCC and FCC type crystals respectively, then the number of atoms of Na and Mg present in the unit cell of their respective crystal is
   - (a) 4 and 2
   - (b) 9 and 14
   - (c) 14 and 9
   - (d) 2 and 4.

3. How many unit cells are present in a cube-shaped ideal crystal of NaCl of mass 1.00 g?
   - [Atomic masses: Na = 23, Cl = 35.5]
   - (a) $5.14 \times 10^{21}$ unit cells
   - (b) $1.28 \times 10^{21}$ unit cells
   - (c) $1.71 \times 10^{21}$ unit cells
   - (d) $2.57 \times 10^{21}$ unit cells

4. Which one of the following characteristics is not correct for physical adsorption?
   - (a) Adsorption increases with increase in temperature
   - (b) Adsorption is spontaneous
   - (c) Both enthalpy and entropy of adsorption are negative
   - (d) Adsorption on solids is reversible

5. What type of crystal defect is indicated in the diagram below?

   - [Diagram showing various types of defects: Na⁺Cl⁻ Na⁺Cl⁻ Na⁺Cl⁻]
   - (a) Interstitial defect
   - (b) Schottky defect
   - (c) Frenkel defect
   - (d) Frenkel and Schottky defects

6. Identify the correct statement regarding enzymes
   - [Diagram showing various enzymes and their properties]
   - (a) Enzymes are specific biological catalysts that cannot be poisoned
   - (b) Enzymes are normally heterogeneous catalysts that are very specific in their action
   - (c) Enzymes are specific biological catalysts that can normally function at very high temperatures (T~1000K)
   - (d) Enzymes are specific biological catalysts that possess well-defined active sites
7. An ionic compound has a unit cell consisting of A ions at the corners of a cube and B ions on the centres of the faces of the cube. The empirical formula for this compound would be [2005]
(a) A₂B  
(b) AB₃  
(c) A₂B  
(d) AB

8. The volume of a colloidal particle, \( V_C \), as compared to the volume of a solute particle in a true solution \( V_S \), could be [2005]
(a) \( \frac{V_C}{V_S} \approx 10^3 \)  
(b) \( \frac{V_C}{V_S} \approx 10^{-3} \)  
(c) \( \frac{V_C}{V_S} \approx 10^{23} \)  
(d) \( \frac{V_C}{V_S} \approx 1 \)

9. The disperse phase in colloidal iron (III) hydroxide and colloidal gold is positively and negatively charged, respectively. Which of the following statements is NOT correct? [2005]
(a) Coagulation in both sols can be brought about by electrophoresis  
(b) Mixing the sols has no effect  
(c) Sodium sulphate solution causes coagulation in both sols  
(d) Magnesium chloride solution coagulates, the gold sol more readily than the iron (III) hydroxide sol

10. Total volume of atoms present in a face-centred cubic unit cell of a metal is \( r \) is atomic radius [2006]
(a) \( \frac{12}{3} \pi r^3 \)  
(b) \( \frac{16}{3} \pi r^3 \)  
(c) \( \frac{20}{3} \pi r^3 \)  
(d) \( \frac{24}{3} \pi r^3 \)

11. In Langmuir’s model of adsorption of a gas on a solid surface [2006]
(a) the mass of gas striking a given area of surface is proportional to the pressure of the gas  
(b) the mass of gas striking a given area of surface is independent of the pressure of the gas  
(c) the rate of dissociation of adsorbed molecules from the surface does not depend on the surface covered  
(d) the adsorption at a single site on the surface may involve multiple molecules at the same time

12. In a compound, atoms of element Y form ccp lattice and those of element X occupy 2/3rd of tetrahedral voids. The formula of the compound will be [2008]
(a) \( X_4 Y_3 \)  
(b) \( X_2 Y_3 \)  
(c) \( X_2 Y \)  
(d) \( X_3 Y_4 \)

13. Gold numbers of protective colloids A, B, C and D are 0.50, 0.01, 0.10 and 0.005, respectively. The correct order of their protective powers is [2008]
(a) \( D < A < C < B \)  
(b) \( C < B < D < A \)  
(c) \( A < C < B < D \)  
(d) \( B < D < A < C \)

14. Which of the following statements is incorrect regarding physisorption? [2009]
(a) More easily liquefiable gases are adsorbed readily.  
(b) Under high pressure it results into multi molecular layer on adsorbent surface.  
(c) Enthalpy of adsorption (\( \Delta H_{\text{adsorption}} \)) is low and positive.  
(d) It occurs because of van der Waal’s forces.

15. Copper crystallises in fcc with a unit cell length of 361 pm. What is the radius of copper atom? [2009]
(a) 127 pm  
(b) 157 pm  
(c) 181 pm  
(d) 108 pm

16. The edge length of a face centered cubic cell of an ionic substance is 508 pm. If the radius of the cation is 110 pm, the radius of the anion is [2010]
(a) 288 pm  
(b) 398 pm  
(c) 618 pm  
(d) 144 pm

17. Percentages of free space in cubic close packed structure and in body centered packed structure are respectively [2010]
(a) 30% and 26%  
(b) 26% and 32%  
(c) 32% and 48%  
(d) 48% and 26%

18. In a face centred cubic lattice, atom A occupies the corner positions and atom B occupies the face centre positions. If one atom of B is missing from one of the face centred points, the formula of the compound is: [2011]
(a) \( A_2 B \)  
(b) \( A B_2 \)  
(c) \( A_2 B_3 \)  
(d) \( A_2 B_2 \)

19. Lithium forms body centred cubic structure. The length of the side of its unit cell is 351 pm. Atomic radius of the lithium will be: [2012]
(a) 75 pm  
(b) 300 pm  
(c) 240 pm  
(d) 152 pm

20. According to Freundlich adsorption isotherm which of the following is correct? [2012]
(a) \( \frac{x}{m} \propto p^0 \)  
(b) \( \frac{x}{m} \propto p^1 \)  
(c) \( \frac{x}{m} \propto p^{1/n} \)  
(d) All the above are correct for different ranges of pressure
21. Which of the following exists as covalent crystals in the solid state? [JEE M 2013]
   (a) Iodine
   (b) Silicon
   (c) Sulphur
   (d) Phosphorus

22. The coagulating power of electrolytes having ions Na$^+$, Al$^{3+}$ and Ba$^{2+}$ for arsenic sulphide sol increases in the order: [JEE M 2013]
   (a) Al$^{3+}$ < Ba$^{2+}$ < Na$^+$  
   (b) Na$^+$ < Ba$^{2+}$ < Al$^{3+}$  
   (c) Ba$^{2+}$ < Na$^+$ < Al$^{3+}$  
   (d) Al$^{3+}$ < Na$^+$ < Ba$^{2+}$

23. CsCl crystallises in body centred cubic lattice. If 'a' is its edge length then which of the following expressions is correct? [JEE M 2014]
   (a) $r_{Cs^+} + r_{Cl^-} = 3a$
   (b) $r_{Cs^+} + r_{Cl^-} = \frac{3a}{2}$
   (c) $r_{Cs^+} + r_{Cl^-} = \frac{\sqrt{3}}{2} a$
   (d) $r_{Cs^+} + r_{Cl^-} = \sqrt{3}a$

24. Sodium metal crystallizes in a body centred cubic lattice with a unit cell edge of 4.29Å. The radius of sodium atom is approximately: [JEE M 2015]
   (a) 5.72Å  
   (b) 0.93Å  
   (c) 1.86Å  
   (d) 3.22Å

25. 3 g of activated charcoal was added to 50 mL of acetic acid solution (0.06N) in a flask. After an hour it was filtered and the strength of the filtrate was found to be 0.042 N. The amount of acetic acid adsorbed (per gram of charcoal) is: [JEE M 2015]
   (a) 42 mg  
   (b) 54 mg  
   (c) 18 mg  
   (d) 36 mg

26. For a linear plot of $\log \left( \frac{x}{m} \right)$ versus $\log p$ in a Freundlich adsorption isotherm, which of the following statements is correct? (k and $n$ are constants) [JEE M 2016]
   (a) Only $1/n$ appears as the slope.
   (b) $\log \left( \frac{1}{n} \right)$ appears as the intercept.
   (c) Both $k$ and $1/n$ appear in the slope term.
   (d) $1/n$ appears as the intercept.
Solutions

Section-A

Fill in the Blanks

1. Given that \( \Delta T_f \) is the depression in freezing point of the solvent in a solution of a non-volatile solute of molality, \( m \), the quantity \( \lim_{m \to 0} \frac{\Delta T_f}{m} \) is equal to .......... . \( \text{1994 - 1 Mark} \)

2. For a dilute solution, Raoult’s law states:

(a) the lowering of vapour pressure is equal to the mole fraction of solute.
(b) the relative lowering of vapour pressure is equal to the mole fraction of solute.
(c) the relative lowering of vapour pressure is proportional to the amount of solute in solution.
(d) the vapour pressure of the solution is equal to the mole fraction of solvent.

3. When mercuric iodide is added to the aqueous solution of potassium iodide then

(a) freezing point is raised.
(b) freezing point is lowered.
(c) freezing point does not change.
(d) boiling point does not change.

4. Which of the following 0.1 M aqueous solutions will have the lowest freezing point?

(a) Potassium sulphate  (b) Sodium chloride  (c) Urea  (d) Glucose

5. The freezing point of equimolar aqueous solutions will be highest for:

(a) \( \text{C}_6\text{H}_5\text{NH}_3\text{Cl} \) (aniline hydrochloride)
(b) \( \text{Ca(NO}_3\text{)}_2 \)
(c) \( \text{La(NO}_3\text{)}_3 \)
(d) \( \text{C}_6\text{H}_12\text{O}_6 \) (glucose)

6. 0.2 molal acid HX is 20% ionised in solution. \( K_f = 1.86 \text{ K molality}^{-1} \). The freezing point of the solution is: \( \text{1995S} \)

(a) -0.45  (b) -0.90  (c) -0.31  (d) -0.53

7. The molecular weight of benzoic acid in benzene as determined by depression in freezing point method corresponds to: \( \text{1996 - 1 Mark} \)

(a) ionization of benzoic acid.
(b) dimerization of benzoic acid.
(c) trimerization of benzoic acid.
(d) solvation of benzoic acid.

8. During depression of freezing point in a solution the following are in equilibrium \( \text{2003S} \)

(a) liquid solvent, solid solvent
(b) liquid solvent, solid solute
(c) liquid solute, solid solute
(d) liquid solute, solid solvent

9. The elevation in boiling point of a solution of 13.44 g of \( \text{CuCl}_2 \) in 1 kg of water using the following information will be \( \text{2005S} \)

(a) 0.16  (b) 0.05  (c) 0.1  (d) 0.2

10. When 20 g of naphthaic acid (\( \text{C}_11\text{H}_8\text{O}_2 \)) is dissolved in 50 g of benzene (\( K_f = 1.72 \text{ K kg mol}^{-1} \)), a freezing point depression of 2K is observed. The Van’t Hoff factor (i) is \( \text{2007} \)

(a) 0.5  (b) 1  (c) 2  (d) 3

11. The Henry’s law constant for the solubility of \( \text{N}_2 \) gas in water at 298 K is \( 1.0 \times 10^{-5} \text{ atm} \). The mole fraction of \( \text{N}_2 \) in air is 0.8. The number of moles of \( \text{N}_2 \) from air dissolved in 10 moles of water at 298 K and 5 atm pressure is \( \text{2009} \)

(a) \( 4.0 \times 10^{-4} \)  (b) \( 4.0 \times 10^{-5} \)  (c) \( 5.0 \times 10^{-4} \)  (d) \( 4.0 \times 10^{-6} \)

12. Dissolving 120 g of urea (mol. wt. 60) in 1000 g of water gave a solution of density 1.15 g/mL. The molarity of the solution is \( \text{2011} \)

(a) 1.78 M  (b) 2.00 M  (c) 2.05 M  (d) 2.22 M
13. The freezing point (in °C) of a solution containing 0.1 g of K₃[Fe(CN)₆] (Mol. wt. 329) in 100 g of water (Kᵥ = 1.86 K kg mol⁻¹) is (2011)
   (a) \(-2.3 \times 10^{-2}\)  (b) \(-5.7 \times 10^{-2}\)
   (c) \(-5.7 \times 10^{-3}\)  (d) \(-1.2 \times 10^{-2}\)

14. For a dilute solution containing 2.5 g of a non-volatile nonelectrolyte solute in 100 g of water, the elevation in boiling point at 1 atm pressure is 2°C. Assuming concentration of solute is much lower than the concentration of solvent, the vapour pressure (mm of Hg) of the solution is (take Kᵥ = 0.76 K kg mol⁻¹) (2012)
   (a) 724  (b) 740
   (c) 736  (d) 718

D) MCQs with One or More Than One Correct

1. In the depression of freezing point experiment, it is found that the vapour pressure of the solution is less than that of pure solvent (1999 - 3 Marks)
   (a) vapour pressure of the solution is less than that of pure solvent
   (b) vapour pressure of the solution is more than that of pure solvent
   (c) only solute molecules solidify at the freezing point
   (d) only solvent molecules solidify at the freezing point

2. Benzene and naphthalene form an ideal solution at room temperature. For this process, the true statement(s) is(are) (JEE Adv. 2013)
   (a) ΔG is positive  (b) ΔS_system is positive
   (c) ΔS_surroundings = 0  (d) ΔH = 0

3. Mixture(s) showing positive deviation from Raoult’s law at 35°C is (are) (JEE Adv. 2016)
   (a) carbon tetrachloride + methanol
   (b) carbon disulphide + acetone
   (c) benzene + toluene
   (d) phenol + aniline

E) Subjective Problems

1. What is the molality and molality of a 13% solution (by weight) of sulphuric acid with a density of 1.02 g/ml? To what volume should 100 ml of this acid be diluted in order to prepare a 1.5 N solution? (1978)
2. A bottle of commercial sulphuric acid (density 1.787 g/ml) is labelled as 86 percent by weight. What is the molality of the acid. What volume of the acid has to be used to make 1 litre of 0.2 M H₂SO₄? (1979)
3. 0.5 gm of fuming H₂SO₄ (Oleum) is diluted with water. This solution is completely neutralized by 26.7 ml of 0.4 N NaOH. Find the percentage of free SO₃ in the sample of oleum. (1980)
4. The vapour pressure of pure benzene is 639.7 mm of mercury and the vapour of a solution of a solute in benzene at the same temperature is 631.9 mm of mercury. Calculate the molality of the solution. (1981 - 3 Marks)
5. An organic compound C₄H₆O₃ was burnt with twice the amount of oxygen needed for complete combustion to CO₂ and H₂O. The hot gases when cooled to 0°C and 1 atm pressure, measured 2.24 liters. The water collected during cooling weighed 0.9 g. The vapour pressure of pure water at 20°C is 17.5 mm Hg and is lowered by 0.104 mm when 50 g of the organic compound are dissolved in 1000 g of water. Give the molecular formula of the organic compound. (1983 - 5 Marks)
6. 'Two volatile and miscible liquids can be separated by fractional distillation into pure component', is true under what conditions? (1984 - 1 Mark)
7. The vapour pressure of ethanol and methanol are 44.5 mm and 88.7 Hg respectively. An ideal solution is formed at the same temperature by mixing 60 g of ethanol with 40 g of methanol. Calculate the total vapour pressure of the solution and the mole fraction of methanol in the vapour. (1986 - 4 Marks)
8. The vapour pressure of a dilute aqueous solution of glucose (C₆H₁₂O₆) is 750 mm of mercury at 373 K. Calculate (i) molality and (ii) mole fraction of the solution. (1989 - 3 Marks)
9. The vapour pressure of pure benzene at a certain temperature is 640 mm Hg. A non-volatile nonelectrolyte solid weighing 2.175 g is added to 39.0 g of benzene. The vapour pressure of the solution is 600 mm Hg. What is the molecular weight of the solid substance? (1990 - 3 Marks)
10. The degree of dissociation of calcium nitrate in a dilute aqueous solution, containing 7.0 g of the salt per 100 g of water at 100°C is 70%. If the vapour pressure of water at 100°C is 760 mm, calculate the vapour pressure of the solution. (1991 - 4 Marks)
11. Addition of 0.643 g of a compound to 50 ml of benzene (density: 0.879 g/ml) lowers the freezing point from 5.1°C to 5.03°C. If Kᵥ for benzene is 5.12 K kg mol⁻¹, calculate the molecular weight of the compound. (1992 - 2 Marks)
12. What weight of the non-volatile solute, urea (NH₂ – CO – NH₂) needs to be dissolved in 100g of water, in order to decrease the vapour pressure of water by 25%? What will be the molality of the solution? (1993 - 3 Marks)
13. The molar volume of liquid benzene (density=0.877 g mL⁻¹) increases by a factor of 2750 as it vapourises at 20°C and that of liquid toluene (density=0.867 g mL⁻¹) increases by a factor of 7720 at 20°C. A solution of benzene and toluene at 20°C has a vapour pressure of 46.0 Torr. Find the mole fraction of benzene in the vapour above the solution. (1996 - 3 Marks)
14. A solution of a nonvolatile solute in water freezes at -0.30°C. The vapour pressure of pure water at 298 K is 23.51 mm Hg and Kᵥ for water is 1.86 K kg mol⁻¹. Calculate the vapour pressure of this solution at 298 K. (1998 - 4 Marks)
15. Nitrobenzene is formed as the major product along with a minor product in the reaction of benzene with a hot mixture of nitric acid and sulphuric acid. The minor product consists of carbon: 42.86%, hydrogen: 2.40%, nitrogen: 16.67%, and oxygen: 38.07% (i) Calculate the empirical formula of the minor product. (ii) When 5.5 g of the minor product is dissolved in 45 g of benzene, the boiling point of the solution is 1.84 °C higher than that of pure benzene. Calculate the molar mass of the minor product and determine its molecular and structural formula. (Molal boiling point elevation constant of benzene is 2.53 K kg mol⁻¹.) (1999 - 10 Marks)

16. To 500 cm³ of water, 3.0 × 10⁻³ kg of acetic acid is added. If 23% of acetic acid is dissociated, what will be the depression in freezing point? K_f and density of water are 1.86 K kg⁻¹ mol⁻¹ and 0.997 g cm⁻³, respectively. (2000 - 3 Marks)

17. 1.22 g of benzoic acid is dissolved in 100 g of acetone and 100 g of benzene separately. Boiling point of the solution in acetone increases by 0.17 °C, while that in the benzene increases by 0.13 °C. K_b for acetone and benzene is 1.7 K kg mol⁻¹ and 2.6 K kg mol⁻¹. Find molecular weight of benzoic acid in two cases and justify your answer. (2004 - 2 Marks)

18. 75.2 g of C₆H₅OH (phenol) is dissolved in a solvent of K_f = 14. If the depression in freezing point is 7 K then find the % of phenol that dimerises. (2006 - 6M)

G Comprehension Based Questions

PASSAGE

Properties such as boiling point, freezing point and vapour pressure of a pure solvent change when solute molecules are added to get homogeneous solution. These are called colligative properties. Application of colligative properties are very useful in day-to-day life. One of its example is the use of ethylene glycol and water mixture as anti-freezing liquid in the radiator of automobiles.

A solution M is prepared by mixing ethanol and water. The mole fraction of ethanol in the mixture is 0.9

Given: Freezing point depression constant of water (K_f, water) = 1.86 K kg mol⁻¹
Freezing point depression constant of ethanol (K_f, ethanol) = 2.0 K kg mol⁻¹
Boiling point elevation constant of water (K_b, water) = 0.52 K kg mol⁻¹
Boiling point elevation constant of ethanol (K_b, ethanol) = 1.2 K kg mol⁻¹

Standard freezing point of water = 273 K
Standard boiling point of water = 155.7 K
Standard boiling point of water = 373 K
Standard boiling point of ethanol = 351.5 K

Vapour pressure of pure water = 32.8 mm Hg
Vapour pressure of pure ethanol = 40 mm Hg
Molecular weight of water = 18 g mol⁻¹
Molecular weight of ethanol = 46 g mol⁻¹

In answering the following questions, consider the solution to be ideal dilute solutions and solutes to be non-volatile and non-dissociative.

1. The freezing point of the solution M is (2008 - 3 Marks)
   (a) 268.7 K     (b) 268.5 K     (c) 234.2 K     (d) 150.9 K

2. The vapour pressure of the solution M is (2008 - 3 Marks)
   (a) 39.3 mm Hg     (b) 36.0 mm Hg     (c) 29.5 mm Hg     (d) 28.8 mm Hg

3. Water is added to the solution M such that the mole fraction of water in the solution becomes 0.9. The boiling point of this solution is (2008 - 3 Marks)
   (a) 380.4 K     (b) 376.2 K     (c) 375.5 K     (d) 354.7 K

I Integer Value Correct Type

1. 29.2% (w/w) HCl stock solution has a density of 1.25 g mL⁻¹. The molecular weight of HCl is 36.5 g mol⁻¹. The volume (mL) of stock solution required to prepare a 200 mL solution of 0.4 M HCl is (2012)

2. MX₂ dissociates into M²⁺ and X⁻ ions in an aqueous solution, with a degree of dissociation (α) of 0.5. The ratio of the observed depression of freezing point of the aqueous solution to the value of the depression of freezing point in the absence of ionic dissociation is (JEE Adv. 2014)

3. A compound H₂X with molar weight of 80 g is dissolved in a solvent having density of 0.4 g mL⁻¹. Assuming no change in volume upon dissolution, the molality of a 3.2 molar solution is (JEE Adv. 2014)

4. If the freezing point of a 0.01 molal aqueous solution of a cobalt(III) chloride-ammonia complex (which behaves as a strong electrolyte) is −0.0558°C, the number of chloride(s) in the coordination sphere of the complex is [K_f, water = 1.86 K kg mol⁻¹] (JEE Adv. 2015)

5. The mole fraction of a solute in a solution is 0.1. At 298 K, molarity of this solution is the same as its molality. Density of this solution at 298 K is 2.0 g cm⁻³. The ratio of the molecular weights of the solute and solvent, \( \frac{\text{MW}_\text{solute}}{\text{MW}_\text{solvent}} \), is (JEE Adv. 2016)
1. Freezing point of an aqueous solution is (-0.186)°C. Elevation of boiling point of the same solution is $K_b = 0.512°C$, $K_f = 1.86°C$, find the increase in boiling point.
   (a) 0.186°C   (b) 0.0512°C   [2002]
   (c) 0.092°C   (d) 0.2372°C.

2. In mixture $A$ and $B$ components show -ve deviation as
   (a) $\Delta V_{mix} < 0$  [2002]
   (b) $\Delta H_{mix} < 0$
   (c) $A - B$ interaction is weaker than $A - A$ and $B - B$
   (d) $A - B$ interaction is stronger than $A - A$ and $B - B$ interaction.

3. If liquids $A$ and $B$ form an ideal solution  [2003]
   (a) the entropy of mixing is zero
   (b) the free energy of mixing is zero
   (c) the free energy as well as the entropy of mixing are each zero
   (d) the enthalpy of mixing is zero

4. In a 0.2 molal aqueous solution of a weak acid $HX$ the degree of ionization is 0.3. Taking $k_f$ for water as 1.85, the freezing point of the solution will be nearest to  [2003]
   (a) $-0.360°C$     (b) $-0.260°C$
   (c) $+0.480°C$     (d) $-0.480°C$

5. A pressure cooker reduces cooking time for food because
   [2003]
   (a) boiling point of water involved in cooking is increased
   (b) the higher pressure inside the cooker crushes the food material
   (c) cooking involves chemical changes helped by a rise in temperature
   (d) heat is more evenly distributed in the cooking space

6. Which one of the following aqueous solutions will exhibit highest boiling point?  [2004]
   (a) 0.015 M urea   (b) 0.01 M KNO$_3$
   (c) 0.01 M Na$_2$SO$_4$   (d) 0.015 M glucose

7. For which of the following parameters the structural isomers $C_4H_8O$ and $C_3H_7OCH_3$ would be expected to have the same values? (Assume ideal behaviour)  [2004]
   (a) Boiling points
   (b) Vapour pressure at the same temperature
   (c) Heat of vaporization
   (d) Gaseous densities at the same temperature and pressure

8. Which of the following liquid pairs shows a positive deviation from Raoult’s law?  [2004]
   (a) Water - nitric acid
   (b) Benzene - methanol
   (c) Water - hydrochloric acid
   (d) Acetone - chloroform

9. Which one of the following statements is FALSE?  [2004]
   (a) The correct order of osmotic pressure for 0.01 M aqueous solution of each compound is $\text{BaCl}_2 > \text{KCl} > \text{CH}_3\text{COOH} > \text{sucrose}$
   (b) The osmotic pressure ($\pi$) of a solution is given by the equation $\pi = MRT$, where $M$ is the molarity of the solution
   (c) Raoult’s law states that the vapour pressure of a component over a solution is proportional to its mole fraction
   (d) Two sucrose solutions of same molality prepared in different solvents will have the same freezing point depression

10. Benzene and toluene form nearly ideal solution. At 20°C, the vapour pressure of benzene is 75 torr and that of toluene is 22 torr. The partial vapour pressure of benzene at 20°C for a solution containing 78 g of benzene and 46 g of toluene in torr is  [2005]
    (a) 53.5      (b) 37.5
    (c) 25        (d) 50

11. Equimolar solutions in the same solvent have  [2005]
    (a) Different boiling and different freezing points
    (b) Same boiling and same freezing points
    (c) Same freezing point but different boiling points
    (d) Same boiling point but different freezing points

12. Among the following mixtures, dipole-dipole as the major interaction, is present in  [2006]
    (a) KCl and water
    (b) benzene and carbon tetrachloride
    (c) benzene and ethanol
    (d) acetonitrile and acetone

13. 18 g of glucose ($C_6H_{12}O_6$) is added to 178.2 g of water. The vapour pressure of water for this aqueous solution at 100°C is  [2006]
    (a) 76.00 Torr       (b) 752.40 Torr
    (c) 759.00 Torr      (d) 7.60 Torr
14. A mixture of ethyl alcohol and propyl alcohol has a vapour pressure of 290 mm at 300 K. The vapour pressure of propyl alcohol is 200 mm. If the mole fraction of ethyl alcohol is 0.6, its vapour pressure (in mm) at the same temperature will be

(a) 360  
(b) 350  
(c) 300  
(d) 700  

15. Equal masses of methane and oxygen are mixed in an empty container at 25°C. The fraction of the total pressure exerted by oxygen is

(a) 1/2  
(b) 2/3  
(c) \( \frac{1}{3} \times \frac{273}{298} \)  
(d) 1/3.  

16. A 5.25% solution of a substance is isotonic with a 1.5% solution of urea (molar mass = 60 g mol\(^{-1}\)) in the same solvent. If the densities of both the solutions are assumed to be equal to 1.0 g cm\(^{-3}\), molar mass of the substance will be

(a) 210.0 g mol\(^{-1}\)  
(b) 90.0 g mol\(^{-1}\)  
(c) 115.0 g mol\(^{-1}\)  
(d) 105.0 g mol\(^{-1}\).  

17. At 80°C, the vapour pressure of pure liquid 'A' is 520 mm Hg and that of pure liquid 'B' is 1000 mm Hg. If a mixture solution of 'A' and 'B' boils at 80°C and 1 atm pressure, the amount of 'A' in the mixture is (1 atm = 760 mm Hg)

(a) 52 mol percent  
(b) 34 mol percent  
(c) 48 mol percent  
(d) 50 mol percent.  

18. The vapour pressure of water at 20°C is 17.5 mm Hg. If 18 g of glucose (C\(_6\)H\(_{12}\)O\(_6\)) is added to 178.2 g of water at 20°C, the vapour pressure of the resulting solution will be

(a) 17.325 mm Hg  
(b) 17.750 mm Hg  
(c) 16.500 mm Hg  
(d) 17.500 mm Hg.  

19. A binary liquid solution is prepared by mixing n-heptane and ethanol. Which one of the following statements is correct regarding the behaviour of the solution?

(a) The solution is non-ideal, showing – ve deviation from Raoult’s Law.  
(b) The solution is non-ideal, showing + ve deviation from Raoult’s Law.  
(c) n-heptane shows + ve deviation while ethanol shows – ve deviation from Raoult’s Law.  
(d) The solution formed is an ideal solution.  

20. Two liquids X and Y form an ideal solution. At 300 K, vapour pressure of the solution containing 1 mol of X and 3 mol of Y is 550 mm Hg. At the same temperature, if 1 mol of Y is further added to this solution, vapour pressure of the solution increases by 10 mm Hg. Vapour pressure (in mm Hg) of X and Y in their pure states will be, respectively:

(a) 300 and 400  
(b) 400 and 600  
(c) 500 and 600  
(d) 200 and 300.  

21. If sodium sulphate is considered to be completely dissociated into cations and anions in aqueous solution, the change in freezing point of water (\(\Delta T_f\)), when 0.01 mol of sodium sulphate is dissolved in 1 kg of water, is \(K_f = 1.86 \text{ K kg mol}^{-1}\)

(a) 0.372 K  
(b) 0.0558 K  
(c) 0.0744 K  
(d) 0.0186 K  

22. On mixing, heptane and octane form an ideal solution. At 373 K, the vapour pressures of the two liquid components (heptane and octane) are 105 kPa and 45 kPa respectively. Vapour pressure of the solution obtained by mixing 25.0 g of heptane and 35 g of octane will be (molar mass of heptane = 100 g mol\(^{-1}\) and of octane = 114 g mol\(^{-1}\)).

(a) 72.0 kPa  
(b) 36.1 kPa  
(c) 96.2 kPa  
(d) 144.5 kPa.  

23. A 5.2 molal aqueous solution of methyl alcohol, CH\(_3\)OH, is supplied. What is the mole fraction of methyl alcohol in the solution?

(a) 0.100  
(b) 0.190  
(c) 0.086  
(d) 0.050.  

24. Ethylene glycol is used as an antifreeze in a cold climate. Mass of ethylene glycol which should be added to 4 kg of water to prevent it from freezing at −6°C will be: \(K_f\) for water = 1.86 K kg mol\(^{-1}\), and molar mass of ethylene glycol = 62 g mol\(^{-1}\)

(a) 804.32 g  
(b) 204.30 g  
(c) 400.00 g  
(d) 304.60 g.  

25. The degree of dissociation (\(\alpha\)) of a weak electrolyte, \(A_xB_y\), is related to van’t Hoff factor (i) by the expression

\[ \alpha = \frac{i-1}{x+y-1} \]  

(a) \[ \alpha = \frac{i-1}{x+y+1} \]  
(b) \[ \alpha = \frac{x+y-1}{i-1} \]  
(c) \[ \alpha = \frac{x+y+1}{i+1} \]  
(d) \[ \alpha = \frac{x+y+1}{i-1} \]  

26. The density of a solution prepared by dissolving 120 g of urea (mol. mass = 60 u) in 1000 g of water is 1.15 g/mL. The molarity of this solution is:

(a) 0.50 M  
(b) 1.78 M  
(c) 1.02 M  
(d) 2.05 M.  

27. \(K_f\) for water is 1.86 K kg mol\(^{-1}\). If your automobile radiator holds 1.0 kg of water, how many grams of ethylene glycol (C\(_2\)H\(_4\)O\(_2\)) must you add to get the freezing point of the solution lowered to −2.8°C?

(a) 72 g  
(b) 93 g  
(c) 39 g  
(d) 27 g.
28. The molarity of a solution obtained by mixing 750 mL of 0.5(M) HCl with 250 mL of 2(M) HCl will be: [JEE M 2013]
(a) 0.875 M  (b) 1.00 M  
(c) 1.75 M  (d) 0.975 M

29. Consider separate solutions of 0.500 M C₃H₇OH(aq), 0.100 M Mg₃(PO₄)₂(aq), 0.250 M KBr(aq) and 0.125 M Na₃PO₄(aq) at 25°C. Which statement is true about these solutions, assuming all salts to be strong electrolytes? [JEE M 2014]
(a) They all have the same osmotic pressure.
(b) 0.100 M Mg₃(PO₄)₂(aq) has the highest osmotic pressure.

30. The vapour pressure of acetone at 20°C is 185 torr. When 1.2 g of a non-volatile substance was dissolved in 100 g of acetone at 20°C, its vapour pressure was 183 torr. The molar mass (g mol⁻¹) of the substance is: [JEE M 2015]
(a) 128  (b) 488  
(c) 32  (d) 64

31. 18 g glucose (C₆H₁₂O₆) is added to 178.2 g water. The vapour pressure of water (in torr) for this aqueous solution is: [JEE M 2016]
(a) 752.4  (b) 759.0  
(c) 7.6  (d) 76.0
CHAPTER 13

Electrochemistry

Section-A

JEE Advanced/ IIT-JEE

A  Fill in the Blanks

1. Of the halide ions, ______ is the most powerful reducing agent. (1978)
2. The more __________ the standard reduction potential, the __________ is its ability to displace hydrogen from acids. (1986 - 1 Mark)
3. The electrical conductivity of a solution of acetic acid will be __________ if a solution of sodium hydroxide is added. (1987 - 1 Mark)

B  True / False

1. The dependence of electrode potential for the electrode M^{n+}/M with concentration under STP conditions is given by the expression: \( E = E^0 + \frac{0.0591}{n} \log_{10}[M^{n+}] \) (1993 - 1 Mark)

C  MCQs with One Correct Answer

1. The standard reduction potentials at 298 K for the following half reactions are given against each other: (1981 - 1 Mark)
   - Zn^{2+} (aq) + 2e -> Zn(s) \(-0.762\)
   - Cr^{3+} (aq) + 2e -> Cr(s) \(-0.740\)
   - 2H^+ (aq) + 2e -> H_2(g) \(0.000\)
   - Fe^{3+} (aq) + 2e -> Fe^{2+} (aq) \(0.770\)
   Which is the strongest reducing agent?
   (a) Zn(s)  (b) Cr(s)  (c) H_2(g)  (d) Fe^{2+} (aq)

2. Faraday's laws of electrolysis are related to the (a) atomic number of the reactants. (1983 - 1 Mark)
   (b) atomic number of the anion.
   (c) equivalent weight of the electrolyte.
   (d) speed of the cation.

3. A solution containing one mole per litre of each Cu(NO_3)_2, AgNO_3, H_2SO_4, and HNO_3 is being electrolysed by using inert electrodes. The values of standard electrode potentials in volts (reduction potentials) are: (1984 - 1 Mark)
   - Ag/Ag^+ = +0.80; 2Hg/Hg^2+ = +0.79
   - Cu/Cu^{2+} = +0.34; Mg/Mg^{2+} = -2.37
   With increasing voltage, the sequence of deposition of metals on the cathode will be:
   (a) Ag, Hg, Cu, Mg  (b) Mg, Cu, Hg, Ag
   (c) Ag, Hg, Cu  (d) Cu, Hg, Ag

4. The electric charge for electrode deposition of one gram equivalent of a substance is: (1984 - 1 Mark)
   (a) one ampere per second.
   (b) 96,500 coulombs per second.
   (c) one ampere for one hour.
   (d) charge on one mole of electrons.

5. The reaction: \( \frac{1}{2} \text{Hg}_2\text{O}_2\text{(s)} + \text{AgCl(s)} \rightarrow \text{H}^+\text{(aq)} + \text{Cl}^-\text{(aq)} + \text{Ag(s)} \) occurs in the galvanic cell
   (a) Ag | AgCl(s) | KCl (s) | AgNO_3 (s) | Ag
   (b) Pt | H_2(g) | HCl (s) | AgNO_3 (s) | Ag
   (c) Pt | H_2(g) | HCl (s) | AgCl(s) | Ag
   (d) Pt | H_2(g) | KCl (s) | AgCl(s) | Ag

6. A solution of sodium sulphate in water is electrolysed using inert electrodes. The products at the cathode and anode are respectively: (1987 - 1 Mark)
   (a) H_2, O_2  (b) O_2, H_2
   (c) O_2, Na  (d) O_2, SO_2

7. The standard oxidation potentials, \( E^0 \), for the half reactions are as follows: (1988 - 1 Mark)
   - Zn = Zn^{2+} + 2e^-; \( E^0 = +0.76 \) V
   - Fe = Fe^{2+} + 2e^-; \( E^0 = +0.41 \) V
   The EMF for the cell reaction:
   \( \text{Fe}^{2+} + \text{Zn} \rightarrow \text{Zn}^{2+} + \text{Fe} \)
   (a) -0.35 V  (b) +0.35 V
   (c) +1.17 V  (d) -1.17 V

8. A dilute aqueous solution of Na_2SO_4 is electrolyzed using platinum electrodes. The products at the anode and cathode are: (1996 - 1 Mark)
   (a) O_2, H_2  (b) S_2O_3^{2-}, Na
   (c) O_2, Na  (d) S_2O_3^{2-}, H_2

9. The standard reduction potentials of Cu^{2+} | Cu and Cu^{2+} | Cu^+ are 0.337 V and 0.153 respectively. The standard electrode potential of Cu^{+} | Cu half cell is: (1997 - 1 Mark)
   (a) 0.184 V  (b) 0.827 V
   (c) 0.521 V  (d) 0.490 V

10. A gas X at 1 atm is bubbled through a solution containing a mixture of 1 M Y^- and M Z^- at 25°C. If the reduction potential of Z > Y > X, then, (1999 - 2 Marks)
    (a) Y will oxidize X and not Z
    (b) Y will oxidize Z and not X
    (c) Y will oxidize both X and Z
    (d) Y will reduce both X and Z
11. For the electrochemical cell, \[ M | M^+ \ | X^- | X, E^0 M^+/M = 0.44 \text{ V} \text{ and } E^0(X/X^-) = 0.33 \text{ V}. \] From this data one can deduce that \( (2000S) \)
(a) \( M + X \rightarrow M^+ + X^- \) is the spontaneous reaction
(b) \( M^+ + X^- \rightarrow M + X \) is the spontaneous reaction
(c) \( E_{\text{cell}} = 0.77 \text{ V} \)
(d) \( E_{\text{cell}} = -0.77 \text{ V} \)

12. Saturated solution of KNO₃ is used to make ‘salt–bridge’ because \( (2001S) \)
(a) velocity of K⁺ is greater than that of NO₃⁻
(b) velocity of NO₃⁻ is greater than that of K⁺
(c) velocities of both K⁺ and NO₃⁻ are nearly the same
(d) KNO₃ is highly soluble in water

13. The correct order of equivalent conductance at infinite dilution of LiCl, NaCl, and KCl is \( (2001S) \)
(a) LiCl > NaCl > KCl
(b) KCl > NaCl > LiCl
(c) NaCl > KCl > LiCl
(d) LiCl > KCl > NaCl

14. Standard electrode potential data are useful for understanding the suitability of an oxidant in a redox titration. Some half cell reactions and their standard potentials are given below: \( (2002S) \)
\[
\begin{align*}
\text{MnO}_4^- (aq.) + 8H^+ (aq.) + 5e^- & \rightarrow Mn^{2+} (aq.) + 4H_2O(l) \quad E^o = 1.51 \text{ V} \\
Cr_2O_7^{2-} (aq.) + 14H^+ (aq.) + 6e^- & \rightarrow 2Cr^{3+} (aq.) + 7H_2O(l) \quad E^o = 1.38 \text{ V} \\
Fe^{3+} (aq.) + e^- & \rightarrow Fe^{2+} (aq.) \quad E^o = 0.77 \text{ V} \\
Cl_2(g) + 2e^- & \rightarrow 2Cl^- (aq.) \quad E^o = 1.40 \text{ V}
\end{align*}
\]
Identify the only incorrect statement regarding the quantitative estimation of aqueous Fe(NO₃)₂
(a) MnO₄⁻ can be used in aqueous HCl
(b) Cr₂O₇²⁻ can be used in aqueous HCl
(c) MnO₄⁻ can be used in aqueous H₂SO₄
(d) Cr₂O₇²⁻ can be used in aqueous H₂SO₄

15. In the electrolytic cell, flow of electrons is from \( (2003S) \)
(a) Cathode to anode in solution
(b) Cathode to anode through external supply
(c) Cathode to anode through internal supply
(d) Anode to cathode through internal supply

16. The emf of the cell \( (2004S) \)
\[
\begin{align*}
\text{Zn} | \text{Zn}^{2+} (0.01 \text{ M}) | \text{Fe}^{2+} (0.001 \text{ M}) | \text{Fe} \\
\text{at} 298 \text{ K} & \text{is} 0.2905 \text{ then the value of equilibrium constant for the cell reaction is}
\end{align*}
\]
(a) \( e^{-0.0295} \)
(b) \( 10^{0.0295} \)
(c) \( 10^{0.0295} \)
(d) \( 10^{-0.0295} \)

17. The rusting of iron takes place as follows \( (2005S) \)
\[
\begin{align*}
2H^+ + 2e^- + \frac{1}{2}O_2 & \rightarrow H_2O(l); E^o = +1.23 \text{ V} \\
Fe^{2+} + 2e^- & \rightarrow Fe(s); E^o = -0.44 \text{ V}
\end{align*}
\]
Calculate \( \Delta G^o \) for the net process
(a) \(-322 \text{ kJ mol}^{-1}\)
(b) \(-161 \text{ kJ mol}^{-1}\)
(c) \(-152 \text{ kJ mol}^{-1}\)
(d) \(-76 \text{ kJ mol}^{-1}\)

18. Electrolysis of dilute aqueous NaCl solution was carried out by passing 10 milli ampere current. The time required to liberate 0.01 mol of H₂ gas at the cathode is \( (1 \text{ Faraday} = 96500 \text{ C mol}^{-1}) \) \( (2008S) \)
(a) \(9.65 \times 10^4 \text{ sec}\)
(b) \(19.3 \times 10^4 \text{ sec}\)
(c) \(28.95 \times 10^4 \text{ sec}\)
(d) \(38.6 \times 10^4 \text{ sec}\)

19. AgNO₃(aq.) was added to an aqueous KCl solution gradually and the conductivity of the solution was measured. The plot of conductance \((\Lambda)\) versus the volume of AgNO₃ is \( (2011) \)

20. Consider the following cell reaction: \( (2011) \)
\[
2Fe(s) + O_2(g) + 4H^+_aq \rightarrow 2Fe^{2+} + 2H_2O(l); E^o = 1.67 \text{ V}
\]
At \([Fe^{2+}] = 10^{-3} \text{ M, P(O}_2) = 0.1 \text{ atm and pH} = 3\), the cell potential at 25°C is
(a) \(1.47 \text{ V}\)
(b) \(1.77 \text{ V}\)
(c) \(1.87 \text{ V}\)
(d) \(1.57 \text{ V}\)

21. For the following electrochemical cell at 298 K, \( Pt(s)|H_2(g, 1 \text{ bar})|H^+(aq, 1 \text{ M}) || M^{4+}(aq), M^{2+}(aq)|Pt(s) \)
\[
E_{\text{cell}} = 0.092 \text{ V when}\]
\[
\frac{M^{2+}(aq)}{M^{4+}(aq)} = 10^x \quad (\text{JEE Adv. 2016})
\]
Given: \( E_{M^{4+}/M^{2+}}^o = 0.151 \text{ V, } 2.303 \ln \frac{RT}{F} = 0.059 \text{ V} \)
The value of \( x \) is
(a) \(-2\)
(b) \(-1\)
(c) \(1\)
(d) \(2\)
MCQs with One or More Than One Correct

1. The standard reduction potential values of three metallic cations, $X$, $Y$ and $Z$ are 0.52, -3.03 and -1.18 V respectively. The order of reducing power of the corresponding metals is $(1998 \text{ - 2 Marks})$
   (a) $Y > Z > X$  
   (b) $X > Y > Z$  
   (c) $Z > Y > X$  
   (d) $Z > X > Y$

2. For the reduction of $\text{NO}_3^-$ ion in an aqueous solution, $E^o$ is +0.96 V. Values of $E^o$ for some metal ions are given below
   $\text{V}^{2+}$ (aq) $+ 2e^- \rightarrow \text{V}$  
   $E^o = -1.19$ V  
   $\text{Fe}^{3+}$ (aq) $+ 3e^- \rightarrow \text{Fe}$  
   $E^o = -0.04$ V  
   $\text{Au}^{3+}$ (aq) $+ 3e^- \rightarrow \text{Au}$  
   $E^o = +1.40$ V  
   $\text{Hg}^{2+}$ (aq) $+ 2e^- \rightarrow \text{Hg}$  
   $E^o = +0.86$ V

   The pair(s) of metals that is(are) oxidized by $\text{NO}_3^-$ ion in aqueous solution is(are) $(2009)$
   (a) $\text{V}$ and $\text{Hg}$  
   (b) $\text{Hg}$ and $\text{Fe}$  
   (c) $\text{Fe}$ and $\text{Au}$  
   (d) $\text{Fe}$ and $\text{V}$

3. In a galvanic cell, the salt bridge $(JEE \text{ Adv. 2014})$
   (a) Does not participate chemically in the cell reaction  
   (b) Stops the diffusion of ions from one electrode to another  
   (c) Is necessary for the occurrence of the cell reaction  
   (d) Ensures mixing of the two electrolytic solutions

Subjective Problems

1. The density of copper is 8.94 g/ml. Find out the number of coulombs needed to plate an area 10 cm $\times$ 10 cm to a thickness 10$^{-2}$ cm using CuSO$_4$ solution as electrolyte. $(1979)$

2. (a) 19 gm of molten SnCl$_2$ is electrolysed for some time. Inert electrodes are used. 0.119 gm of Sn is deposited at the cathode. No substance is lost during the electrolysis. Find the ratio of the weights of SnCl$_2$ : SnCl$_4$ after electrolysis.
   (b) A hot solution of NaCl in water is electrolysed. Iron electrodes are used. Diaphragm cell is not used. Give equations for all the chemical reactions that take place during electrolysis.
   (c) Find the charge in coulombs of 1 gram ion of $\text{N}_3^{-}$ $(1980)$

3. Complete and balance the following equations $(1980)$
   (i) $\text{KNO}_3 + \text{FeSO}_4 + \text{H}_2\text{SO}_4(\text{conc}) \rightarrow$  
   (ii) $\text{H}_2\text{S} + \text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4 \rightarrow$  
   (iii) $\text{KI} + \text{H}_2\text{SO}_4(\text{conc}) \rightarrow$  
   (iv) $\text{Mg}_3\text{N}_2 + \text{H}_2\text{O} \rightarrow$  
   (v) $\text{Al} + \text{KMnO}_4 + \text{H}_2\text{SO}_4 \rightarrow$

4. Consider the cell $(1982 \text{ - 2 Marks})$
   $\text{Zn} | \text{Zn}^{2+} (\text{aq}) (1.0 \text{M}) || \text{Cu}^{2+} (\text{aq}) (1.0 \text{M}) | \text{Cu}$
   The standard reduction potentials are:
   +0.350 volts for $2e^- + \text{Cu}^{2+} (\text{aq}) \rightarrow \text{Cu}$ and -0.763 volts for $2e^- + \text{Zn}^{2+} (\text{aq}) \rightarrow \text{Zn}$
   (i) Write down the cell reaction.
   (ii) Calculate the emf of the cell.
   (iii) Is the cell reaction spontaneous or not?

5. In an electrolysis experiment current was passed for 5 hours through two cells connected in series. The first cell contains a solution of gold and the second contains copper sulphate solution. 9.85 g of gold was deposited in the first cell. If the oxidation number of gold is +3, find the amount of copper deposited on the cathode of the second cell. Also calculate the magnitude of the current in amperes. $(1 \text{ faraday} = 96,500 \text{ coulombs})$ $(1983 \text{ - 3 Marks})$

6. How long a current of 3 amperes has to be passed through a solution of silver nitrate to coat a metal surface of 80 cm$^2$ with a 0.005 mm thick layer? Density of silver is 10.5 g/cm$^3$ $(1985 \text{ - 3 Marks})$

7. The EMF of a cell corresponding to the reaction:
   $\text{Zn} (s) + 2\text{H}^+ (\text{aq}) \rightarrow \text{Zn}^{2+} + (0.1 \text{ M}) + \text{H}_2 (g) (1 \text{ atm})$
   is 0.28 volt at 25°C.
   Write the half-cell reactions and calculate the pH of the solution at the hydrogen electrode.
   $E^o_{\text{Zn}^{2+}/\text{Zn}} = -0.76$ volt, $E^o_{\text{H}^+/\text{H}_2} = 0$ $(1986 \text{ - 4 Marks})$

8. During the discharge of a lead storage battery, the density of sulphuric acid fell from 1.294 to 1.139 g/ml. Sulphuric acid of density 1.294 g/ml is 39% by weight and that of 1.139 g/ml is 20% $\text{H}_2\text{SO}_4$ by weight. The battery holds 3.5 litres of the acid and the volume remained practically constant during the discharge.
   Calculate the number of ampere-hours for which the battery must have been used. The charging and discharging reactions are:
   $(1986 \text{ - 5 Marks})$
   **Anode**:  
   $\text{Pb} + \text{SO}_4^{2-} \rightarrow \text{PbSO}_4 + 2e^-$ (discharging)  
   **Cathode**:  
   $\text{PbO}_2 + 4\text{H}^+ + \text{SO}_4^{2-} + 2e^- \rightarrow \text{PbSO}_4 + 2\text{H}_2\text{O}$ (discharging)
   **Note**: Both the reactions take place at the anode and cathode respectively during discharge. Both reaction get reverse during charging.

9. A 100 watt, 110 volt incandescent lamp is connected in series with an electrolyte cell containing cadmium sulphate solution. What weight of cadmium will be deposited by the current flowing for 10 hours? $(1987 \text{ - 5 Marks})$

10. A cell contains two hydrogen electrodes. The negative electrode is in contact with a solution of $10^{-6}$ M hydrogen ions. The EMF of the cell is 0.118 V at 25°C. Calculate the concentration of hydrogen ions at the positive electrode. $(1988 \text{ - 2 Marks})$
11. In a fuel cell hydrogen and oxygen react to produce electricity. In the process hydrogen gas is oxidised at the anode and oxygen at the cathode. If 67.2 litre of H₂ at STP react in 15 minutes, what is the average current produced?
If the entire current is used for electro deposition of copper from copper (II) solution, how many grams of copper will be deposited?

\[ \text{Anode reaction: } \text{H}_2 + 2\text{OH}^- \rightarrow 2\text{H}_2\text{O} + 2\text{e}^- \]
\[ \text{Cathode reaction: } \frac{1}{2} \text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{OH}^- . \]

\[ (1988 - 4 \text{ Marks}) \]

12. An acidic solution of Cu²⁺ salt containing 0.4 g of Cu²⁺ is electrolysed until all the copper is deposited. The electrolysis is continued for seven more minutes with the volume of solution kept at 100 ml and the current at 1.2 amp. Calculate the volume of gases evolved at NTP during the entire electrolysis.

\[ (1989 - 5 \text{ Marks}) \]

13. The standard reduction potential at 25°C of the reaction,
\[ 2\text{H}_2\text{O} + 2\text{e}^- \rightleftharpoons \text{H}_2 + 2\text{OH}^- \text{is} -0.8277V. \]
Calculate the equilibrium constant for the reaction \[ 2\text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{O}^+ + \text{OH}^- \text{at} 25°C. \]

\[ (1989 - 3 \text{ Marks}) \]

14. The standard reduction potential of Cu⁺⁺/Cu and Ag⁺/Ag electrodes are 0.337 and 0.799 volt respectively. Construct a galvanic cell using these electrodes so that its standard e.m.f. is positive. For what concentration of Ag⁺ will the e.m.f. of the cell, at 25°C, be zero if the concentration of Cu⁺⁺ is 0.01 M?

\[ (1990 - 3 \text{ Marks}) \]

15. Calculate the quantity of electricity that would be required to reduce 12.3 g of nitrobenzene to aniline, if the current efficiency for the process is 50 per cent. If the potential drop across the cell is 3.0 volts, how much energy will be consumed?

\[ (1990 - 3 \text{ Marks}) \]

16. Zinc granules are added in excess to a 500 ml of 1.0 M nickel nitrate solution at 25°C until the equilibrium is reached. If the standard reduction potential of Zn²⁺ / Zn and Ni²⁺ / Ni are \(-0.75 \text{ V and } -0.24 \text{ V} \) respectively, find out the concentration of Ni²⁺ in solution at equilibrium.

\[ (1991 - 2 \text{ Marks}) \]

17. A current of 1.70 A is passed through 300.0 ml of 0.160 M solution of a ZnSO₄ for 230 sec. with a current efficiency of 90%. Find out the molarity of Zn²⁺ after the deposition of Zn. Assume the volume of the solution to remain constant during the electrolysis.

\[ (1991 - 4 \text{ Marks}) \]

18. For the galvanic cell,

\[ \text{Ag} / \text{AgCl} / \text{KCl}(0.2 M) \| \text{KBr}(0.001 M), \text{AgBr} / \text{Ag} \]
Calculate the EMF generated and assign correct polarity to each electrode for a spontaneous process after taking into account the cell reaction at 25°C.

\[ K_{sp}(\text{AgCl}) = 2.8 \times 10^{-10}, K_{sp}(\text{AgBr}) = 3.3 \times 10^{-13} \]

\[ (1992 - 4 \text{ Marks}) \]

19. An aqueous solution of NaCl on electrolysis gives H₂(g), Cl₂(g) and NaOH according to the reaction:

\[ 2\text{Cl}^-(\text{aq}) + 2\text{H}_2\text{O} = 2\text{OH}^-(\text{aq}) + \text{H}_2(\text{g}) + \text{Cl}_2(\text{g}). \]

A direct current of 25 amperes with a current efficiency of 62% is passed through 20 litres of NaCl solution (20% by weight). Write down the reactions taking place at the anode and the cathode. How long will it take to produce 1 kg of Cl₂? What will be the molarity of the solution with respect to hydroxide ion? (Assume no loss due to evaporation.)

\[ (1992 - 3 \text{ Marks}) \]

20. The standard reduction potential for the half-cell

\[ \text{NO}_3^- (\text{aq}) + 2\text{H}^+ (\text{aq}) + e \rightarrow \text{NO}_2^- (\text{g}) + \text{H}_2\text{O} \text{ is} 0.78 \text{V}. \]

(i) Calculate the reduction potential in 8 M H⁺
(ii) What will be the reduction potential of the half-cell in a neutral solution? Assume all the other species to be at unit concentration.

\[ (1993 - 2 \text{ Marks}) \]

21. Chromium metal can be plated out from an acidic solution containing CrO₃ according to the following equation.

\[ \text{CrO}_3 (\text{aq}) + 6\text{H}^+ (\text{aq}) + 6e^- \rightarrow \text{Cr(s)} + 3\text{H}_2\text{O} \]

Calculate (i) how many grams of chromium will be plated out by 24,000 coulombs and (ii) how long will it take to plate out 1.5 g of chromium by using 12.5 amp current.

\[ (1993 - 2 \text{ Marks}) \]

22. The standard reduction potential of the Ag⁺ / Ag electrode at 298 K is 0.799 V. Given that for AgI, \( K_{sp} = 8.7 \times 10^{-17} \), evaluate the potential of the Ag⁺/Ag electrode in a saturated solution of AgI. Also calculate the standard reduction potential of the I⁻/AgI/Ag electrode.

\[ (1994 - 3 \text{ Marks}) \]

23. The Edison storage cells is represented as

\[ \text{Fe(s)} | \text{FeO(s)} | \text{KOH(aq)} | \text{Ni}_2\text{O}_3(s) | \text{Ni(s)} \]
The half-cell reactions are:

\[ \text{Ni}_2\text{O}_3(s) + \text{H}_2\text{O}(l) + 2e^- \rightleftharpoons 2\text{NiO}(s) + 2\text{OH}^- ; \]

\[ E^0 = +0.40 \text{V} \]

\[ \text{FeO}(s) + \text{H}_2\text{O}(l) + 2e^- \rightleftharpoons \text{Fe(s)} + 2\text{OH}^- ; \]

\[ E^0 = -0.87 \text{V} \]

(i) What is the cell reaction ?
(ii) What is the cell e.m.f ? How does it depend on the concentration of KOH?
(iii) What is the maximum amount of electrical energy that can be obtained from one mole of \( \text{Ni}_2\text{O}_3 \)?

\[ (1994 - 4 \text{ Marks}) \]

24. Although aluminium is above hydrogen in the electrochemical series, it is stable in air and water. Explain.

\[ (1994 - 1 \text{ Mark}) \]
25. An excess of liquid mercury is added to an acidified solution of $1.0 \times 10^{-3}$ M Fe$^{3+}$. It is found that 5% of Fe$^{3+}$ remains at equilibrium at 25°C. Calculate $E^\circ_{Hg_2^{2+}/Hg}$, assuming that the only reaction that occurs is

$$2\text{Hg} + 2\text{Fe}^{3+} \rightarrow \text{Hg}_2^{2+} + 2\text{Fe}^{2+}. \quad (1995 - 4\text{ Marks})$$

26. The standard reduction potential for Cu$^{2+}$/Cu is +0.34 V. Calculate the reduction potential at pH = 14 for the above couple. $K_{sp}$ of Cu(OH)$_2$ is $1.0 \times 10^{-19}$ \hfill (1996 - 3 Marks)

27. How many grams of silver could be plated out on a serving tray by electrolysis of a solution containing silver in +1 oxidation state for a period of 8.0 hours at a current of 8.46 amperes? What is the area of the tray if the thickness of the silver plating is 0.00254 cm? Density of silver is 10.5 g/cm$^3$. \hfill (1997 - 3 Marks)

28. Calculate the equilibrium constant for the reaction

$$\text{Fe}^{2+} + \text{Ce}^{4+} \rightleftharpoons \text{Fe}^{3+} + \text{Ce}^{3+} \quad (1997 - 2\text{ Marks})$$

(given $E^\circ_{\text{Ce}^{4+/\text{Ce}^{3+}}} = 1.44$ V; $E^\circ_{\text{Fe}^{3+/\text{Fe}^{2+}}} = 0.68$ V)

29. Calculate the equilibrium constant for the reaction,

$$2\text{Fe}^{2+} + 3\text{I}^- \rightleftharpoons 2\text{Fe}^{2+} + \text{I}_3^-.$$ The standard reduction potentials in acidic conditions are 0.77 V and 0.54 V respectively for Fe$^{3+}$/Fe$^{2+}$ and I$_3^-$/I$^-$ couples. \hfill (1998 - 3 Marks)

30. Find the solubility product of a saturated solution of Ag$_2$CrO$_4$ in water at 298 K if the emf of the cell Ag | Ag$^+$ (std. Ag$_2$CrO$_4$ soln.) | Ag$^+$ (0.1M) Ag is 0.164 V at 298 K. \hfill (1998 - 6 Marks)

31. A cell, Ag | Ag$^+$ | Cu$^{2+}$/Cu, initially contains 1 M Ag$^+$ and 1 M Cu$^{2+}$ ions. Calculate the change in the cell potential after the passage of 9.65 A for 1 hour. \hfill (1999 - 6 Marks)

32. Copper sulphate solution (250 mL) was electrolysed using a platinum anode and a copper cathode. A constant current of 2 mA was passed for 16 minutes. It was found that after electrolysis the absorbance of the solution was reduced to 50% of its original value. Calculate the concentration of copper sulphate in the solution to begin with. \hfill (2000 - 3 Marks)

33. The following electrochemical cell has been set up.

Pt(1) | [Fe$^{3+},$ Fe$^{2+} | \text{(a = 1)} | \text{Ce}^{4+}, \text{Ce}^{3+} | \text{(a = 1)} | \text{Pt}(2)

$$E^\circ (\text{Fe}^{3+}, \text{Fe}^{2+}) = 0.77 \text{ V;} \quad E^\circ (\text{Ce}^{4+/\text{Ce}^{3+}}) = 1.61 \text{ V}$$

If an ammeter is connected between the two platinum electrodes, predict the direction of flow of current. Will the current increase or decrease with time? \hfill (2000 - 2 Marks)

34. The standard potential of the following cell is 0.23 V at 15°C and 0.21 V at 35°C. \hfill (2001 - 10 Marks)

Pt | H$_2$(g) | HCl(aq) | AgCl(s) | Ag(s)

(i) Write the cell reaction.
(ii) Calculate $\Delta H^\circ$ and $\Delta S^\circ$ for the cell reaction by assuming that these quantities remain unchanged in the range 15°C to 35°C.
(iii) Calculate the solubility of AgCl in water at 25°C.

Given: The standard reduction potential of the Ag$^+(aq)$ / Ag(s) couple is 0.80 V at 25°C.

35. Two students use same stock solution of ZnSO$_4$ and a solution of CuSO$_4$. The emf of one cell is 0.03 V higher than the other. The conc. of CuSO$_4$ in the cell with higher emf value is 0.5 M. Find out the conc. of CuSO$_4$ in the other cell (2.203 RT/F = 0.06). \hfill (2003 - 2 Marks)

36. Find the equilibrium constant for the reaction,

$$\text{In}^{2+} + \text{Cu}^{2+} \rightleftharpoons \text{In}^{3+} + \text{Cu}^+$$ at 298 K

given:

$$E^\circ_{\text{In}^{2+/\text{In}^+}} = -0.40 \text{ V;} \quad E^\circ_{\text{In}^{3+/\text{In}^+}} = 0.15 \text{ V}$$

\hfill (2004 - 4 Marks)

37. (a) For the reaction

$$\text{Ag}^+(aq) + \text{Cl}^-(aq) \rightleftharpoons \text{AgCl(s)}$$

Given:

<table>
<thead>
<tr>
<th>Species</th>
<th>$\Delta G^\circ$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag$^+$ (aq)</td>
<td>+77</td>
</tr>
<tr>
<td>Cl$^-$ (aq)</td>
<td>-129</td>
</tr>
<tr>
<td>AgCl(s)</td>
<td>-109</td>
</tr>
</tbody>
</table>

Write the cell representation of above reaction and calculate $E^\circ_{\text{cell}}$ at 298 K. Also find the solubility product of AgCl.

(b) If 6.539 $\times$ 10$^{-2}$ g of metallic zinc is added to 100 ml saturated solution of AgCl. Find the value of $\log_{10} \frac{[\text{Zn}^{2+}]}{[\text{Ag}^+]}$.

How many moles of Ag will be precipitated in the above reaction. Given that

Ag$^+ + e^- \rightarrow$ Ag; $E^\circ = 0.80$ V ;

$\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn}; E^\circ = -0.76$ V \hfill (2005 - 6 Marks)

(It was given that Atomic mass of Zn = 65.39)

38. We have taken a saturated solution of AgBr. $K_{sp}$ of AgBr is $12 \times 10^{-14}$. If 10$^{-7}$ mole of AgNO$_3$ are added to 1 litre of this solution find conductivity (specific conductance) of this solution in terms of 10$^{-7}$ S m$^{-1}$ units. Given, Molar conductance of Ag$^+$, Br$^-$ and NO$_3^-$ are $6 \times 10^{-3}$ Sm$^2$mol$^{-1}$, $8 \times 10^{-3}$ Sm$^2$mol$^{-1}$ and $7 \times 10^{-3}$ Sm$^2$mol$^{-1}$. \hfill (2006 - 6M)
**Match the Following**

**DIRECTION (for Q. 1):** Each question contains statements given in two columns, which have to be matched. The statements in Column I are labelled A, B, C and D, while the statements in Column II are labelled p, q, r, s and t. Any given statement in Column-I can have correct matching with ONE OR MORE statement(s) in Column-II. The appropriate bubbles corresponding to the answers to these questions have to be darkened as illustrated in the following example:

If the correct matches are A-p, s and t; B-q and r; C-p and q; and D-s then the correct darkening of bubbles will look like the given.

1. Match the reactions in Columns I with nature of the reactions/type of the products in Column II. Indicate your answer by darkening the appropriate bubbles of the $4 \times 4$ matrix given in the ORS.

<table>
<thead>
<tr>
<th>Column I</th>
<th>Column II</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A) $O_2 \rightarrow O_2 + O_2^2-$</td>
<td>(p) redox reaction</td>
</tr>
<tr>
<td>(B) $CrO_4^{2-} + H^+ \rightarrow$</td>
<td>(q) one of the products has trigonal planar structure</td>
</tr>
<tr>
<td>(C) $MnO_4^- + NO_2 + H^+ \rightarrow$</td>
<td>(r) dimeric bridged tetrahedral metal ion</td>
</tr>
<tr>
<td>(D) $NO_3^- + H_2SO_4 + Fe^{2+} \rightarrow$</td>
<td>(s) disproportionation</td>
</tr>
</tbody>
</table>

**DIRECTION (for Q. 2 & 3):** Following questions have matching lists. The codes for the lists have choices (a), (b), (c) and (d) out of which ONLY ONE is correct.

2. An aqueous solution of X is added slowly to an aqueous solution of Y as shown in List I. The variation in conductivity of these reactions is given in List II. Match List I with List II and select the correct answer using the code given below the lists:

<table>
<thead>
<tr>
<th>List I</th>
<th>List II</th>
</tr>
</thead>
<tbody>
<tr>
<td>P. $(C_6H_5)_3N + CH_3COOH \Xrightarrow{X} Y$</td>
<td>1. Conductivity decreases and then increases</td>
</tr>
<tr>
<td>Q. $KI(0.1M) + AgNO_3(0.01M) \Xrightarrow{X} Y$</td>
<td>2. Conductivity decreases and then does not change much</td>
</tr>
<tr>
<td>R. $CH_3COOH + KOH \Xrightarrow{X} Y$</td>
<td>3. Conductivity increases and then does not change much</td>
</tr>
<tr>
<td>S. $NaOH + HCl \Xrightarrow{X} Y$</td>
<td>4. Conductivity does not change much and then increases</td>
</tr>
</tbody>
</table>

**Codes:**
- P
- Q
- R
- S
- (a) 3 4 2 1
- (b) 4 3 2 1
- (c) 2 3 4 1
- (d) 1 4 3 2

3. The standard reduction potential data at 25°C is given below:

$E^0(Fe^{3+}, Fe^{2+}) = +0.77 V; E^0(Fe^{3+}, Fe) = -0.44 V; E^0(Cu^{2+}, Cu) = +0.34 V; E^0(Cu^{+}, Cu) = +0.52 V$

$E^0[O_2(g) + 4H^+ + 4e^- \rightarrow 2H_2O] = +1.23 V; E^0[O_2(g) + 2H_2O + 4e^- \rightarrow 4OH^-] = +0.40 V$

$E^0(Cr^{3+}, Cr) = -0.74 V; E^0(Cr^{2+}, Cr) = -0.91 V$

Match $E^0$ of the redox pair in List I with the values given in List II and select the correct answer using the code given below the lists:

<table>
<thead>
<tr>
<th>List I</th>
<th>List II</th>
</tr>
</thead>
<tbody>
<tr>
<td>P. $E^0(Fe^{3+}, Fe)$</td>
<td>1. $-0.18 V$</td>
</tr>
<tr>
<td>Q. $E^0(4H_2O \rightleftharpoons 4H^+ + 4OH^-)$</td>
<td>2. $-0.4 V$</td>
</tr>
<tr>
<td>R. $E^0(Cu^{2+}, Cu)$</td>
<td>3. $-0.04 V$</td>
</tr>
<tr>
<td>S. $E^0(Cr^{3+}, Cr^{2+})$</td>
<td>4. $-0.83 V$</td>
</tr>
</tbody>
</table>

**Codes:**
- P
- Q
- R
- S
- (a) 4 1 2 3
- (b) 2 3 4 1
- (c) 1 2 3 4
- (d) 3 4 1 2
**G Comprehension Based Questions**

**PASSAGE I**

Tollen’s test is given by aldehydes.

\[ Ag^+ + e^- \rightarrow Ag; \ E_{ox}^{0} = +0.800 \text{ V} \]

\[ \text{C}_6\text{H}_5\text{O}_6^+ + \text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_5\text{O}_7^- + 2\text{H}^+ + 2e^-; \ E_{ox}^{0} = -0.05V \]

\[ \text{Gluconic acid} \]

\[ [\text{Ag(NH}_3)\text{H}]^+ + e^- \rightarrow \text{Ag} + 2\text{NH}_3; \ E_{ox}^{0} = 0.373 \text{ V} \]

Given \[ \frac{2.303RT}{F} = 0.0591 \text{ & } \left( \frac{F}{RT} \right) = 38.92 \text{V}^{-1} \]

1. Calculate \( (\ln K) \) for

\[ \text{C}_6\text{H}_5\text{O}_6^+ + 2\text{Ag}^+ + \text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_5\text{O}_7^- + 2\text{H}^+ + 2\text{Ag} \]

(a) 55.6 \hspace{1cm} (b) 29.6 \hspace{1cm} (2006 - 5M, -2)

(c) 66 \hspace{1cm} (d) 38.38

2. On adding \( \text{NH}_3 \), pH of the solution increases to 11 then, identify the effect on potential of half-cell \((2006 - 5M, -2)\)

(a) \( E_{ox} \) increased from \( E_{ox}^{0} \) by 0.65 V

(b) \( E_{ox} \) decreased from \( E_{ox}^{0} \) by 0.65 V

(c) \( E_{red} \) decreased from \( E_{red}^{0} \) by 0.65 V

(d) \( E_{red} \) decreased from \( E_{red}^{0} \) by 0.65 V

3. \( \text{NH}_3 \) is used in this reaction rather than any other base. Select the correct statement out of the following \((2006 - 5M, -2)\)

(a) \[ [\text{Ag(NH}_3)\text{H}]^+ \] is a weaker oxidizing agent than \( \text{Ag}^+ \)

(b) to dissolve the insoluble silver oxide formed under the reaction conditions

(c) Ag precipitates gluconic acid as its silver salt

(d) \( \text{NH}_3 \) changes the standard reduction potential of \[ [\text{Ag(NH}_3)\text{H}]^+ \]

**PASSAGE II**

Chemical reactions involve interaction of atoms and molecules. A large number of atoms/molecules (approximately \( 6.023 \times 10^{23} \)) are present in a few grams of any chemical compound varying with their atomic/molecular masses. To handle such large numbers conveniently, the mole concept was introduced. This concept has implications in diverse areas such as analytical chemistry, biochemistry, electrochemistry and radiochemistry. The following example illustrates a typical case, involving chemical/electrochemical reaction, which requires a clear understanding of the mole concept.

A 4.0 molar aqueous solution of \( \text{NaCl} \) is prepared and 500 mL of this solution is electrolysed. This leads to the evolution of chlorine gas at one of the electrodes (atomic mass: \( \text{Na} = 23, \text{Hg} = 200; \) 1 Faraday = 96500 coulombs).

4. The total number of moles of chlorine gas evolved is \((2007)\)

(a) 0.5 \hspace{1cm} (b) 1.0

(c) 2.0 \hspace{1cm} (d) 3.0

5. If the cathode is a Hg electrode, the maximum weight (g) of amalgam formed from this solution is \((2007)\)

(a) 200 \hspace{1cm} (b) 225

(c) 400 \hspace{1cm} (d) 446

6. The total charge (coulombs) required for complete electrolysis is \((2007)\)

(a) 24125 \hspace{1cm} (b) 48250

(c) 96500 \hspace{1cm} (d) 193000

**PASSAGE III**

Redox reactions play a pivotal role in chemistry and biology. The values of standard redox potential \( (E^0) \) of two half-cell reactions decide which way the reaction is expected to proceed. A simple example is the Daniel cell in which zinc goes into solution and copper gets deposited. Given below are a set of half-cell reactions (acidic medium) along with their \( E^0 \) (V with respect to normal hydrogen electrode) values. Using this data obtain the correct explanations to questions given.

\[ \text{I}_2 + 2e^- \rightarrow 2\text{I}^- \hspace{1cm} E^0 = 0.54 \]

\[ \text{Cl}_2 + 2e^- \rightarrow 2\text{Cl}^- \hspace{1cm} E^0 = 1.36 \]

\[ \text{Mn}^{2+} + e^- \rightarrow \text{Mn}^{3+} \hspace{1cm} E^0 = 1.50 \]

\[ \text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+} \hspace{1cm} E^0 = 0.77 \]

\[ \text{O}_2 + 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2\text{O} \hspace{1cm} E^0 = 1.23 \]

7. Among the following, identify the correct statement.

(a) \( \text{Cl}^- \) is oxidised by \( \text{O}_2 \) \((2007)\)

(b) \( \text{Fe}^{3+} \) is oxidised by iodine

(c) Iodide ion is oxidised by chlorine

(d) \( \text{Mn}^{2+} \) is oxidised by chlorine

8. While \( \text{Fe}^{3+} \) is stable, \( \text{Mn}^{3+} \) is not stable in acid solution because \((2007)\)

(a) \( \text{O}_2 \) oxidises \( \text{Mn}^{2+} \) to \( \text{Mn}^{3+} \)

(b) \( \text{O}_2 \) oxidises both \( \text{Mn}^{2+} \) to \( \text{Mn}^{3+} \) and \( \text{Fe}^{2+} \) to \( \text{Fe}^{3+} \)

(c) \( \text{Fe}^{3+} \) oxidises \( \text{H}_2\text{O} \) to \( \text{O}_2 \)

(d) \( \text{Mn}^{3+} \) oxidises \( \text{H}_2\text{O} \) to \( \text{O}_2 \)

9. Sodium fusion extract, obtained from aniline, on treatment with iron (II) sulphate and \( \text{H}_2\text{SO}_4 \) in presence of air gives a Prussian blue precipitate. The blue colour is due to the formation of \((2007)\)

(a) \( \text{Fe}_3[\text{Fe(CN)}]_8 \)

(b) \( \text{Fe}_2[\text{Fe(CN)}]_8 \)

(c) \( \text{Fe}[\text{Fe(CN)}]_2 \)

(d) \( \text{Fe}_2[\text{Fe(CN)}]_6 \)

**PASSAGE IV**

The concentration of potassium ions inside a biological cell is atleast twenty times higher than the outside. The resulting potential difference across the cell is important in several processes such as transmission of nerve impulses and maintaining the ion balance. A simple model for such a concentration cell involving a metal M is

\[ \text{M}^+ (\text{aq}; 0.05 \text{molar} \) || M$^+$ (aq; 1 molar) || M(s) \]

For the above electrolytic cell the magnitude of the cell potential \[ |E_{cell}| = 70 \text{ mV} \] \((2010)\)

10. For the above cell

(a) \( E_{cell} < 0; \Delta G > 0 \) \hspace{1cm} (b) \( E_{cell} > 0; \Delta G < 0 \)

(c) \( E_{cell} < 0; \Delta G^o > 0 \) \hspace{1cm} (d) \( E_{cell} > 0; \Delta G^o < 0 \)

11. If the 0.05 molar solution of \( M^+ \) is replaced by a 0.0025 molar \( M^+ \) solution, then the magnitude of the cell potential would be

(a) 35mV \hspace{1cm} (b) 70mV \hspace{1cm} (c) 140mV \hspace{1cm} (d) 700mV
PASSAGE: V

The electrochemical cell shown below is a concentration cell.

\[ \text{M} | \text{M}^{2+} (\text{saturated solution of a sparingly soluble salt, MX}_2) | [\text{M}^{2+}(0.001 \text{ mol dm}^{-3})] | \text{M} \]

The emf of the cell depends on the difference in concentrations of \( \text{M}^{2+} \) ions at the two electrodes. The emf of the cell at 298 K is 0.059 V (2012)

12. The value of \( \Delta G \) (kJ mol\(^{-1}\)) for the given cell is (take 1F = 96500 C mol\(^{-1}\))
   (a) \(-5.7\) (b) 5.7 (c) 11.4 (d) \(-11.4\)

13. The solubility product (\( K_{sp} \), mol\(^3\) dm\(^{-6}\)) of MX\(_2\) at 298 K based on the information available for the given concentration cell is (take \( 2.303 \times R \times 298/|F| = 0.059 \) V)
   (a) \( 1 \times 10^{-15} \) (b) \( 4 \times 10^{-15} \)
   (c) \( 1 \times 10^{-12} \) (d) \( 4 \times 10^{-12} \)

Section-B

**JEE Main / AIEEE**

1. Conductivity (unit Siemen's S) is directly proportional to area of the vessel and the concentration of the solution in it and is inversely proportional to the length of the vessel then the unit of the constant of proportionality is
   (a) Sm\(^{-1}\) (b) Sm\(^2\)mol\(^{-1}\) (2002)
   (c) S\(^{-2}\)m\(^2\)mol\(^{-1}\) (d) S\(^{-1}\)m\(^{-2}\)mol\(^{-2}\).

2. EMF of a cell in terms of reduction potential of its left and right electrodes is
   (a) \( E = E_{\text{left}} - E_{\text{right}} \) (b) \( E = E_{\text{left}} + E_{\text{right}} \) (2002)
   (c) \( E = E_{\text{right}} - E_{\text{left}} \) (d) \( E = -(E_{\text{right}} + E_{\text{left}}) \)

3. What will be the emf for the given cell
   \[ \text{Pt} \mid \text{H}_2(\text{P}_1) \mid \text{H}^+ (\text{aq}) | | \text{H}_2(\text{P}_2) | \text{Pt} \]
   \( \frac{RT}{F} \log_{e} \frac{P_1}{P_2} \) (b) \( \frac{RT}{2F} \log_{e} \frac{P_1}{P_2} \)
   (c) \( \frac{RT}{F} \log_{e} \frac{P_2}{P_1} \) (c) None of these.

4. Which of the following reaction is possible at anode?
   (a) \( 2\text{Cr}^{3+} + 7\text{H}_2\text{O} \rightarrow \text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ \) (2002)
   (b) \( \text{F}_2 \rightarrow 2\text{F}^- \)
   (c) \((1/2)\text{O}_2 + 2\text{H}^+ \rightarrow \text{H}_2\text{O} \)
   (d) None of these.

5. When the sample of copper with zinc impurity is to be purified by electrolysis, the appropriate electrodes are
   \[ \text{Cathode} | \text{Anode} \]
   (a) pure zinc | pure copper (2002)
   (b) impure sample | pure copper
   (c) impure zinc | impure sample
   (d) pure copper | impure sample.

6. Which of the following is a redox reaction?
   (a) \( \text{NaCl} + \text{KNO}_3 \rightarrow \text{NaNO}_3 + \text{KCl} \) (2002)
   (b) \( \text{CaC}_2\text{O}_4 + 2\text{HCl} \rightarrow \text{CaCl}_2 + \text{H}_2\text{C}_2\text{O}_4 \)

7. The molar conductivity of a solution of a weak acid HX (0.01 M) is 10 times smaller than the molar conductivity of a solution of a weak acid HY (0.10 M). If \( \lambda_X^0 \approx \lambda_Y^0 \), the difference in their p\( K_a \) values, p\( K_a \)(HX) – p\( K_a \)(HY), is (consider degree of ionization of both acids to be <1)

8. Standard reduction electrode potentials of three metals A, B & C are respectively +0.5 V, −3.0 V & −1.2 V. The reducing powers of these metals are
   (a) A > B > C (b) C > B > A (2003)
   (c) C > A > B (d) B > C > A

9. When during electrolysis of a solution of AgNO\(_3\) 9650 coulombs of charge pass through the electroplating bath, the mass of silver deposited on the cathode will be
   (a) 10.8 g (b) 21.6 g (2003)
   (c) 108 g (d) 1.08 g

10. For the redox reaction
    \[ \text{Zn(s)} + \text{Cu}^{2+} (0.1\text{M}) \rightarrow \text{Zn}^{2+} (1\text{M}) + \text{Cu(s)} \]
    taking place in a cell, \( E_{\text{cell}}^* \) is 1.10 volt. \( E_{\text{cell}}^* \) for the cell will be \( 2.303 \frac{RT}{F} = 0.591 \)
    (a) 1.80 volt (b) 1.07 volt (2003)
    (c) 0.82 volt (d) 2.14 volt

11. Several blocks of magnesium are fixed at the bottom of a ship to
    (a) make the ship lighter (2003)
    (b) prevent action of water and salt
    (c) prevent puncturing by under-sea rocks
    (d) keep away the sharks
12. In a hydrogen-oxygen fuel cell, combustion of hydrogen occurs to
   (a) produce high purity water
   (b) create potential difference between two electrodes
   (c) generate heat
   (d) remove adsorbed oxygen from electrode surfaces

13. Consider the following E° values:
   \[ E^\circ_{Fe^{3+}/Fe^{2+}} = +0.77\text{V}; \quad E^\circ_{Sn^{2+}/Sn} = -0.14\text{V} \]

   Under standard conditions the potential for the reaction:
   \[ Sn_{(s)} + 2Fe^{3+}_{(aq)} \rightarrow 2Fe^{2+}_{(aq)} + Sn^{2+}_{(aq)} \]
   is
   (a) 0.91 V
   (b) 1.40 V
   (c) 1.68 V
   (d) 0.63 V

14. The standard e.m.f. of a cell involving one electron change
   is found to be 0.591 V at 25°C. The equilibrium constant of
   the reaction is \( K = 96,500 \text{C mol}^{-1} \cdot R = 8.314 \text{JK}^{-1} \text{mol}^{-1} \)
   (a) \( 1.0 \times 10^{10} \)
   (b) \( 1.0 \times 10^{5} \)
   (c) \( 1.0 \times 1 \)
   (d) \( 1.0 \times 30 \)

15. The limiting molar conductivities \( \Lambda^\circ \) for NaCl, KBr and KCl
   are 126, 152 and 150 S cm\(^{-2}\) mol\(^{-1}\) respectively. The \( \Lambda^\circ \) for
   NaBr is
   (a) 278 S cm\(^{-2}\) mol\(^{-1}\)
   (b) 176 S cm\(^{-2}\) mol\(^{-1}\)
   (c) 128 S cm\(^{-2}\) mol\(^{-1}\)
   (d) 302 S cm\(^{-2}\) mol\(^{-1}\)

16. In a cell that utilises the reaction:
   \[ Zn_{(s)} + 2H^+_{(aq)} \rightarrow Zn^{2+}_{(aq)} + H_2_{(g)} \]
   addition of \( H_2SO_4 \) to cathode compartment, will
   (a) increase the E and shift equilibrium to the right
   (b) lower the E and shift equilibrium to the right
   (c) lower the E and shift equilibrium to the left
   (d) increase the E and shift equilibrium to the left

17. The \( E^\circ_{M^{3+}/M^{2+}} \) values for Cr, Mn, Fe and Co are \(-0.41,+1.57,+0.77\) and \(+1.97\) respectively. For which one of these
   metals the change in oxidation state from +2 to +3 is easiest?
   (a) Fe
   (b) Mn
   (c) Cr
   (d) Co

18. For a spontaneous reaction the \( \Delta G \), equilibrium constant
   (K) and \( E^\circ_{\text{cell}} \) will be respectively
   (a) \(-ve, >1, -ve\)
   (b) \(-ve, <1, -ve\)
   (c) \(+ve, >1, -ve\)
   (d) \(+ve, >1, +ve\)

19. The highest electrical conductivity of the following aqueous
   solutions is of
   (a) 0.1 M difluoroacetic acid
   (b) 0.1 M fluoroacetic acid
   (c) 0.1 M chloroacetic acid
   (d) 0.1 M acetic acid

20. Aluminium oxide may be electrolysed at 1000°C to furnish
   aluminium metal (At. Mass = 27 amu; 1 Faraday = 96,500
   Coulombs). The cathode reaction is:
   \( Al^{3+} + 3e^- \rightarrow Al^{0} \)
   To prepare 5.12 kg of aluminium metal by this method we require

21. Calculate \( \Lambda^\circ_{NaOAc} \) using appropriate molar conductances
   of the electrolytes listed above at infinite dilution in \( H_2O \)
   at 25°C
   (a) 217.5
   (b) 390.7
   (c) 552.7
   (d) 517.2

22. Which of the following chemical reactions depict the oxidizing
   behaviour of \( H_2SO_4 \)?
   (a) \( NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl \)
   (b) \( 2PCl_3 + H_2SO_4 \rightarrow 2POCl_3 + 2HCl + SO_2Cl_2 \)
   (c) \( 2HI + H_2SO_4 \rightarrow I_2 + SO_2 + 2H_2O \)
   (d) \( Ca(OH)_2 + H_2SO_4 \rightarrow CaSO_4 + 2H_2O \)

23. The molar conductivities \( \Lambda^\circ_{NaOAc} \) and \( \Lambda^\circ_{HCl} \) at infinite
   dilution in water at 25°C are 91.0 and 426.2 S cm\(^{-2}\)mol\(^{-1}\)
   respectively. To calculate \( \Lambda^\circ_{NaOAc} \), the additional value
   required is
   (a) \( \Lambda^\circ_{NaOH} \)
   (b) \( \Lambda^\circ_{NaCl} \)
   (c) \( \Lambda^\circ_{H_2O} \)
   (d) \( \Lambda^\circ_{KCl} \)

24. Resistance of a conductivity cell filled with a solution of
   an electrolyte of concentration 0.1 M is 100 \Omega. The conductivity
   of this solution is 1.29 S m\(^{-1}\). Resistance of the same cell
   when filled with 0.2 M of the same solution is 520 \Omega. The
   molar conductivity of 0.2 M solution of electrolyte will be
   (a) \( 1.24 \times 10^{-4} \) S m\(^{-2}\) mol\(^{-1}\)
   (b) \( 12.4 \times 10^{-4} \) S m\(^{-2}\) mol\(^{-1}\)
   (c) \( 124 \times 10^{-4} \) S m\(^{-2}\) mol\(^{-1}\)
   (d) \( 1240 \times 10^{-4} \) S m\(^{-2}\) mol\(^{-1}\)

25. The equivalent conductances of two strong electrolytes at
   infinite dilution in \( H_2O \) (where ions move freely through a
   solution) at 25°C are given below:
   \( \Lambda^\circ_{CH_3COO^-} = 91.0 \text{S cm}^2 \text{mol}^{-1} \text{equiv} \)
   \( \Lambda^\circ_{HCl} = 426.2 \text{S cm}^2 \text{mol}^{-1} \text{equiv} \)
   What additional information/quantity one needs to calculate
   \( \Lambda^\circ \) of an aqueous solution of acetic acid?
   (a) \( \Lambda^\circ \) of chloroacetic acid (ClCH_2COOH)
   (b) \( \Lambda^\circ \) of NaCl
   (c) \( \Lambda^\circ \) of CH_3COOK
   (d) the limiting equivalent conductance of \( H^+ (\Lambda^\circ_{H^+}) \).
26. The cell, $Zn | Zn^{2+}(1 M) || Cu^{2+}(1 M) | Cu$ (E°cell = 1.10 V) was allowed to be completely discharged at 298 K. The relative concentration of $Zn^{2+}$ to $Cu^{2+}$ \( \frac{[Zn^{2+}]}{[Cu^{2+}]} \) is [2007]

(a) \(9.65 \times 10^4\)  
(b) antilog(24.08)  
(c) 37.3  
(d) \(10^{37.3}\)

27. Given $E°_{Cr^{3+}/Cr} = -0.72$ V, $E°_{Fe^{2+}/Fe} = -0.42$ V. The potential for the cell 

\[Cr(Cr^{3+}(0.1 M)||Fe^{2+}(0.01 M)|Fe] \] 

is [2008]

(a) 0.26 V  
(b) 0.336 V  
(c) -0.339 V  
(d) 0.26 V

28. In a fuel cell methanol is used as fuel and oxygen gas is used as an oxidizer. The reaction is 

\[CH_3OH(l) + 3/2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)\] 

At 298 K standard Gibb's energies of formation for $CH_3OH(l)$, $H_2O(l)$ and and $CO_2(g)$ are $-166.2 - 237.2$ and $-394.4$ kJ mol$^{-1}$ respectively. If standard enthalpy of combustion of methanol is $-726$ kJ mol$^{-1}$, efficiency of the fuel cell will be:

(a) \(87\%\)  
(b) \(90\%\)  
(c) \(97\%\)  
(d) \(80\%\)

29. Given:

\[E°_{Fe^{3+}/Fe} = -0.036 V, E°_{Fe^{2+}/Fe} = -0.439 V\] 

The value of standard electrode potential for the change, 

\[Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)\] 

will be [2009]

(a) 0.385 V  
(b) 0.770 V  
(c) -0.270 V  
(d) -0.072 V

30. The Gibb's energy for the decomposition of $Al_2O_3$ at 500°C is as follows:

\[\frac{2}{3}Al_2O_3 \rightarrow \frac{4}{3}Al + O_2, \Delta_rG = +966 kJ mol^{-1}\] 

The potential difference needed for electrolytic reduction of $Al_2O_3$ at 500°C is at least [2010]

(a) 4.5 V  
(b) 3.0 V  
(c) 2.5 V  
(d) 5.0 V

31. The correct order of $E°_{M^{2+}/M}$ values with negative sign for the four successive elements Cr, Mn, Fe and Co is [2010]

(a) Mn > Cr > Fe > Co  
(b) Cr < Fe > Mn > Co  
(c) Fe > Mn > Cr > Co  
(d) Cr > Mn > Fe > Co

32. The reduction potential of hydrogen half-cell will be negative if:

(a) \(p(H_2) = 1 \text{ atm and } [H^+] = 2.0 \text{ M}\) [2011]  
(b) \(p(H_2) = 1 \text{ atm and } [H^+] = 1.0 \text{ M}\)  
(c) \(p(H_2) = 2 \text{ atm and } [H^+] = 1.0 \text{ M}\)  
(d) \(p(H_2) = 2 \text{ atm and } [H^+] = 2.0 \text{ M}\)

33. The standard reduction potentials for $Zn^{2+}/Zn$, $Ni^{2+}/Ni$ and $Fe^{2+}/Fe$ are $-0.76, -0.23$ and $-0.44$ V respectively.

The reaction $X + Y^{2+} \rightarrow X^{2+} + Y$ will be spontaneous when:

(a) $X = Ni, Y = Fe$  
(b) $X = Ni, Y = Zn$  
(c) $X = Fe, Y = Zn$  
(d) $X = Zn, Y = Ni$

34. Given: 

\[E°_{Cr^{3+}/Cr} = -0.74 \text{ V}, E°_{MnO_4^−/Mn^{2+}} = 1.51 \text{ V}\] 

\[E°_{CrO_4^{2−}/Cr^{3+}} = 1.33 \text{ V}, E°_{Cl/Cl^−} = 1.36 \text{ V}\] 

Based on the data given above, strongest oxidizing agent will be: [JEE M 2013]

(a) Cl  
(b) Cr$^{3+}$  
(c) Mn$^{2+}$  
(d) MnO$^4_4^−$

35. Resistance of 0.2 M solution of an electrolyte is 50 Ω. The specific conductance of the solution is 1.4 S m$^{-1}$. The resistance of 0.5 M solution of the same electrolyte is 280 Ω. The molar conductivity of 0.5 M solution of the electrolyte in S m$^{-2}$ mol$^{-1}$ is:

(a) \(5 \times 10^{-4}\)  
(b) \(5 \times 10^{-3}\)  
(c) \(5 \times 10^{-2}\)  
(d) \(5 \times 10^{2}\)

36. Given below are the half-cell reactions: [JEE M 2014]

\[Mn^{2+} + 2e^- \rightarrow Mn; E° = -1.18 \text{ V}\] 

\[2(Mn^{3+} + e^- \rightarrow Mn^{2+}); E° = +1.51 \text{ V}\] 

The $E°$ for $3Mn^{2+} \rightarrow Mn + 2Mn^{3+}$ will be:

(a) \(-2.69 \text{ V}\)  
(b) \(-2.69 \text{ V}\)  
(c) \(-0.33 \text{ V}\)  
(d) \(-0.33 \text{ V}\)

37. The equivalent conductance of NaCl at concentration C and at infinite dilution are $\lambda_C$ and $\lambda_{\infty}$, respectively. The correct relationship between $\lambda_C$ and $\lambda_{\infty}$ is given as:

Where the constant B is positive [JEE M 2014]

(a) $\lambda_C = \lambda_{\infty} + (B)C$  
(b) $\lambda_C = \lambda_{\infty} - (B)C$  
(c) $\lambda_C = \lambda_{\infty} - (B)\sqrt{C}$  
(d) $\lambda_C = \lambda_{\infty} + (B)\sqrt{C}$

38. Two Faraday of electricity is passed through a solution of CuSO$_4$. The mass of copper deposited at the cathode is (at. mass of Cu = 63.5 amu)

(a) 2g  
(b) 127g  
(c) 0g  
(d) 63.5g

39. Galvanization is applying a coating of: [JEE M 2016]

(a) Cu  
(b) Zn  
(c) Pb  
(d) Cr
CHAPTER 14

Chemical Kinetics and Nuclear Chemistry

Section-A

A. Fill in the Blanks

1. An element $^A_2M$ undergoes an α-emission followed by two successive β-emissions. The element formed is ............... . (1982 - 1 Mark)

2. The rate of chemical change is directly proportional to ............... . (1985 - 1 Mark)

3. The number of neutrons in the parent nucleus which gives $^{14}_7N$ on beta emission is ............... . (1985 - 1 Mark)

4. The hydrolysis of ethyl acetate in ............... medium is a ............... order reaction. (1986 - 1 Mark)

5. A radioactive nucleus decays emitting one alpha and two beta particles; the daughter nucleus is ............... of the parent. (1989 - 1 Mark)

6. For the reaction $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$, under certain conditions of temperature and partial pressure of the reactants, the rate of formation of $NH_3$ is $0.001 \text{ kg h}^{-1}$. The rate of conversion of $H_2$ under the same condition is...........$\text{kg h}^{-1}$. (1994 - 1 Mark)

7. In the Arrhenius equation, $k = A \exp \left(-E_a/RT\right)$, $A$ may be termed as the rate constant at ............... . (1997 - 1 Mark)

B. True / False

1. For a first order reaction, the rate of the reaction doubles as the concentration of the reactant (s) doubles. (1986 - 1 Mark)

2. Catalyst makes a reaction more exothermic. (1987 - 1 Mark)

3. Catalyst does not affect the energy of activation in a chemical reaction. (1989 - 1 Mark)

4. In β-emission from a nucleus the atomic number of the daughter element decreases by one. (1990 - 1 Mark)

5. The rate of an exothermic reaction increases with increasing temperature. (1990 - 1 Mark)

C. MCQs with One Correct Answer

1. If uranium (mass number 238 and atomic number 92) emits an α-particle, the product has mass no. and atomic no. (1981 - 1 Mark)
   (a) 236 and 92      (b) 234 and 90
   (c) 238 and 90      (d) 236 and 90

2. The rate constant of a reaction depends on (1981 - 1 Mark)
   (a) temperature      (b) initial concentration of the reactants
   (c) time              (d) extent of reaction

3. The specific rate constant of a first order reaction depends on the (1983 - 1 Mark)
   (a) concentration of the reactant (b) concentration of the product
   (c) time (d) temperature

4. A catalyst is a substance which (1983 - 1 Mark)
   (a) increases the equilibrium concentration of the product
   (b) changes the equilibrium constant of the reaction
   (c) shortens the time to reach equilibrium
   (d) supplies energy to the reaction

5. The radiations from a naturally occurring radioactive substance, as seen after deflection by a magnetic field in one direction, are: (1984 - 1 Mark)
   (a) definitely alpha rays (b) definitely beta rays
   (c) both alpha and beta rays (d) either alpha or beta rays

6. The half-life period of a radioactive element is 140 days. After 560 days, one gram of the element will reduced to: (1986 - 1 Mark)
   (a) $\frac{1}{2}$ g      (b) $\frac{1}{4}$ g
   (c) $\frac{1}{8}$ g      (d) $\frac{1}{16}$ g

7. The rate constant, the activation energy and the Arrhenius parameter of a chemical reaction at 25°C are $3.0 \times 10^{-4} \text{s}^{-1}$, $104.4 \text{ kJ mol}^{-1}$ and $6.0 \times 10^{14} \text{s}^{-1}$ respectively. The value of the rate constant as $T \rightarrow \infty$ is, (1996 - 1 Mark)
8. \(^{27}_{13}\text{Al}\) is a stable isotope, \(^{29}_{13}\text{Al}\) is expected to disintegrate by \((1996 - 1\text{ Mark})\)
(a) \(\alpha\)-emission  (b) \(\beta\)-emission  
(c) posion emission  (d) proton emission

9. The number of neutrons accompanying the formation of \(^{\text{139}}_{\text{54}}\text{Xe}\) and \(^{\text{94}}_{\text{38}}\text{Sr}\) from the absorption of a slow neutron by \(^{\text{235}}_{\text{92}}\text{U}\), followed by nuclear fission is, \((1999 - 2\text{ Marks})\)
(a) 0  (b) 2  
(c) 1  (d) 3

10. The rate constant for the reaction, 
\(2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2\), is \(3.0 \times 10^{-5}\text{ sec}^{-1}\). If the rate is \(2.40 \times 10^{-5}\text{ mol litre}^{-1}\text{ sec}^{-1}\), then the concentration of \(\text{N}_2\text{O}_5\) (in mol litre\(^{-1}\)) is \((2000\text{S})\)
(a) 1.4  (b) 1.2  
(c) 0.04  (d) 0.8

11. If ‘I’ is the intensity of absorbed light and ‘C’ is the concentration of \(AB\) for the photochemical process, \(AB + \text{hv} \rightarrow AB^*\), the rate of formation of \(AB^*\) is directly proportional to \((2001\text{S})\)
(a) C  (b) I  
(c) \(\frac{1}{I}\)  (d) CI

12. Consider the chemical reaction, \(\text{N}_2\text{(g)} + 3\text{H}_2\text{(g)} \rightarrow 2\text{NH}_3\text{(g)}\). The rate of this reaction can be expressed in terms of the concentration of \(\text{N}_2\text{(g)}, \text{H}_2\text{(g)}\) or \(\text{NH}_3\text{(g)}\). Identify the correct relationship amongst the rate expressions. \((2002\text{S})\)
(a) Rate = \(-d[\text{N}_2]/dt = -1/3d[\text{H}_2]/dt = 1/2d[\text{NH}_3]/dt\)  
(b) Rate = \(-d[\text{N}_2]/dt = -3d[\text{H}_2]/dt = 2d[\text{NH}_3]/dt\)
(c) Rate = \(-d[\text{N}_2]/dt = 1/3d[\text{H}_2]/dt = 1/2d[\text{NH}_3]/dt\)
(d) Rate = \(-d[\text{N}_2]/dt = -d[\text{H}_2]/dt = d[\text{NH}_3]/dt\)

13. In a first order reaction the concentration of reactant decreases from 800 mol dm\(^{-3}\) to 50 mol dm\(^{-3}\) in 2 \times 10\(^4\) sec. The rate constant of reaction in sec\(^{-1}\) is \((2003\text{S})\)
(a) \(2 \times 10^4\)  (b) \(3.45 \times 10^5\)  
(c) \(1.386 \times 10^{-4}\)  (d) \(2 \times 10^{-4}\)

14. \(^{22}\text{Na}\) is the more stable isotope of Na. Find out the process by which \(^{24}\text{Na}\) can undergo radioactive decay \((2003\text{S})\)
(a) \(\beta^-\) emission  (b) \(\alpha\) emission  
(c) \(\beta^+\) emission  (d) K electron capture

15. The reaction, \(A \rightarrow \text{Product}\), follows first order kinetics. In 40 minutes the concentration of A changes from 0.1 to 0.025 M. The rate of reaction, when concentration of A is 0.01 M is \((2004\text{S})\)
(a) \(1.73 \times 10^{-4}\text{ M min}^{-1}\)  (b) \(3.47 \times 10^{-5}\text{ M min}^{-1}\)  
(c) \(3.47 \times 10^{-4}\text{ M min}^{-1}\)  (d) \(1.73 \times 10^{-5}\text{ M min}^{-1}\)

16. Which one of the following statement for order of reaction is not correct? \((2005\text{S})\)
(a) Order can be determined experimentally  
(b) Order of reaction is equal to sum of the powers of concentration terms in differential rate law.  
(c) It is not affected with the stoichiometric coefficient of the reactants  
(d) Order cannot be fractional.

17. \(\text{Ag}^+ + \text{NH}_3 \rightleftharpoons [\text{Ag(NH}_3]^+\); \(k_1 = 6.8 \times 10^{-3}\) \([\text{Ag(NH}_3]^+ + \text{NH}_3 \rightleftharpoons [\text{Ag(NH}_3]_2]^+\); \(k_2 = 1.6 \times 10^{-3}\) then the formation constant of \([\text{Ag(NH}_3]_2]^+\) is \((2006 - 3\text{M}, -1)\)
(a) \(6.8 \times 10^{-6}\)  (b) \(1.08 \times 10^{-5}\)  
(c) \(1.08 \times 10^{-6}\)  (d) \(6.8 \times 10^{-5}\)

18. Consider a reaction \(aG + bH \rightarrow \text{Products}\). When the concentration of both the reactants \(G\) and \(H\) is doubled, the rate increases by eight times. However, when concentration of \(G\) is doubled keeping the concentration of \(H\) fixed, the rate is doubled. The overall order of the reaction is \((2007)\)
(a) 0  (b) 1  
(c) 2  (d) 3

19. A positron is emitted from \(^{23}_{11}\text{Na}\). The ratio of the atomic mass and atomic number of the resulting nuclide is \((2007)\)
(a) 22/10  (b) 22/11  
(c) 23/10  (d) 23/12

20. Under the same reaction conditions, initial concentration of 1.386 mol dm\(^{-3}\) of a substance becomes half in 40 seconds and 20 seconds through first order and zero order kinetics, respectively. Ratio \((k_1/k_0)\) of the rate constant for first order \((k_1)\) and zero order \((k_0)\) of the reaction is \((2008)\)
(a) \(0.5 \text{ mol dm}^{-3}\)  (b) \(1.0 \text{ mol dm}^{-3}\)  
(c) \(1.5 \text{ mol dm}^{-3}\)  (d) \(2.0 \text{ mol dm}^{-3}\)

21. For a first order reaction \(A \rightarrow P\), the temperature \((T)\) dependent rate constant \((k)\) was found to follow the equation \(\log k = -\frac{1}{T} + 6.0\). The pre-exponential factor \(A\) and the activation energy \(E_a\), respectively, are \((2009)\)
(a) \(1.0 \times 10^6 \text{ s}^{-1}\) and \(9.2 \text{ kJ mol}^{-1}\)  
(b) \(6.0 \text{ s}^{-1}\) and \(16.6 \text{ kJ mol}^{-1}\)  
(c) \(1.0 \times 10^6 \text{ s}^{-1}\) and \(16.6 \text{ kJ mol}^{-1}\)  
(d) \(1.0 \times 10^6 \text{ s}^{-1}\) and \(38.3 \text{ kJ mol}^{-1}\)

22. Plots showing the variation of the rate constant \((k)\) with temperature \((T)\) are given below. The plot that follows Arrhenius equation is \((2010)\)
23. Bombardment of aluminium by α-particle leads to its artificial disintegration in two ways, (i) and (ii) as shown. Products X, Y and Z respectively are,

\[
\begin{align*}
\text{(i)} & \quad 27_{13} \text{Al} \rightarrow 30_{15} \text{P} + Y \\
\text{(ii)} & \quad 30_{15} \text{P} + X \rightarrow 30_{14} \text{Si} + Z
\end{align*}
\]

(a) proton, neutron, positron
(b) neutron, positron, proton
(c) proton, positron, neutron
(d) positron, proton, neutron

24. In the reaction,

\[
P + Q \rightarrow R + S
\]

The time taken for 75% reaction of P is twice the time taken for 50% reaction of P. The concentration of Q varies with reaction time as shown in the figure. The overall order of the reaction is

\[
\frac{[Q]}{[Q_0]} = k_1 t
\]

(a) 2 \hspace{1cm} (b) 3
(c) 0 \hspace{1cm} (d) 1

25. For the elementary reaction \( M \rightarrow N \), the rate of disappearance of \( M \) increases by a factor of 8 upon doubling the concentration of \( M \). The order of the reaction with respect to \( M \) is

\[
JEE \text{ Adv. 2014}
\]

(a) 4 \hspace{1cm} (b) 3
(c) 2 \hspace{1cm} (d) 1

D \hspace{1cm} \text{MCQs with One or More Than One Correct}

1. A catalyst:

\[
\text{(JEE Adv. 1984 - 1 Mark)}
\]

(a) increases the average kinetic energy of reacting molecules
(b) decreases the activation energy
(c) alters the reaction mechanism
(d) increases the frequency of collisions of reacting species

2. The rate law for the reaction:

\[
\text{RCl} + \text{NaOH(aq)} \rightarrow \text{ROH} + \text{NaCl}
\]

is given by, \( \text{Rate} = k_1 [\text{RCl}] \). The rate of the reaction will be

\( \text{(a) doubled on doubling the concentration of sodium hydroxide.} \)

(b) halved on reducing the concentration of alkyl halide to one half.

(c) increased on increasing the temperature of the reaction.

(d) unaffected by increasing the temperature of the reaction.

3. Nuclear reactions accompanied with emission of neutron(s) are:

\[
\text{(JEE Adv. 1988 - 1 Mark)}
\]

(a) \( ^{17}_{13} \text{Al} + ^2_1 \text{H} \rightarrow ^{30}_{15} \text{P} \)

(b) \( ^{12}_6 \text{C} + ^1_1 \text{H} \rightarrow ^{13}_7 \text{N} \)

(c) \( ^{30}_{15} \text{P} \rightarrow ^{30}_{14} \text{Si} + ^0_1 \text{e} \)

(d) \( ^{241}_{96} \text{Am} + ^4_2 \text{He} \rightarrow ^{244}_{97} \text{Bk} + ^0_1 \text{e} \)

4. For a first order reaction,

\[
\text{(JEE Adv. 1998 - 2 Marks)}
\]

(a) the degree of dissociation is equal to \( (1-e^{-kt}) \)

(b) a plot of reciprocal concentration of the reactant vs time gives a straight line.

(c) the time taken for the completion of 75% reaction is thrice the \( t_{1/2} \) of the reaction

(d) the pre-exponential factor in the Arrhenius equation has the dimension of time, \( T^{-1} \).

5. The following statement(s) is (are) correct:

\[
\text{(JEE Adv. 1999 - 3 Marks)}
\]

(a) A plot of \( \log K \) versus \( 1/T \) is linear

(b) A plot of \( \log [X] \) versus time is linear for a first order reaction, \( X \rightarrow P \)

(c) A plot of \( P \) versus \( 1/T \) is linear at constant volume

(d) A plot of \( P \) versus \( 1/T \) is linear at constant

6. For the first order reaction

\[
2\text{N}_2\text{O}_3(g) \rightarrow 4\text{NO}_2(g) + \text{O}_2(g)
\]

(a) the concentration of the reactant decreases exponentially with time

(b) the half-life of the reaction decreases with increasing temperature

(c) the half-life of the reaction depends on the initial concentration of the reactant

(d) the reaction proceeds to 99.6% completion in eight half-life duration

7. In the nuclear transmutation

\[
\text{(JEE Adv. 2013)}
\]

\[^9_4 \text{Be} + X \rightarrow ^8_4 \text{Be} + ^1_0 \text{Y} \] (X, Y) is(are)

(a) (γ, n) \hspace{1cm} (b) (p, D)
(c) (n, D) \hspace{1cm} (d) (γ, p)

8. According to the Arrhenius equation,

\[
\text{(JEE Adv. 2016)}
\]

(a) a high activation energy usually implies a fast reaction.

(b) rate constant increases with increase in temperature. This is due to a greater number of collisions whose energy exceeds the activation energy.

(c) higher the magnitude of activation energy, stronger is the temperature dependence of the rate constant.

(d) the pre-exponential factor is a measure of the rate at which collisions occur, irrespective of their energy.

9. A plot of the number of neutrons (N) against the number of protons (P) of stable nuclei exhibits upward deviation from linearity for atomic number, \( Z > 20 \). For an unstable nucleus having N/P ratio less than 1, the possible mode(s) of decay is(are)

\[
\text{(JEE Adv. 2016)}
\]

(a) \( \beta^- \)-decay (β emission)

(b) orbital or K-electron capture

(c) neutron emission

(d) \( \beta^- \)-decay (positron emission)
Subjective Problems

1. Rate of a reaction \( A + B \rightarrow \) products, is given below as a function of different initial concentrations of \( A \) and \( B \):

\[
\begin{array}{cccc}
[A] (\text{mol/l}) & [B] (\text{mol/l}) & \text{Initial rate (mol/l/min)} \\
0.01 & 0.01 & 0.005 \\
0.02 & 0.01 & 0.010 \\
0.01 & 0.02 & 0.005 \\
\end{array}
\]

Determine the order of the reaction with respect to \( A \) and with respect to \( B \). What is the half-life of \( A \) in the reaction?

(1982 - 4 Marks)

2. Radioactive decay is a first order process. Radioactive carbon in wood sample decays with a half life of 5770 years. What is the rate constant (in years\(^{-1}\)) for the decay? What fraction would remain after 11540 years? (1984 - 3 Marks)

3. While studying the decomposition of gaseous \( N_2O_5 \) it is observed that a plot of log of partial pressure versus time is linear. What kinetic parameters can be obtained from this observation? (1985 - 2 Marks)

4. \(^{234}\text{Th}\) disintegrates to give \(^{206}\text{Pb}\) as the final product. How many alpha and beta particles are emitted during this process? (1986 - 2 Marks)

5. A first order reaction has \( K = 1.5 \times 10^{-4} \) per second at 200°C. If the reaction is allowed to run for 10 hours, what percentage of the initial concentration would have changed in the product? What is the half life of this reaction? (1987 - 5 Marks)

6. A first order reaction is 50% complete in 30 minutes at 27°C and in 10 minutes at 47°C. Calculate the rate constant at 27°C and the energy of activation of the reaction in kJ/mole. (1988 - 3 Marks)

7. An experiment requires minimum beta activity product at the rate of 346 beta particles per minute. The half life period of \(^{99}\text{Mo}\), which is a beta emitter is 66.6 hours. Find the minimum amount of \(^{99}\text{Mo}\) required to carry out the experiment in 6.909 hours. (1989 - 5 Marks)

8. In the Arrhenius equation for a certain reaction, the value of \( A \) and \( E_a \) (activation energy) are \( 4 \times 10^{13} \) sec\(^{-1}\) and 98.6 kJ mol\(^{-1}\) respectively. If the reaction is of first order, at what temperature will its half-life period be ten minutes? (1990 - 3 Marks)

9. The decomposition of \( N_2O_5 \) according to the equation:

\[
2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)
\]

is a first order reaction. After 30 min. from the start of the decomposition in a closed vessel, the total pressure developed is found to be 284.5 mm of Hg and on complete decomposition, the total pressure is 584.5 mm of Hg. Calculate the rate constant of the reaction. (1991 - 6 Marks)

10. Two reactions \( A \rightarrow \) products, \( B \rightarrow \) products, follows first order kinetics. The rate of the reaction : \( (i) \) is doubled when the temperature is raised from 300K to 310K. The half life for this reaction at 310K is 30 minutes. At the same temperature \( B \) decomposes twice as fast as \( A \). If the energy of activation for the reaction, \( (ii) \) is half that of reaction \( (i) \), calculate the rate constant of the reaction \( (ii) \) at 300K. (1992 - 3 Marks)

11. The nucleic ratio, \( ^{3}\text{H} \) to \( ^{1}\text{H} \) in a sample of water is \( 8.0 \times 10^{-18} \). 1. Tritium undergoes decay with a half life period of 12.3 years. How many tritium atoms would 10.0 g of such a sample contain 40 years after the original sample is collected? (1992 - 4 Marks)

12. A first order reaction \( A \rightarrow B \), requires activation energy of 70kJ mol\(^{-1}\). When a 20% solution of \( A \) was kept at 25°C for 20 minutes, 25% decomposition took place. What will be the percent decomposition in the same time in a 30% solution maintained at 40°C? Assume that activation energy remains constant in this range of temperature. (1993 - 4 Marks)

13. The gas phase decomposition of dimethyl ether follows first order kinetics.

\[
\text{CH}_3-\text{O-CH}_3(g) \rightarrow \text{CH}_4(g) + \text{H}_2(g) + \text{CO}_2(g)
\]

The reaction is carried out in a constant volume container at 500°C and has a half life of 14.5 minutes. Initially, only dimethyl ether is present at a pressure of 0.40 atmosphere. What is the total pressure of the system after 12 minutes? Assume ideal gas behaviour. (1993 - 4 Marks)

14. The progress of the reaction, \( A \rightleftharpoons nB \), with time, is presented in figure given below. Determine

(i) the value of \( n \)
(ii) the equilibrium constant, \( K \) and
(iii) the initial rate of conversion of \( A \). (1994 - 3 Marks)

15. From the following data for the reaction between \( A \) and \( B \). (1994 - 5 Marks)

<table>
<thead>
<tr>
<th>( [A] \text{ mol litre}^{-1} )</th>
<th>( [B] \text{ mol litre}^{-1} )</th>
<th>Initial rate ( \text{mole litre}^{-1} \text{s}^{-1} ) at</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 1 )</td>
<td>( 2.5 \times 10^{-3} )</td>
<td>( 3.0 \times 10^{-3} )</td>
</tr>
<tr>
<td>( II )</td>
<td>( 5.0 \times 10^{-4} )</td>
<td>( 6.0 \times 10^{-3} )</td>
</tr>
<tr>
<td>( III )</td>
<td>( 1.0 \times 10^{-3} )</td>
<td>( 6.0 \times 10^{-3} )</td>
</tr>
</tbody>
</table>

Calculate
(i) the order of the reaction with respect to \( A \) and with respect to \( B \),
(ii) the rate constant at 300K,
(iii) the energy of activation, and
(iv) the pre-exponential factor.

16. One of the hazards of nuclear explosion is the generation of \( ^{90}\text{Sr} \) and its subsequent incorporation in bones. This
nuclide has a half-life of 28.1 years. Suppose one microgram was absorbed by a newborn child, how much $^{90}$Sr will remain in his bones after 20 years? (1995 - 2 Marks)

17. At 380°C, the half-life period for the first-order decomposition of $\text{H}_2\text{O}_2$ is 360 min. The energy of activation of the reaction is 200 kJ mol$^{-1}$. Calculate the time required for 75% decomposition at 450°C. (1995 - 4 Marks)

18. $^{227}$Ac has a half-life of 21.8 years with respect to radioactive decay. The decay follows two parallel paths. One leading to $^{227}$Th and the other to $^{223}$Fr. The percentage yields of these two daughter nuclides are 1.2 and 98.8 respectively. What are the decay constants ($\lambda$) for each of the separate paths? (1996 - 2 Marks)

19. The ionisation constant of $\text{NH}_4^+$ in water is $5.6 \times 10^{-10}$ at 25°C. The rate constant for the reaction of $\text{NH}_4^+$ and $\text{OH}^-$ to form $\text{NH}_3$ and $\text{H}_2\text{O}$ at 25°C is $3.4 \times 10^{10}$ L mol$^{-1}$s$^{-1}$. Calculate the rate constant for proton transfer from water to $\text{NH}_3$. (1996 - 3 Marks)

20. The rate constant for the first order decomposition of a certain reaction is described by the equation

$$\log (K) = 14.34 - \frac{1.25 \times 10^4 K}{T}$$

(1997 - 5 Marks)

(i) What is the energy of activation for this reaction?
(ii) At what temperature will its half-life period be 256 minutes?

21. Write a balanced equation for the reaction of $^{14}$N with $\alpha$-particle. (1997 - 1 Mark)

22. The rate constant of a reaction is $1.5 \times 10^7$ s$^{-1}$ at 50°C and $4.5 \times 10^5$ s$^{-1}$ at 100°C. Evaluate the Arrhenius parameters $A$ and $E_a$. (1998 - 5 Marks)

23. The rate constant for an isomerisation reaction, $A \rightarrow B$ is $4.5 \times 10^{-3}$ min$^{-1}$. If the initial concentration of $A$ is 1 M, calculate the rate of the reaction after 1 h. (1999 - 4 Marks)

24. $^{238}_{92}$U is radioactive and it emits $\alpha$ and $\beta$ particles to form $^{206}_{82}$Pb. Calculate the number of $\alpha$ and $\beta$ particles emitted in this conversion. An ore of $^{238}_{92}$U is found to contain $^{238}_{92}$U and $^{206}_{82}$Pb in the weight ratio of 1:0.1. The half-life period of $^{238}_{92}$U is $4.5 \times 10^9$ years. Calculate the age of the ore. (2000 - 5 Marks)

25. A hydrogenation reaction is carried out at 500 K. If the same reaction is carried out at a temperature 50°C higher at the same rate, the temperature required is 400 K. Calculate the activation energy of the reaction if the catalyst lowers the activation barrier by 20 kJ mol$^{-1}$. (2000 - 3 Marks)

26. The rate of a first-order reaction is 0.04 mol litre$^{-1}$ s$^{-1}$ at 10 minutes and 0.03 mol litre$^{-1}$ s$^{-1}$ at 20 minutes after initiation. Find the half-life of the reaction. (2001 - 5 Marks)

27. The vapour pressure of the two miscible liquids (A) and (B) are 300 and 500 mm of Hg respectively. In a flask 10 moles of (A) is mixed with 12 moles of (B). However, as soon as (B) is added, (A) starts polymerizing into a completely insoluble solid. The polymerization follows first-order kinetics. After 100 minutes, 0.525 mole of a solution is dissolved which arrested the polymerization completely. The final vapour pressure of the solution is 400 mm of Hg. Estimate the rate of constant of the polymerization reaction. Assume negligible volume change on mixing and polymerization and ideal behaviour for the final solution. (2001 - 10 Marks)

28. $^{64}$Cu (half-life = 12.8 h) decays by $\beta^-$ emission (38%), $\beta^+$ emission (19%) and electron capture (43%). Write the decay products and calculate partial half-lives for each of the decay processes. (2002 - 5 Marks)

29. For the given reactions, $A + B \rightarrow \text{Products}$, following data were obtained.

<table>
<thead>
<tr>
<th>$[A]_0$</th>
<th>$[B]_0$</th>
<th>$R_0$ (mol L$^{-1}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>0.2</td>
<td>0.05</td>
</tr>
<tr>
<td>2.0</td>
<td>0.2</td>
<td>0.10</td>
</tr>
<tr>
<td>3.0</td>
<td>0.1</td>
<td>0.05</td>
</tr>
</tbody>
</table>

(a) Write the rate law expression
(b) Find the rate constant

30. Complete and balance the following reactions.

(i) $^{\gamma}^{92}$Th$^{234}$ $\rightarrow$ .......... $+^{7}2\text{He}^{4} + 6\beta^{0}$ (2004 - 1 Mark)

(ii) $^{92}$U$^{235} + \gamma n^{1} \rightarrow$ .......... $+^{52}\text{Te}^{137} + ^{40}\text{Zn}^{92}$ (2005 - 1 Mark)

(iii) $^{34}$Se$^{86} \rightarrow 2^{+1}\text{e}^{0} +$ ............... (2005 - 1 Mark)

31. At constant temperature and volume, $X$ decomposes as $2X(g) \rightarrow 3Y(g) + 2Z(g)$; $P_x$ is the partial pressure of $X$.

<table>
<thead>
<tr>
<th>Observation No.</th>
<th>Time (in minute)</th>
<th>$P_x$ (in mm of Hg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>800</td>
</tr>
<tr>
<td>2</td>
<td>100</td>
<td>400</td>
</tr>
<tr>
<td>3</td>
<td>200</td>
<td>200</td>
</tr>
</tbody>
</table>

(i) What is the order of reaction with respect to $X$?
(ii) Find the rate constant.
(iii) Find the time for 75% completion of the reaction.
(iv) Find the total pressure when pressure of $X$ is 700 mm of Hg.

G Comprehension Based Questions

Several short-lived radioactive species have been used to determine the age of wood or animal fossils. One of the most interesting substances is $^{14}$C (half-life 5760 years) which is used in determining the age of carbon-bearing materials (e.g. wood, animal fossils, etc.). Carbon-14 is produced by the bombardment of nitrogen atoms present in the upper atmosphere with neutrons (from cosmic rays).

$^{\gamma}^{14}N + n^{1} \rightarrow ^{6}C^{14} + ^{1}H^{1}$
Thus carbon-14 is oxidised to CO₂ and eventually ingested by plants and animals. The death of plants or animals put an end to the intake of C^{14} from the atmosphere. After this the amount of C^{14} in the dead tissues starts decreasing due to its disintegration as per the following reaction:

$$^{6}C^{14} \rightarrow ^{7}N^{14} + ^{0}\beta^{0}$$

The C^{14} isotope enters the biosphere when carbon dioxide is taken up in plant photosynthesis. Plants are eaten by animals, which exhale C^{14} as CO₂. Eventually, C^{14} participates in many aspects of the carbon cycle. The C^{14} lost by radioactive decay is constantly replenished by the production of new isotopes in the atmosphere. In this decay-replenishment process, a dynamic equilibrium is established whereby the ratio of C^{14} to C^{12} remains constant in living matter. But when an individual plant or an animal dies, the C^{14} isotope in it is no longer replenished, so the ratio decreases as C^{14} decays. So, the number of C^{14} nuclei after time t (after the death of living matter) would be less than in a living matter. The decay constant can be calculated using the following formula,

$$t_{1/2} = \frac{0.693}{\lambda}$$

The intensity of the cosmic rays have remain the same for 30,000 years. But since some years the changes in this are observed due to excessive burning of fossil fuel and nuclear tests.

1. Why do we use the carbon dating to calculate the age of the fossil? (2006 - 5 M, -2)
   (a) Rate of exchange of carbon between atmosphere and living is slower than decay of C^{14}
   (b) It is not appropriate to use C^{14} dating to determine age
   (c) Rate of exchange of C^{14} between atmosphere and living organism is so fast that an equilibrium is set up between the intake of C^{14} by organism and its exponential decay
   (d) none of the above

2. What should be the age of the fossil for meaningful determination of its age? (2006 - 5 M, -2)
   (a) 6 years
   (b) 6000 years
   (c) 60,000 years
   (d) can be used to calculate any age

3. A nuclear explosion has taken place leading to increase in concentration of C^{14} in nearby areas. C^{14} concentration is C₁ in nearby areas and C₂ in areas far away. If the age of the fossil is determined to be T₁ and T₂ at the respective places then (2006 - 5 M, -2)
   (a) The age of the fossil will increase at the place where explosion has taken place and T₁ - T₂ = \frac{\ln C₁}{\ln C₂}
   (b) The age of the fossil will decrease at the place where explosion has taken place and T₁ - T₂ = \frac{\ln C₁}{\ln C₂}
   (c) The age of fossil will be determined to be same
   (d) \frac{T₁}{T₂} = \frac{C₁}{C₂}

### Assertion & Reason Type Questions

1. Read the following assertion and statement and answer as per the options given below:
   **Assertion**: For each ten degree rise of temperature the specific rate constant is nearly doubled.
   **Statement**: Energy-wise distribution of molecules in a gas is an experimental function of temperature.

   (1989 - 2 Marks)
   (a) If both assertion and statement are correct and statement is an explanation of assertion.
   (b) If assertion is correct and statement is wrong, statement is not an explanation of assertion.
   (c) If assertion is wrong and statement is correct, statement is not an explanation of assertion.
   (d) If both assertion and statement are wrong and statement is not explanation of assertion.

### Integer Value Correct Type

1. The total number of α and β particles emitted in the nuclear reaction \( ^{238}_{92}U \rightarrow ^{214}_{82}Pb \) is (2009)

2. The concentration of R in the reaction R → P was measured as a function of time and the following data is obtained:

<table>
<thead>
<tr>
<th>[R] (molar)</th>
<th>1.0</th>
<th>0.75</th>
<th>0.40</th>
<th>0.10</th>
</tr>
</thead>
<tbody>
<tr>
<td>t (min)</td>
<td>0.00</td>
<td>0.05</td>
<td>0.12</td>
<td>0.18</td>
</tr>
</tbody>
</table>

   The order of reaction is (2010)

3. The number of neutrons emitted when \( ^{235}_{92}U \) undergoes controlled nuclear fission to \( ^{142}_{54}Xe \) and \( ^{90}_{38}Sr \) is (2010)

4. An organic compound undergoes first-order decomposition. The time taken for its decomposition to 1/8 and 1/10 of its initial concentration are \( t_{1/8} \) and \( t_{1/10} \) respectively. What is the value of \( \frac{t_{1/8}}{t_{1/10}} \times 10 \) ? (\log_{10} 8 = 0.3) (2012)

5. The periodic table consists of 18 groups. An isotope of copper, on bombardment with protons, undergoes a nuclear reaction yielding element X as shown below. To which group, element X belongs in the periodic table? (2012)

   \( ^{63}_{29}Cu + ^{1}_{1}H \rightarrow ^{60}_{29}Cu + ^{2}_{2}H_{2} + ^{4}_{1}He + ^{1}_{1}H + X \)

6. A closed vessel with rigid walls contains 1 mol of \( ^{238}_{92}U \) and 1 mol of air at 298 K. Considering complete decay of \( ^{238}_{92}U \) to \( ^{206}_{82}Pb \), the ratio of the final pressure to the initial pressure of the system at 298 K is (JEE Adv. 2015)

7. In dilute aqueous H₂SO₄, the complex diaquodioxalatoferrate(II) is oxidized by MnO₄⁻. For this reaction, the ratio of the rate of change of [H⁺] to the rate of change of
1. Units of rate constant of first and zero order reactions in terms of molarity M unit are respectively [2002]
   (a) sec⁻¹, M sec⁻¹  (b) sec⁻¹, M
   (c) M sec⁻¹, sec⁻¹  (d) M, sec⁻¹.

2. For the reaction \( A + 2B \rightarrow C \), rate is given by \( R = [A][B]^2 \)
   then the order of the reaction is [2002]
   (a) 3  (b) 6
   (c) 5  (d) 7.

3. The differential rate law for the reaction
   \[ \text{H}_2 + \text{I}_2 \rightarrow 2\text{HI} \]
   is [2002]
   (a) \( -\frac{d[\text{H}_2]}{dt} = -\frac{d[\text{I}_2]}{dt} = -\frac{d[\text{HI}]}{dt} \)
   (b) \( \frac{d[\text{H}_2]}{dt} = \frac{d[\text{I}_2]}{2 dt} = \frac{d[\text{HI}]}{2 dt} \)
   (c) \( \frac{1}{2} \frac{d[\text{H}_2]}{dt} = \frac{1}{2} \frac{d[\text{I}_2]}{dt} = -\frac{d[\text{HI}]}{dt} \)
   (d) \( -\frac{2}{2} \frac{d[\text{H}_2]}{dt} = -\frac{2}{2} \frac{d[\text{I}_2]}{dt} = \frac{d[\text{HI}]}{dt} \)

4. If half-life of a substance is 5 yrs, then the total amount of substance left after 15 years, when initial amount is 64 grams is [2002]
   (a) 16 grams  (b) 2 grams
   (c) 32 grams  (d) 8 grams.

5. The integrated rate equation is [2002]
   \( Rt = \log C_0 - \log C_f \)
   The straight line graph is obtained by plotting
   (a) time vs \( \log C_f \)  (b) \( \frac{1}{\text{time}} \) vs \( C_f \)
   (c) time vs \( C_f \)  (d) \( \frac{1}{\text{time}} \) vs \( \frac{1}{C_f} \)

6. \( \beta \)-particle is emitted in radioactivity by [2002]
   (a) conversion of proton to neutron
   (b) from outermost orbit
   (c) conversion of neutron to proton
   (d) \( \beta \)-particle is not emitted.

7. The radionuclide \( ^{234}_{90}\text{Th} \) undergoes two successive \( \beta \)-decays followed by one \( \alpha \)-decay. The atomic number and the mass number respectively of the resulting radionuclide are [2003]
   (a) 94 and 230  (b) 90 and 230
   (c) 92 and 230  (d) 92 and 234

8. The half-life of a radioactive isotope is three hours. If the initial mass of the isotope were 256 g, the mass of it remaining undecayed after 18 hours would be [2003]
   (a) 8.0 g  (b) 12.0 g
   (c) 16.0 g  (d) 4.0 g

9. In respect of the equation \( k = A e^{-E_a/RT} \) in chemical kinetics, which one of the following statements is correct? [2003]
   (a) \( A \) is adsorption factor
   (b) \( E_a \) is energy of activation
   (c) \( R \) is Rydberg's constant
   (d) \( k \) is equilibrium constant

10. The rate law for a reaction between the substances A and B is given by
    \[ \text{Rate} = k [A]^m [B]^n \]
    On doubling the concentration of A and halving the concentration of B, the ratio of the new rate to the earlier rate of the reaction will be as [2003]
    (a) \( (m+n) \)  (b) \( (n-m) \)
    (c) \( 2^{(n-m)} \)  (d) \( \frac{1}{2^{(m+n)}} \)

11. For the reaction system:
    \[ 2\text{NO}(g) + \text{O}_2(g) \rightarrow 2 \text{NO}_2(g) \]
    volume is suddenly reduced to half its value by increasing the pressure on it. If the reaction is of first order with respect to \( \text{O}_2 \) and second order with respect to \( \text{NO} \), the rate of reaction will [2003]
    (a) diminish to one-eighth of its initial value
    (b) increase to eight times of its initial value
    (c) increase to four times of its initial value
    (d) diminish to one-fourth of its initial value

12. In a first order reaction, the concentration of the reactant, decreases from 0.8 M to 0.4 M is 15 minutes. The time taken for the concentration to change from 0.1 M to 0.025 M is [2004]
    (a) 7.5 minutes  (b) 15 minutes
    (c) 30 minutes  (d) 60 minutes

13. The rate equation for the reaction \( 2\text{A} + \text{B} \rightarrow \text{C} \) is found to be: \( \text{rate} = k[A][B] \). The correct statement in relation to this reaction is that the [2004]
    (a) rate of formation of \( \text{C} \) is twice the rate of disappearance of \( \text{A} \)
    (b) \( t_{1/2} \) is a constant
    (c) unit of \( k \) must be s⁻¹
    (d) value of \( k \) is independent of the initial concentrations of \( \text{A} \) and \( \text{B} \)
14. Consider the following nuclear reactions:

\[ ^{238}_{92} M \rightarrow ^{\chi}_{\chi} N + 2^{4}_{2} He \; ; \; ^{\chi}_{\chi} N \rightarrow ^{16}_{8} L + 2^{\beta+} \]

The number of neutrons in the element L is

(a) 140  (b) 144  (c) 142  (d) 146

15. The half-life of a radioisotope is four hours. If the initial mass of the isotope was 200 g, the mass remaining after 24 hours undecayed is

(a) 3.125 g  (b) 2.084 g  (c) 1.042 g  (d) 4.167 g

16. Hydrogen bomb is based on the principle of

(a) artificial radioactivity  (b) nuclear fusion  (c) natural radioactivity  (d) nuclear fission

17. A reaction involving two different reactants can never be

(a) bimolecular reaction  (b) second order reaction  (c) first order reaction  (d) unimolecular reaction

18. A schematic plot of \( \ln K_{eq} \) versus inverse of temperature for a reaction is shown below

\[
\begin{array}{c}
\text{ln} \; K_{eq} \\
2.0 \times 10^{-3} \; \frac{1}{T} (K^{-1}) \; 2.0 \times 10^{-3}
\end{array}
\]

The reaction must be

(a) highly spontaneous at ordinary temperature  (b) one with negligible enthalpy change  (c) endothermic  (d) exothermic

19. A photon of hard gamma radiation knocks a proton out of

\[ ^{24}_{12} Mg \] nucleus to form

(a) the isobar of \( ^{23}_{11} Na \)  (b) the nuclide \( ^{23}_{11} Na \)  (c) the isobar of parent nucleus  (d) the isotope of parent nucleus

20. \( t_{1/4} \) can be taken as the time taken for the concentration of a reactant to drop to \( \frac{3}{4} \) of its initial value. If the rate constant for a first order reaction is \( K \), the \( t_{1/4} \) can be written as

(a) 0.75/K  (b) 0.69/K  (c) 0.29/K  (d) 0.10/K

21. A reaction was found to be second order with respect to the concentration of carbon monoxide. If the concentration of carbon monoxide is doubled, with everything else kept the same, the rate of reaction will

(a) increase by a factor of 4  (b) double  (c) remain unchanged  (d) triple

22. Rate of a reaction can be expressed by Arrhenius equation as:

\[ k = A e^{-E/RT} \]

In this equation, \( E \) represents

(a) the total energy of the reacting molecules at a temperature, \( T \)  (b) the fraction of molecules with energy greater than the activation energy of the reaction  (c) the energy above which all the colliding molecules will react  (d) the energy below which all the colliding molecules will react

23. In the transformation of \( ^{238}_{92} \text{U} \) to \( ^{234}_{92} \text{U} \), if one emission is an \( \alpha \)-particle, what should be the other emission(s)?

(a) one \( \beta^- \) and one \( \gamma \)  (b) one \( \beta^+ \) and one \( \beta^- \)  (c) two \( \beta^- \)  (d) two \( \beta^- \) and one \( \beta^+ \)

24. The following mechanism has been proposed for the reaction of NO with \( \text{Br}_2 \) to form \( \text{NOBr} \):

\[
\text{NO(g)} + \text{Br}_2(g) \leftrightarrow \text{NOBr}_2(g)
\]

\[
\text{NOBr}_2(g) + \text{NO(g)} \rightarrow 2\text{NOBr(g)}
\]

If the second step is the rate determining step, the order of the reaction with respect to \( \text{NO(g)} \) is

(a) 3  (b) 2  (c) 1  (d) 0

25. The energies of activation for forward and reverse reactions for \( A_2 + B_2 \rightarrow 2\text{AB} \) are 180 kJ mol\(^{-1}\) and 200 kJ mol\(^{-1}\) respectively. The presence of a catalyst lowers the activation energy of both (forward and reverse) reactions by 100 kJ mol\(^{-1}\). The enthalpy change of the reaction \( (A_2 + B_2 \rightarrow 2\text{AB}) \) in the presence of a catalyst will be (in kJ mol\(^{-1}\))
32. Consider the reaction:

\[ \text{Cl}_2(\text{aq}) + \text{H}_2\text{S}(\text{aq}) \rightarrow \text{S}(\text{s}) + 2\text{H}^+ (\text{aq}) + 2\text{Cl}^- (\text{aq}) \]

The rate equation for this reaction is

\[ \text{rate} = k[\text{Cl}_2][\text{H}_2\text{S}] \]

Which of these mechanisms is/are consistent with this rate equation? [2010]

A. \[ \text{Cl}_2 + \text{H}_2\text{S} \rightarrow \text{H}^+ + \text{Cl}^- + \text{Cl}^+ + \text{HS}^- \] (slow)

B. \[ \text{Cl}^+ + \text{HS}^- \rightarrow \text{H}^+ + \text{Cl}^- + \text{S} \] (fast)

C. \[ \text{H}_2\text{S} \Leftrightarrow \text{H}^+ + \text{HS}^- \] (fast equilibrium)

D. \[ \text{Cl}_2 + \text{HS}^- \rightarrow 2\text{Cl}^- + \text{H}^+ + \text{S} \] (Slow)

(a) B only (b) Both A and B
(c) Neither A nor B (d) A only

33. The rate of a chemical reaction doubles for every 10°C rise of temperature. If the temperature is raised by 50°C, the rate of the reaction increases by about: [2011]

(a) 10 times (b) 24 times
(c) 32 times (d) 64 times

34. For a first order reaction \( \text{A} \rightarrow \) products the concentration of \( \text{A} \) changes from 0.1 M to 0.025 M in 40 minutes.

The rate of reaction when the concentration of \( \text{A} \) is 0.01 M is:

(a) \( 1.73 \times 10^{-5} \) M/min (b) \( 3.47 \times 10^{-4} \) M/min
(c) \( 3.47 \times 10^{-5} \) M/min (d) \( 1.73 \times 10^{-4} \) M/min

35. The rate of a reaction doubles when its temperature changes from 300 K to 310 K. Activation energy of such a reaction will be: \( R = 8.314 \text{JK}^{-1}\text{mol}^{-1} \) and \log 2 = 0.301 [JEE M 2013]

(a) 53.6 kJ mol\(^{-1}\) (b) 48.6 kJ mol\(^{-1}\)
(c) 58.5 kJ mol\(^{-1}\) (d) 60.5 kJ mol\(^{-1}\)

36. For the non - stoichiometry reaction \( 2\text{A} + \text{B} \rightarrow \text{C} + \text{D} \), the following kinetic data were obtained in three separate experiments, all at 298 K. [JEE M 2014]

<table>
<thead>
<tr>
<th>Initial Concentration (A)</th>
<th>Initial Concentration (B)</th>
<th>Initial rate of formation of C (mol L(^{-1}) s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 M</td>
<td>0.1 M</td>
<td>( 1.2 \times 10^{-3} )</td>
</tr>
<tr>
<td>0.1 M</td>
<td>0.2 M</td>
<td>( 1.2 \times 10^{-3} )</td>
</tr>
<tr>
<td>0.2 M</td>
<td>0.1 M</td>
<td>( 2.4 \times 10^{-3} )</td>
</tr>
</tbody>
</table>
The rate law for the formation of C is:

(a) \( \frac{dc}{dt} = k[A][B] \)  \( \frac{dc}{dt} = k[A]^2[B] \)

(c) \( \frac{dc}{dt} = k[A][B]^2 \)  \( \frac{dc}{dt} = k[A] \)

37. Higher order (>3) reactions are rare due to:
   (a) shifting of equilibrium towards reactants due to elastic collisions
   (b) loss of active species on collision
   (c) low probability of simultaneous collision of all the reacting species
   (d) increase in entropy and activation energy as more molecules are involved

38. Decomposition of \( \text{H}_2\text{O}_2 \) follows a first order reaction. In fifty minutes the concentration of \( \text{H}_2\text{O}_2 \) decreases from 0.5 to 0.125 M in one such decomposition. When the concentration of \( \text{H}_2\text{O}_2 \) reaches 0.05 M, the rate of formation of \( \text{O}_2 \) will be:
   (a) 2.66 L\text{ min}^{-1} \text{ at STP}
   (b) \( 1.34 \times 10^{-2} \text{ mol min}^{-1} \)
   (c) \( 6.96 \times 10^{-2} \text{ mol min}^{-1} \)
   (d) \( 6.93 \times 10^{-4} \text{ mol min}^{-1} \)
General Principles and Processes of Isolation of Elements

Section-A

A Fill in the Blanks

2. In the thermite process .......... is used as reducing agent. (1980)
3. In the basic Bessemer process for the manufacture of steel the lining of the converter is made of .......... The slag formed consists of .......... (1980)
4. In extractive metallurgy of zinc partial fusion of ZnO with coke is called .......... and reduction of the ore to the molten metal is called .......... (smelting, calcining, roasting, sintering) (1988 - 1 Mark)

C MCQs with One Correct Answer

1. Copper can be extracted from (1978)
   (a) Kupfernical
   (b) Dolomite
   (c) Malachite
   (d) Galena

2. In the alumino-thermite process, aluminium acts as (1983 - 1 Mark)
   (a) an oxidizing agent
   (b) a flux
   (c) a reducing agent
   (d) a solder

3. The chemical composition of ‘slag’ formed during the smelting process in the extraction of copper is (2001)
   (a) Cu₂O + FeS
   (b) FeSiO₃
   (c) CuFeS₂
   (d) Cu₂S + FeO

4. Which of the following process is used in the extractive metallurgy of magnesium? (2002)
   (a) fused salt electrolysis
   (b) self reduction
   (c) aqueous solution electrolysis
   (d) thermite reduction

5. Which ore contains both iron and copper? (2005)
   (a) Cuprite
   (b) Chalcocite
   (c) Chalcopyrite
   (d) Malachite

6. Extraction of zinc from zinc blende is achieved by (2007)
   (a) electrolytic reduction
   (b) roasting followed by reduction with carbon
   (c) roasting followed by reduction with another metal
   (d) roasting followed by self-reduction

7. Oxidation states of the metal in the minerals haematite and magnetite, respectively, are (2011)
   (a) II, III in haematite and III in magnetite
   (b) II, III in haematite and II in magnetite
   (c) II in haematite and II, III in magnetite
   (d) III in haematite and II, III in magnetite

8. In the cyanide extraction process of silver from argentite ore, the oxidising and reducing agents used are (2012)
   (a) O₂ and CO respectively
   (b) O₂ and Zn dust respectively
   (c) HNO₃ and Zn dust respectively
   (d) HNO₃ and CO respectively

9. Sulfide ores are common for the metals (JEE Adv. 2013)
   (a) Ag, Cu and Pb
   (b) Ag, Mg and Pb
   (c) Ag, Cu and Sn
   (d) Al, Cu and Pb

D MCQs with One or More Than One Correct

1. Of the following, the metals that cannot be obtained by electrolysis of the aqueous solution of their salts are : (1990 - 1 Mark)
   (a) Ag
   (b) Mg
   (c) Cu
   (d) Al
   (e) Cr
2. Extraction of metal from the ore cassiterite involves
   (a) carbon reduction of an oxide ore
   (b) self-reduction of a sulphide ore
   (c) removal of copper impurity
   (d) removal of iron impurity

3. The carbon-based reduction method is NOT used for the extraction of
   (JEE Adv. 2013)
   (a) Tin from SnO₂
   (b) Iron from Fe₂O₃
   (c) Aluminium from Al₂O₃
   (d) Magnesium from MgCO₃CaCO₃

4. Upon heating with Cu₂S, the reagent(s) that give copper metal is/are
   (JEE Adv. 2014)
   (a) CuFeS₂
   (b) CuO
   (c) Cu₂O
   (d) CuSO₄

5. Copper is purified by electrolytic refining of blister copper.
   The correct statement(s) about this process is/are
   (JEE Adv. 2015)
   (a) Impure Cu strip is used as cathode
   (b) Acidified aqueous CuSO₄ is used as electrolyte
   (c) Pure Cu deposits at cathode
   (d) Impurities settle as anode-mud

6. Extraction of copper from copper pyrite (CuFeS₂) involves
   (JEE Adv. 2016)
   (a) crushing followed by concentration of the ore by froth-flotation
   (b) removal of iron as slag
   (c) self-reduction step to produce ‘blister copper’ following evolution of SO₂
   (d) refining of ‘blister copper’ by carbon reduction

E Subjective Problems

1. (a) Write the chemical equations involved in the extraction of lead from galena by self reduction process.
   (b) Match the following extraction processes with the appropriate metals listed below:
   (i) Silver
   (ii) Calcium
   (iii) Zinc
   (iv) Iron
   (v) Copper
   (A) Fused salt electrolysis
   (B) Carbon reduction
   (C) Carbon monoxide reduction
   (D) Amalgamation
   (E) Self reduction
   (1979)

2. Write the matching pairs:
   (1980)
   Bleaching agent
   Aluminium
   Smelling salt
   Carbon
   Cryolite
   Tin
   Bell metal
   Ammonium carbonate
   Fluorspar
   Ammonium phosphate
   Fertilizer
   Calcium
   Anthracite
   Chlorine

Examples:
   Bleaching agent
   Chlorine
   Smelling salt
   Ammonium carbonate

3. Give reasons for the following:
   (i) Metals can be recovered from their ores by chemical methods.
   (1984 - 1 Mark)
   (ii) High purity metals can be obtained by zone refining method.
   (1984 - 1 Mark)
   (iii) Why is chalsecite roasted and not calcinated during recovery of copper?
   (1987 - 1 Mark)

4. Give the equations for the recovery of lead from Galena by air reduction.
   (1987 - 1 Mark)

F Match the Following

Each question contains statements given in two columns, which have to be matched. The statements
in Column-I are labelled A, B, C and D, while the statements in Column-II are labelled p, q, r, s and
t. Any given statement in Column-I can have correct matching with ONE OR MORE statement(s) in
Column-II. The appropriate bubbles corresponding to the answers to these questions have to be
darkened as illustrated in the following example:
If the correct matches are A-p, s and t; B-q and r; C-p and q; and D-s then the correct darkening of
bubbles will look like the given.
1. Match the extraction processes listed in Column I with metals listed in Column II:

<table>
<thead>
<tr>
<th>Column I</th>
<th>Column II</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A) Self-reduction</td>
<td>(p) PbO</td>
</tr>
<tr>
<td>(B) Carbon reduction</td>
<td>(q) CaO</td>
</tr>
<tr>
<td>(C) Complex formation</td>
<td>(r) Zn</td>
</tr>
<tr>
<td>(D) Decomposition</td>
<td>(s) Cu</td>
</tr>
</tbody>
</table>

2. Match the conversions in Column I with the type(s) of reaction(s) given in Column II:

<table>
<thead>
<tr>
<th>Column I</th>
<th>Column II</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A) PbS → PbO</td>
<td>(p) roasting</td>
</tr>
<tr>
<td>(B) CaCO₃ → CaO</td>
<td>(q) calcination</td>
</tr>
<tr>
<td>(C) ZnS → Zn</td>
<td>(r) carbon reduction</td>
</tr>
<tr>
<td>(D) Cu₂S → Cu</td>
<td>(s) self reduction</td>
</tr>
</tbody>
</table>

3. Match the anionic species given in Column-I that are present in the ore(s) given in Column-II. *(JEE Adv. 2015)*

<table>
<thead>
<tr>
<th>Column I</th>
<th>Column II</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A) Carbonate</td>
<td>(p) Siderite</td>
</tr>
<tr>
<td>(B) Sulphide</td>
<td>(q) Malachite</td>
</tr>
<tr>
<td>(C) Hydroxide</td>
<td>(r) Bauxite</td>
</tr>
<tr>
<td>(D) Oxide</td>
<td>(s) Calamine</td>
</tr>
<tr>
<td></td>
<td>(t) Argentite</td>
</tr>
</tbody>
</table>

---

**Section-B**

1. Aluminium is extracted by the electrolysis of
   (a) bauxite
   (b) alumina
   (c) alumina mixed with molten cryolite
   (d) molten cryolite.

2. The metal extracted by leaching with a cyanide is
   (a) Mg
   (b) Ag
   (c) Cu
   (d) Na.

3. Which one of the following ores is best concentrated by froth-flotation method?
   (a) Galena
   (b) Cassiterite
   (c) Magnetite
   (d) Malachite

4. During the process of electrolytic refining of copper, some metals present as impurity settle as ‘anode mud’. These are
   (a) Fe and Ni
   (b) Ag and Au
   (c) Pb and Zn
   (d) Sn and Ag

5. Which of the following factors is of **no significance** for roasting sulphide ores to the oxides and not subjecting the sulphide ores to carbon reduction directly?
   (a) Metal sulphides are thermodynamically more stable than CS₂
   (b) CO₂ is thermodynamically more stable than CS₂
   (c) Metal sulphides are less stable than the corresponding oxides
   (d) CO₂ is more volatile than CS₂

6. 29.5 mg of an organic compound containing nitrogen was digested according to Kjeldahl’s method and the evolved ammonia was absorbed in 20 mL of 0.1 M HCl solution. The excess of the acid required 15 mL of 0.1 M NaOH solution for complete neutralization. The percentage of nitrogen in the compound is
   (a) 59.0
   (b) 47.4
   (c) 23.7
   (d) 29.5

7. Which method of purification is represented by the following equation?
   \[ \text{Ti}(s) + 2\text{I}_2(g) \xrightarrow{523K} \text{TiI}_4(g) \xrightarrow{1700K} \text{Ti}(s) + 2\text{I}_2(g) \]
   (a) Zone refining
   (b) Cupellation
   (c) Polling
   (d) VanArkel
8. The metal that cannot be obtained by electrolysis of an aqueous solution of its salts is:  
   (a) Ag  
   (b) Ca  
   (c) Cu  
   (d) Cr

9. In the context of the Hall - Heroult process for the extraction of Al, which of the following statements is false?  
   (a) \( \text{Al}^{3+} \) is reduced at the cathode to form Al  
   (b) \( \text{Na}_3\text{AlF}_6 \) serves as the electrolyte  
   (c) CO and \( \text{CO}_2 \) are produced in this process  
   (d) \( \text{Al}_2\text{O}_3 \) is mixed with \( \text{CaF}_2 \) which lowers the melting point of the mixture and brings conductivity

10. Which one of the following ores is best concentrated by froth floatation method?  
    (a) Galena  
    (b) Malachite  
    (c) Magnetite  
    (d) Siderite
CHAPTER 16
The p-Block Elements

Section-A

JEE Advanced/ IIT-JEE

A  Fill in the Blanks

1. The lowest possible oxidation state of nitrogen is \( \text{(1980)} \)
2. Iodine reacts with hot NaOH solution. The products are NaI and ....... \( \text{(1980)} \)
3. ................. is a weak acid. (HF, HCl, HI) \( \text{(1981 - 1 Mark)} \)
4. The increase in the solubility of iodine in an aqueous solution of potassium iodide is due to the formation of .......... \( \text{(1982 - 1 Mark)} \)
5. Hydrogen gas is liberated by the action of aluminium with concentrated solution of .......... \( \text{(1987 - 1 Mark)} \)
6. ................. phosphorus is reactive because of its highly strained tetrahedral structure. \( \text{(1987 - 1 Mark)} \)
7. .......... acid gives hypo ............... ion. (hydrobromic, hypobromous, perbromic, bromide, bromate, perbromate) \( \text{(1988 - 1 Mark)} \)
8. Sulphur acts as ............... agent in vulcanization of rubber. \( \text{(1989 - 1 Mark)} \)
9. The basicity of phosphorous acid (\( \text{H}_3\text{PO}_3 \)) is .......... . \( \text{(1990 - 1 Mark)} \)
10. The hydrolysis of alkyl substituted chlorosilanes gives .......... \( \text{(1991 - 1 Mark)} \)
11. In \( \text{P}_4\text{O}_{10} \), the number of oxygen atoms bonded to each phosphorus atom is .......... . \( \text{(1992 - 1 Mark)} \)
12. The lead chamber process involves oxidation of \( \text{SO}_2 \) by atomic oxygen under the influence of .......... as catalyst. \( \text{(1992 - 1 Mark)} \)
13. The hydrolysis of trialkylchlorosilane \( \text{R}_3\text{SiCl} \), yields ............ \( \text{(1994 - 1 Mark)} \)
14. One recently discovered allotrope of carbon (e.g., \( \text{C}_{60} \)) is commonly known as .......... \( \text{(1994 - 1 Mark)} \)
15. Solubility of iodine in water is greatly increased by the addition of iodide ions because of the formation of .......... \( \text{(1994 - 1 Mark)} \)
16. A liquid which is permanently supercooled is frequently called a ............. \( \text{(1997 - 1 Mark)} \)
17. Compounds that formally contain \( \text{Pb}^{4+} \) are easily reduced to \( \text{Pb}^{2+} \). The stability of the lower oxidation state is due to .......... \( \text{(1997 - 1 Mark)} \)

B  True / False

1. Red phosphorus is less volatile than white phosphorus because the former has a tetrahedral structure. \( \text{(1982 - 1 Mark)} \)
2. When \( \text{PbO}_2 \) reacts with a dilute acid, it gives hydrogen peroxide. \( \text{(1982 - 1 Mark)} \)
3. Carbon tetrachloride burns in air when lighted to give phosgene. \( \text{(1983 - 1 Mark)} \)
4. Dil. HCl oxidizes metallic Fe to Fe\(^{2+}\). \( \text{(1983 - 1 Mark)} \)
5. In aqueous solution chlorine is a stronger oxidizing agent than fluorine. \( \text{(1984 - 1 Mark)} \)
6. The H-N-H bond angle in \( \text{NH}_3 \) is greater than the H-As-H bond angle in \( \text{AsH}_3 \). \( \text{(1984 - 1 Mark)} \)
7. Carbon tetrachloride is inflammable. \( \text{(1985 - ½ Mark)} \)
8. Graphite is better lubricant on the moon than on the earth. \( \text{(1987 - 1 Mark)} \)
9. All the Al–Cl bonds in \( \text{Al}_2\text{Cl}_6 \) are equivalent. \( \text{(1989 - 1 Mark)} \)
10. Nitric oxide, though an odd electron molecule, is diamagnetic in liquid state. \( \text{(1991 - 1 Mark)} \)
11. Diamond is harder than graphite. \( \text{(1993 - 1 Mark)} \)
12. The tendency for catenation is much higher for C than for Si. \( \text{(1993 - 1 Mark)} \)
13. HBr is a stronger acid than HI because of hydrogen bonding. \( \text{(1993 - 1 Mark)} \)

C  MCQs with One Correct Answer

1. The reddish brown coloured gas formed when nitric oxide is oxidised by air is \( \text{(1979)} \)
   a) \( \text{N}_2\text{O}_5 \)    b) \( \text{N}_2\text{O}_4 \)
   c) \( \text{NO}_2 \)    d) \( \text{N}_2\text{O}_3 \)
2. The temporary hardness of water due to calcium carbonate can be removed by adding – \( \text{(1979)} \)
   a) \( \text{CaCO}_3 \)    b) \( \text{Ca(OH)}_2 \)
   c) \( \text{CaCl}_2 \)    d) HCl
3. Which of the following is most stable to heat \( \text{(1980)} \)
   a) HCl    b) HOCI
   c) HBr    d) HI
4. White P reacts with caustic soda. The products are PH$_3$ and NaH$_2$PO$_3$. This reaction is an example of *(1980)*
   (a) Oxidation     (b) Reduction
   (c) Oxidation and reduction     (d) Neutralisation
5. A solution of KBr is treated with each of the following. Which one would liberate bromine *(1980)*
   (a) Cl$_2$     (b) HI
   (c) I$_2$     (d) SO$_2$
6. Which of the following is coloured *(1980)*
   (a) NO     (b) N$_2$O
   (c) SO$_3$     (d) None
7. Lead pencil contains *(1980)*
   (a) Pb     (b) FeS
   (c) Graphite     (d) PbS
8. Ammonia can be dried by *(1980)*
   (a) Conc. H$_2$SO$_4$     (b) P$_2$O$_5$
   (c) Anhydrous CuSO$_4$     (d) None
9. HBr and HI reduce sulphuric acid, HCl can reduce KMnO$_4$ and HF can reduce *(1981 - 1 Mark)*
   (a) H$_2$SO$_4$     (b) KMnO$_4$
   (c) K$_2$Cr$_2$O$_7$     (d) None of the above
10. Which of the following statements about anhydrous aluminium chloride is correct? *(1981 - 1 Mark)*
    (a) It exists as AlCl$_4$ molecules
    (b) It is not easily hydrolysed
    (c) It sublimes at 100°C under vacuum
    (d) It is a strong Lewis base
11. Moderate electrical conductivity is shown by *(1982 - 1 Mark)*
    (a) Silica     (b) Graphite
    (c) Diamond     (d) Carborundum
12. Chlorine acts as a bleaching agent only in presence of *(1983 - 1 Mark)*
    (a) Dry air     (b) Moisture
    (c) Sunlight     (d) Pure oxygen
13. Nitrogen dioxide cannot be obtained by heating *(1985 - 1 Mark)*
    (a) KNO$_3$     (b) Pb(NO$_3$)$_2$
    (c) Cu(NO$_3$)$_2$     (d) AgNO$_3$
14. A gas that cannot be collected over water is: *(1985 - 1 Mark)*
    (a) N$_2$     (b) O$_2$
    (c) SO$_2$     (d) PH$_3$
15. The compound which gives off oxygen on moderate heating is: *(1986 - 1 Mark)*
    (a) Cupric oxide     (b) Mercuric oxide
    (c) Zinc oxide     (d) Aluminium oxide
16. The bonds present in N$_2$O are: *(1986 - 1 Mark)*
    (a) Only ionic     (b) Covalent and coordinate
    (c) Only covalent     (d) Covalent and ionic
17. Which of the following oxides of nitrogen is a coloured gas? *(1987 - 1 Mark)*
    (a) N$_2$O     (b) NO
    (c) N$_2$O$_5$     (d) NO$_2$
18. Amongst the trihalides of nitrogen which one is least basic? *(1987 - 1 Mark)*
    (a) NF$_3$     (b) NCl$_3$
    (c) NBr$_3$     (d) NI$_3$
19. Bromine can be liberated from potassium bromide solution by the action of *(1987 - 1 Mark)*
    (a) Iodine solution     (b) Chlorine water
    (c) Sodium chloride     (d) Potassium iodide
20. There is no S–S bond in: *(1991 - 1 Mark)*
    (a) S$_2$O$_4^{2–}$     (b) S$_2$O$_5^{2–}$
    (c) S$_2$O$_3^{2–}$     (d) S$_2$O$_7^{2–}$
21. In P$_4$O$_{10}$ each P atom is linked with ........ O atoms *(1995S)*
    (a) 2     (b) 3
    (c) 4     (d) 5
22. H$_2$SO$_4$ cannot be used to prepare HBr from NaBr as it: *(1995S)*
    (a) Reacts slowly with NaBr     (b) Oxidises HBr
    (c) Reduces HBr     (d) Disproportionates HBr
23. Hydrolysis of one mole of peroxodisulphuric acid produces *(1996 - 1 Mark)*
    (a) Two moles of sulphuric acid
    (b) Two moles of peroxomonsulphuric acid
    (c) One mole of sulphuric acid and one mole of peroxomonsulphuric acid
    (d) One mole of sulphuric acid, one mole of peroxomonsulphuric acid and one mole of hydrogen peroxide.
24. Which of the following statements is correct for CsBr$_3$? *(1996 - 1 Mark)*
    (a) It is a covalent compound.
    (b) It contains Cs$^{3+}$ and Br$^-$. ions.
    (c) It contains Cs$^+$ and Br$_3^-$ ions.
    (d) It contains Cs$^+$, Br$^-$ and lattice Br$_2$ molecule.
25. KF combines with HF to form KHF$_2$. The compound contains the species. *(1996 - 1 Mark)*
    (a) K$^+$, F$^-$ and H$^+$     (b) K$^+$, F$^-$ and HF
    (c) K$^+$ and [HF$_2]$$^-$.     (d) [KHF]$^+$ and F$^-$
26. Sodium thiosulphate is prepared by *(1996 - 1 Mark)*
    (a) Reducing Na$_2$SO$_4$ solution with H$_2$S
    (b) Boiling Na$_2$SO$_4$ solution with S in alkaline medium
    (c) Neutralising H$_2$SO$_4$ solution with NaOH
    (d) Boiling Na$_2$SO$_4$ solution with S in acidic medium
27. Which of the following halides is least stable and has doubtful existence? *(1996 - 1 Mark)*
    (a) Cl$_4$     (b) GeI$_4$
    (c) SnI$_4$     (d) PbI$_4$
28. Which one of the following oxides is neutral? *(1997 - 1 Mark)*
    (a) CO     (b) SnO$_2$
    (c) ZnO     (d) SO$_3$
29. Which one of the following species is not a pseudohalide? *(1997 - 1 Mark)*
    (a) CNO$^-$     (b) RCOO$^-$
    (c) OCN$^-$     (d) NNN$^-$
30. One mole of calcium phosphate on reaction with excess water gives *(1999 - 2 Marks)*
    (a) One mole of phosphine
    (b) Two moles of phosphoric acid
    (c) Two moles of phosphate
    (d) One mole of phosphorus pentoxide
31. On heating ammonium dichromate, the gas evolved is
   \((1999 - 2 \text{ Marks})\)
   (a) oxygen \(\quad\) (b) ammonia \(\quad\)
   (c) nitrous oxide \(\quad\) (d) nitrogen

32. In the commercial electrochemical process for aluminium extraction the electrolyte used is
   \((1999 - 2 \text{ Marks})\)
   (a) \(\text{Al(OH)}_3\) in \(\text{NaOH}\) solution
   (b) an aqueous solution of \(\text{Al}_2(\text{SO}_4)_3\)
   (c) a molten mixture of \(\text{Al}_2\text{O}_3\) and \(\text{Na}_2\text{AlF}_6\)
   (d) a molten mixture of \(\text{Al}2(\text{OH})_2\) and \(\text{Al(OH)}_3\)

33. In compounds of type \(\text{ECl}_3\), where \(\text{E} = \text{B, P, As or Bi}\), the angles \(\text{Cl} - \text{E} - \text{Cl}\) for different \(\text{E}\) are in the order
   \((1999 - 2 \text{ Marks})\)
   (a) \(\text{B} > \text{P} = \text{As} = \text{Bi}\) \(\quad\) (b) \(\text{B} > \text{P} > \text{As} > \text{Bi}\)
   (c) \(\text{B} < \text{P} = \text{As} = \text{Bi}\) \(\quad\) (d) \(\text{B} < \text{P} < \text{As} < \text{Bi}\)

34. Electrolytic reduction of alumina to aluminium by Hall-Heroult process is carried out
   \((2000S)\)
   (a) in the presence of \(\text{NaCl}\)
   (b) in the presence of cryolite
   (c) in the presence of cryolite which forms a melt with lower melting temperature
   (d) in the presence of cryolite which forms a melt with higher melting temperature

35. The number of \(\text{P} - \text{O} - \text{P}\) bonds in cyclic metaphosphoric acid is
   \((2000S)\)
   (a) zero \(\quad\) (b) two \(\quad\)
   (c) three \(\quad\) (d) four

36. Ammonia can be dried by
   \((2000S)\)
   (a) conc. \(\text{H}_2\text{SO}_4\) \(\quad\) (b) \(\text{P}_4\text{O}_{10}\)
   (c) \(\text{CaO}\) \(\quad\) (d) anhydrous \(\text{CaCl}_2\)

37. The number of \(\text{S} - \text{S}\) bonds in sulphur trioxide trimer \((\text{S}_3\text{O}_6)\) is
   \((2001S)\)
   (a) three \(\quad\) (b) two \(\quad\)
   (c) one \(\quad\) (d) zero

38. Polyphosphates are used as water softening agents because they
   \((2002S)\)
   (a) form soluble complexes with anionic species \(\quad\)
   (b) precipitate anionic species \(\quad\)
   (c) form soluble complexes with cationic species \(\quad\)
   (d) precipitate cationic species

39. For \(\text{H}_3\text{PO}_3\) and \(\text{H}_2\text{PO}_4\) the correct choice is:
   \((2003S)\)
   (a) \(\text{H}_3\text{PO}_3\) is dibasic and reducing \(\quad\)
   (b) \(\text{H}_2\text{PO}_3\) is dibasic and non-reducing \(\quad\)
   (c) \(\text{H}_2\text{PO}_4\) is tribasic and reducing \(\quad\)
   (d) \(\text{H}_2\text{PO}_3\) is tribasic and non-reducing

40. \(\text{H}_3\text{BO}_3\) is
   \((2003S)\)
   (a) Monobasic and weak Lewis acid \(\quad\)
   (b) Monobasic and weak Bronsted acid \(\quad\)
   (c) Monobasic and strong Lewis acid \(\quad\)
   (d) Tribasic and weak Bronsted acid

41. \((\text{Me})_2\text{SiCl}_2\) on hydrolysis will produce \((2003S)\)
   (a) \((\text{Me})_2\text{Si(OH)}_2\) \(\quad\) (b) \((\text{Me})_2\text{Si} = \text{O}\)
   (c) \(-[\text{O}-(\text{Me})_2\text{Si}-\text{O}]_n-\) \(\quad\) (d) \((\text{Me})_2\text{Si(OH)}_3\)

42. Total number of lone pair of electrons in \(\text{XeOF}_4\) is \((2004S)\)
   (a) 0 \(\quad\) (b) 1 \(\quad\)
   (c) 2 \(\quad\) (d) 3

43. The acid having \(\text{O} - \text{O}\) bond is \((2004S)\)
   (a) \(\text{H}_2\text{SiO}_3\) \(\quad\) (b) \(\text{H}_2\text{SiO}_6\)
   (c) \(\text{H}_2\text{SiO}_8\) \(\quad\) (d) \(\text{H}_2\text{SiO}_6\)

44. Pb and Sn are extracted from their chief ores by \((2004S)\)
   (a) carbon reduction and self reduction respectively
   (b) self reduction and carbon reduction respectively
   (c) electrolysis and self reduction respectively
   (d) self reduction and electrolysis respectively

45. Name of the structure of silicates in which three oxygen atoms of \([\text{SiO}_4]^{4-}\) are shared. \((2005S)\)
   (a) Pyrosilicate \(\quad\) (b) Sheet silicate
   (c) Linear chain silicate \(\quad\) (d) Three dimensional silicate

46. Which is the most thermodynamically stable allotropic form of phosphorus? \((2005S)\)
   (a) red \(\quad\) (b) white
   (c) black \(\quad\) (d) yellow

47. Which of the following is not oxidized by \(\text{O}_3\) ? \((2005S)\)
   (a) \(\text{KI}\) \(\quad\) (b) \(\text{FeSO}_4\)
   (c) \(\text{K}_2\text{MnO}_4\) \(\quad\) (d) \(\text{K}_2\text{MnO}_4\)

48. Blue liquid which is obtained on reacting equimolar amounts of two gases at \(-30^\circ\text{C}\) is? \((2005S)\)
   (a) \(\text{N}_2\text{O}\) \(\quad\) (b) \(\text{N}_2\text{O}_3\)
   (c) \(\text{N}_2\text{O}_4\) \(\quad\) (d) \(\text{N}_2\text{O}_3\)

49. When \(\text{PbO}_2\) reacts with conc. \(\text{HNO}_3\) the gas evolved is \((2005S)\)
   (a) \(\text{NO}_2\) \(\quad\) (b) \(\text{O}_2\)
   (c) \(\text{N}_2\) \(\quad\) (d) \(\text{N}_2\text{O}\)

50. How can the following reaction be made to proceed in forward direction? \((2006 - 3M, -1)\)
   \(\text{B(OH)}_3 + \text{NaOH} \rightleftharpoons \text{NaBO}_2 + \text{Na[B(OH)}_4\] + \(\text{H}_2\text{O}\)
   (a) addition of borax \(\quad\)
   (b) addition of \(\text{cis}-1,2\)-diol \(\quad\)
   (c) addition of \(\text{Na}_2\text{HPO}_4\) \(\quad\)
   (d) addition of \(\text{trans}-1,2\)-diol

51. The percentage of \(\pi\)-character in the orbitals forming \(\text{P} - \text{P}\) bonds in \(\text{P}_4\) is \((2007)\)
   (a) 25 \(\quad\) (b) 33 \(\quad\)
   (c) 50 \(\quad\) (d) 75

52. Aqueous solution of \(\text{Na}_2\text{S}_2\text{O}_3\) on reaction with \(\text{Cl}_2\) gives – \((2008)\)
   (a) \(\text{Na}_2\text{S}_2\text{O}_6\) \(\quad\) (b) \(\text{NaH}\text{SO}_4\)
   (c) \(\text{NaCl}\) \(\quad\) (d) \(\text{NaOH}\)

53. The reaction of \(\text{P}_4\) with \(\text{X}\) leads selectively to \(\text{P}_4\text{O}_6\). The \(\text{X}\) is \((2009)\)
   (a) \(\text{Dry O}_2\) \(\quad\)
   (b) A mixture of \(\text{O}_2\) and \(\text{N}_2\)
   (c) Moist \(\text{O}_2\) \(\quad\)
   (d) \(\text{O}_2\) in the presence of aqueous \(\text{NaOH}\)
54. Extra pure N₂ can be obtained by heating
(a) NH₃ with CuO
(b) NH₄NO₃
(c) (NH₄)₂Cr₂O₇
(d) Ba(N₂)₂

55. Which ordering of compounds is according to the decreasing order of the oxidation state of nitrogen?
(a) HNO₃, NO, NH₃Cl, N₂
(b) HNO₃, NO, N₂, NH₄Cl
(c) HNO₃, NH₃Cl, NO, N₂
(d) NO, HNO₃, NH₃Cl, N₂

56. The reaction of white phosphorus with aqueous NaOH gives phosphine along with another phosphorus containing compound. The reaction type; the oxidation states of phosphorus in phosphine and the other product are respectively
(a) redox reaction; – 3 and – 5
(b) redox reaction; + 3 and + 5
(c) disproportionation reaction; – 3 and + 5
(d) disproportionation reaction; – 3 and + 3

57. The shape of XeO₄F₂ molecule is
(a) trigonal bipyramidal
(b) square planar
(c) tetrahedral
(d) see-saw

58. Concentrated nitric acid, upon long standing, turns yellow brown due to the formation of
(a) NO
(b) NO₂
(c) N₂O
(d) N₂O₄

59. The product formed in the reaction of SOCl₂ with white phosphorous is
(a) PCl₃
(b) SO₂Cl₂
(c) SCl₂
(d) POCl₃

60. Under ambient conditions, the total number of gases released as products in the final step of the reaction scheme shown below is

\[ \text{XeF}_6 \xrightarrow{\text{Hydrolysis}} \text{P} + \text{Other product} \]
\[ \xrightarrow{\text{OH}_2\text{H}_2\text{O}} \]
\[ \xrightarrow{\text{Q}} \]
\[ \text{Slow disproportionation in OH}_2\text{H}_2\text{O} \]
\[ \xrightarrow{\text{Products}} \]

61. The increasing order of atomic radii of the following Group 13 elements is
(a) Al < Ga < In < Tl
(b) Ga < Al < In < Tl
(c) Al < In < Ga < Tl
(d) Al < Ga < Tl < In

62. In the following reaction sequence in aqueous solution, the species X, Y and Z, respectively, are

\[ \text{S}_2\text{O}_3^{2-} \xrightarrow{\text{Ag}^+} \text{X} \xrightarrow{\text{Ag}^+} \text{Y} \]

\[ \text{with time} \]
\[ \text{Z} \]

(a) \[\text{[Ag(S}_2\text{O}_3)_2]^{3-}; \text{Ag}_2\text{S}_2\text{O}_3; \text{Ag}_2\text{S}\]
(b) \[\text{[Ag(S}_2\text{O}_3)_3]^{3-}; \text{Ag}_2\text{SO}_3; \text{Ag}_2\text{S}\]
(c) \[\text{[Ag(S}_2\text{O}_3)_2]^{3-}; \text{Ag}_2\text{S}_2\text{O}_3; \text{Ag}\]
(d) \[\text{[Ag(S}_2\text{O}_3)_3]^{3-}; \text{Ag}_2\text{SO}_4; \text{Ag}\]

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**MCQs with One or More Than One Correct**

1. In the electrolysis of alumina, cryolite is added to:
   (a) lower the melting point of alumina
   (b) increase the electrical conductivity
   (c) minimise the anode effect
   (d) remove impurities from alumina

2. Nitrogen(I) oxide is produced by:
   (a) thermal decomposition of ammonium nitrate
   (b) disproportionation of N₂O₄
   (c) thermal decomposition of ammonium nitrate
   (d) interaction of hydroxylamine and nitrous acid.

3. The compounds used as refrigerant are
   (a) NH₃
   (b) CCl₄
   (c) CF₄
   (d) CF₂Cl₂
   (e) CH₂F₂

4. The major role of fluor spar (CaF₂), which is added in small quantities in the electrolytic reduction of alumina dissolved in fused cryolite (Na₃AlF₆), is
   (a) as a catalyst
   (b) to make the fused mixture very conducting
   (c) to lower the temperature of the melt
   (d) to decrease the rate of oxidation of carbon at the anode.

5. The material used in the solar cells contains
   (a) Cs
   (b) Si
   (c) Sn
   (d) Ti

6. Sodium nitrate decomposes above 800°C to give
   (a) N₂
   (b) O₂
   (c) NO₂
   (d) Na₂O
7. White phosphorus (P$_2$) has \(1998 - 2\) Marks
   (a) six P-P single bonds
   (b) four P-P single bonds
   (c) four lone pairs of electrons
   (d) PPP angle of 60°

8. Ammonia, on reaction with hypochlorite anion, can form \(1999 - 3\) Marks
   (a) NO
   (b) NH$_4$Cl
   (c) N$_2$H$_4$
   (d) HNO$_2$

9. A solution of colourless salt H on boiling with excess NaOH produces a non-flammable gas. The gas evolution ceases after sometime. Upon addition of Zn dust to the same solution, the gas evolution restarts. The colourless salt $(s)$ H is (are) \(2008\)
   (a) NH$_4$NO$_3$
   (b) NH$_4$NO$_2$
   (c) NH$_4$Cl
   (d) (NH$_4$)$_2$SO$_4$

10. The nitrogen oxide(s) that contain(s) N-N bond(s) is(are) \(2009\)
    (a) N$_2$O
    (b) N$_2$O$_3$
    (c) N$_2$O$_4$
    (d) N$_2$O$_5$

11. Which of the following halides react(s) with AgNO$_3$(aq) to give a precipitate that dissolves in Na$_2$S$_2$O$_3$(aq)? \(2012\)
    (a) HCl
    (b) HF
    (c) HBr
    (d) HI

12. With respect to graphite and diamond, which of the statement(s) given below is (are) correct? \(2012\)
    (a) Graphite is harder than diamond.
    (b) Graphite has higher electrical conductivity than diamond.
    (c) Graphite has higher thermal conductivity than diamond.
    (d) Graphite has higher C–C bond order than diamond.

13. The correct statement(s) about O$_3$ is(are) \(2013-11\)
    (a) O–O bond lengths are equal
    (b) Thermal decomposition of O$_3$ is endothermic
    (c) O$_3$ is diamagnetic in nature
    (d) O$_3$ has a bent structure

14. For the reaction \(2014\)
    \[ \Gamma^- + ClO_3^- + H_2SO_4 \rightarrow Cl^- + HSO_4^- + I_2 \]
    The correct statement(s) in the balanced equation is/are
    (a) Stoichiometric coefficient of HSO$_4^-$ is 6
    (b) Iodide is oxidized
    (c) Sulphur is reduced
    (d) H$_2$O is one of the products

15. The correct statement(s) for orthoboric acid is(are) \(2014\)
    (a) It behaves as a weak acid in water due to self ionization.
    (b) Acidity of its aqueous solution increases upon addition of ethylene glycol
    (c) It has a three dimensional structure due to hydrogen bonding
    (d) It is a weak electrolyte in water

16. The correct statement(s) regarding, (i) HClO, (ii) HClO$_2$, (iii) HClO$_3$ and (iv) HClO$_4$, is(are) \(2015\)
    (a) The number of Cl–O bonds in (ii) and (iii) together is two
    (b) The number of lone pairs of electrons on Cl in (ii) and (iii) together is three
    (c) The hybridization of Cl in (iv) is sp$^3$
    (d) Amongst (i) to (iv), the strongest acid is (i)

17. Under hydrolytic conditions, the compounds used for preparation of linear polymer and for chain termination, respectively, are \(2015\)
    (a) CH$_3$SiCl$_3$ and Si(CH$_3$)$_4$
    (b) (CH$_3$)$_2$SiCl$_2$ and (CH$_3$)$_3$SiCl
    (c) (CH$_3$)$_2$SiCl$_2$ and CH$_3$SiCl$_3$
    (d) SiCl$_4$ and (CH$_3$)$_3$SiCl

18. The crystalline form of borax has \(2016\)
    (a) tetranuclear [B$_4$O$_6$(OH)$_4$]$^{2-}$ unit
    (b) all boron atoms in the same plane
    (c) equal number of sp$^2$ and sp$^3$ hybridized boron atoms
    (d) one terminal hydroxide per boron atom

19. The nitrogen containing compound produced in the reaction of HNO$_3$ with P$_2$O$_{10}$ \(2016\)
    (a) can also be prepared by reaction of P$_4$ and HNO$_3$
    (b) is diamagnetic
    (c) contains one N-N bond
    (d) reacts with Na metal producing a brown gas

E. Subjective Problems

1. Account for the following. Limit your answer to two sentences
   (i) Hydrogen bromide cannot be prepared by action of concentrated sulphuric acid or sodium bromide.
   (ii) When a blue litmus paper is dipped into a solution of hypochlorous acid, it first turns red and then later gets decolourised.

2. Write balanced equation involved in the preparation of
   (i) Anhydrous aluminium chloride from alumina.
   (ii) Bleaching powder from slaked lime.
   (iii) Tin metal from cassiterite
   (iv) Chlorine from sodium chloride.
   (v) Nitric oxide from nitric acid.

3. State with balanced equations, what happens when:
   (i) Tin is treated with moderately concentrated nitric acid.
   (ii) Aluminium is reacted with hot concentrated caustic soda solution

4. Give structural formula for the following:
   (i) Phosphorous acid, H$_3$PO$_3$ \(1981 - 1\) Mark
   (ii) Pyrophosphoric acid, H$_4$P$_2$O$_7$ \(1981 - 1\) Mark
5. Complete the following equations (no balancing is needed)
   (i) \( \text{HCO}_3^- + \text{Al}^{3+} \rightarrow \text{Al(OH)}_3 + \ldots \) (1981 - 1 Mark)
   (ii) \( \text{AlBr}_3 + \text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{PO}_4 \rightarrow \text{K}_3\text{PO}_4 + \text{AlPO}_4 + \text{H}_2\text{O} + \ldots + \ldots \) (1981 - 1 Mark)

6. Give reasons for the following:
   (i) Carbon acts as an abrasive and also as a lubricant. (1981 - 1 Mark)
   (ii) Sulphur melts to a clear mobile liquid at 119°C, but on further heating above 160°C, it becomes viscous. (1981 - 1 Mark)
   (iii) In the preparation of hydrogen iodide from alkali iodides, phosphoric acid is preferred to sulphuric acid (1982 - 1 Mark)
   (iv) Orthophosphoric acid, \( \text{H}_3\text{PO}_4 \), is tribasic, but phosphorous acid, \( \text{H}_3\text{P} = \text{O}_3 \), is dibasic. (1982 - 1 Mark)
   (v) A bottle of liquor ammonia should be cooled before opening the stopper. (1983 - 1 Mark)
   (vi) Solid carbon dioxide is known as dry ice. (1983 - 1 Mark)
   (vii) Anhydrous \( \text{HCl} \) is a bad conductor of electricity but aqueous \( \text{HCl} \) is a good conductor. (1985 - 1 Mark)
   (viii) Graphite is used as a solid lubricant; (1985 - 1 Mark)
   (ix) Fluorine cannot be prepared from fluorides by chemical oxidation. (1985 - 1 Mark)
   (x) The mixture of hydrazine and hydrogen peroxide with a copper(II) catalyst is used as a rocket propellant. (1987 - 1 Mark)
   (xi) Orthophosphorus acid is not tribasic acid. (1987 - 1 Mark)
   (xii) The molecule of magnesium chloride is linear whereas that of stannous chloride is angular. (1987 - 1 Mark)
   (xiii) Valency of oxygen is generally two whereas sulphur shows valency of two, four and six. (1988 - 1 Mark)
   (xiv) \( \text{H}_3\text{PO}_3 \) is a dibasic acid. (1989 - 1 Mark)
   (xv) Phosgene has lower boiling point than ammonia. (1989 - 1 Mark)
   (xvi) Ammonium chloride is acidic in liquid ammonia solvent. (1991 - 1 Mark)
   (xvii) The hydroxides of aluminium and iron are insoluble in water. However, \( \text{NaOH} \) is used to separate one from the other. (1991 - 1 Mark)
   (xviii) Bond dissociation energy of \( \text{F}_2 \) is less than that of \( \text{Cl}_2 \). (1992 - 1 Mark)
   (xix) Sulphur dioxide is a more powerful reducing agent in an alkaline medium than in acidic medium. (1992 - 1 Mark)

7. State with balanced equations what happens when:
   (i) White phosphorous \( (\text{P}_4) \) is boiled with a strong solution of sodium hydroxide in an inert atmosphere. (1982/87 - 1 Mark)
   (ii) Sodium iodate is treated with sodium bisulphite solution. (1982 - 1 Mark)
   (iii) Dilute nitric acid is slowly reacted with metallic tin. (1987 - 1 Mark)
   (iv) Potassium permanganate is reacted with warm solution of oxalic acid in the presence of sulphuric acid. (1987 - 1 Mark)
   (v) Iodate ion reacts with bisulphite ion to liberate iodine. (1988 - 1 Mark)
   (vi) Phosphorus reacts with nitric acid to give equimolar ratio of nitric oxide and nitrogen dioxide. (1988 - 1 Mark)
   (vii) Hypophosphorous acid \( (\text{H}_3\text{P}_2\text{O}_5) \) is heated. (1989 - 1 Mark)
   (viii) Sodium bromate reacts with fluorine in presence of alkali. (1989 - 1 Mark)
   (ix) Sodium chlorate reacts with sulphur dioxide in dilute sulphuric acid medium. (1989 - 1 Mark)
   (x) Write balanced equations for the preparation of crystalline silicon from \( \text{SiCl}_4 \). (1990 - 1 Mark)
   (xi) Write balanced equations for the preparation of phosphine from \( \text{CaO} \) and white phosphorus. (1990 - 2 Marks)
   (xii) Write balanced equations for the preparation of ammonium sulphate from gypsum, ammonia and carbon dioxide. (1990 - 1 Mark)
   (xiii) Aqueous solution of sodium nitrate is heated with zinc dust and caustic soda solution. (1990 - 1 Mark)
   (xiv) Sodium iodate is added to a solution of sodium bisulphite. (1990 - 1 Marks)
   (xv) Sodium nitrite is produced by absorbing the oxides of nitrogen in aqueous solution of washing soda. (1991 - 1 Mark)
   (xvi) Nitrogen is obtained in the reaction of aqueous ammonia with potassium permanganate. (1991 - 1 Mark)
(xvii) Elemental phosphorus reacts with conc. HNO₃ to give phosphoric acid. \(1991 - 1 \text{ Mark}\)

(xviii) Sulphur is precipitated in the reaction of hydrogen sulphide with sodium bisulphite solution. \(1991 - 1 \text{ Mark}\)

(xix) Phosphorus is treated with concentrated nitric acid. \(1997 - 1 \text{ Mark}\)

**OR**

Manufacture of phosphoric acid from phosphorus. \(1997 - 1 \text{ Mark}\)

(xx) Reaction of aluminium with aqueous sodium hydrosolate. \(1997 - 1 \text{ Mark}\)

(xxi) Aluminium sulphide gives a foul odour when it becomes damp. Write a balanced chemical equation for the reaction. \(1997 - 2 \text{ Marks}\)

(xxii) \(P_4O_{10} + PCl_5 \rightarrow\) \(1998 - 1 \text{ Mark}\)

(xxiii) \(SnCl_4 + C_2H_4Cl + Na \rightarrow\) \(1998 - 1 \text{ Mark}\)

8. Show with equations how the following compound is prepared (equations need not be balanced) sodium thiosulphate from sodium sulphite. \(1982 - 1 \text{ Mark}\)

9. Give balanced equations for the extraction of aluminium from bauxite by electrolysis. \(1982 - 2 \text{ Marks}\)

10. State the conditions under which the following preparation is carried out. Give the necessary equations which need not be balanced: Alumina from aluminium. \(1983 - 1 \text{ Mark}\)

11. Write down the resonance structures of nitrous oxide. \(1985 - 2 \text{ Marks}\)

**OR**

Write the two resonance structures of \(N_2O\) that satisfy the octet rule. \(1990 - 1 \text{ Mark}\)

12. Write down the balanced equations for the reactions when:

(i) a mixture of potassium chlorate, oxalic acid and sulphuric acid is heated; \(1985 - 1 \text{ Mark}\)

(ii) ammonium sulphate is heated with a mixture of nitric oxide and nitrogen dioxide. \(1985 - 1 \text{ Mark}\)

13. What happens when:

(i) hydrogen sulphide is bubbled through an aqueous solution of sulphur dioxide. \(1985 - 1 \text{ Mark}\)

(ii) tin is treated with concentrated nitric acid. \(1985 - 1 \text{ Mark}\)

(iii) \(PbO_4\) is treated with nitric acid. \(1985 - 1 \text{ Mark}\)

14. Arrange the following in:

(i) increasing bond strength \(1986 - 1 \text{ Mark}\)

HCl, HBr, HF, HI

(ii) HOCl, HOClO₂, HOClO₃, HOCIO in increasing order of thermal stability. \(1988 - 1 \text{ Mark}\)

(iii) \(CO_2, N_2O_5, SiO_2, SO_3\) in the order of increasing acidic character. \(1988 - 1 \text{ Mark}\)

(iv) Increasing order of extent of hydrolysis:

\(CCl_4, MgCl_2, AlCl_3, PCl_5, SiCl_4\) \(1991 - 1 \text{ Mark}\)

15. Mention the products formed in the following:

(i) Chlorine gas is bubbled through a solution of ferrous bromide. \(1986 - 1 \text{ Mark}\)

(ii) Iodine is added to a solution of stannous chloride. \(1986 - 1 \text{ Mark}\)

(iii) Sulphur dioxide gas, water vapour and air are passed over heated sodium chloride. \(1986 - 1 \text{ Mark}\)

16. Write the two resonance structures of ozone which satisfy the octet rule. \(1991 - 1 \text{ Mark}\)

17. \(PbS \xrightarrow{\text{heat in air}} A + PbS \xrightarrow{B} Pb + SO_2\); Identify A and B. \(1991 - 2 \text{ Marks}\)

18. Complete and balance the following chemical reactions:

(i) Red phosphorus is reacted with iodine in presence of water. \(1992 - 1 \text{ Mark}\)

\(P + I_2 + H_2O \rightarrow \ldots \ldots + \ldots \ldots\)

(ii) Anhydrous potassium nitrate is heated with excess of metallic potassium. \(1992 - 1 \text{ Mark}\)

\(KNO_3(s) + K(s) \rightarrow \ldots \ldots + \ldots \ldots\)

(iii) \(NH_3 + NaClO \rightarrow \ldots \ldots + \ldots \ldots\) \(1993 - 1 \text{ Mark}\)

(iv) \(Sn + 2KOH + 4H_2O \rightarrow \ldots \ldots + \ldots \ldots\) \(1994 - 1 \text{ Mark}\)

19. Draw the structure of \(P_4O_{10}\) and identify the number of single and double \(P=O\) bonds. \(1996 - 3 \text{ Marks}\)

20. Gradual addition of \(KI\) solution to \(Bi(NO_3)_3\) solution initially produces a dark brown precipitate which dissolves in excess of \(KI\) to give a clear yellow solution. Write chemical equations for the above reactions. \(1996 - 2 \text{ Marks}\)

21. Complete the following chemical equations:

(a) \(KI + Cl_2 \rightarrow\) \(b) KClO₃ + I₂ \rightarrow\)

Justify the formation of the products in the above reactions. \(1996 - 2 \text{ Marks}\)

22. A soluble compound of a poisonous element \(M\), when heated with \(Zn/HSO_4\) gives a colourless and extremely poisonous gaseous compound \(N\), which on passing through a heated tube gives a silvery mirror of element \(M\). Identify \(M\) and \(N\). \(1997 - 2 \text{ Marks}\)

23. Draw the structure of a cyclic silicate, \((Si_2O_5)_x\) with proper labelling. \(1998 - 4 \text{ Marks}\)

24. Thionyl chloride can be synthesized by chlorinating \(SO_2\) using \(PCl_5\). Thionyl chloride is used to prepare anhydrous ferric chloride starting from its hexahydrated salt. Alternatively, the anhydrous ferric chloride can also be prepared from its hexahydrated salt by treating with 2, 2 - dimethoxypropane. Discuss all this using balanced chemical equations. \(1998 - 6 \text{ Marks}\)
25. Reaction of phosphoric acid with Ca₃(PO₄)₂F yields a fertilizer “triple superphosphate”. Represent the same through balanced chemical equation. *(1998 - 2 Marks)*

26. In the following equation, *(1999 - 6 Marks)*
\[ A + 2B + H₂O \rightarrow C + 2D \]
\( A = HNO₂, B = H₂SO₃, C = NH₂OH \). Identify D. Draw the structures of A, B, C and D.

27. In the contact process for industrial manufacture of sulphuric acid some amount of sulphuric acid is used as a starting material. Explain briefly. What is the catalyst used in the oxidation of SO₂? *(1999 - 4 Marks)*

28. The Haber process can be represented by the following scheme;

![Haber process diagram](image)

Identify A, B, C, D and E. *(1999 - 5 Marks)*

29. Give an example of oxidation of one halide by another halogen. Explain the feasibility of the reaction *(2000 - 2 Marks)*.

30. Draw the molecular structures of XeF₂, XeF₄ and XeO₂F₂ indicating the location of lone pair(s) of electrons. *(2000 - 3 Marks)*

31. Give reason(s) why elemental nitrogen exists as a diatomic molecule whereas elemental phosphorus as a tetraatomic molecule. *(2000 - 2 Marks)*

32. Compound (X) on reduction with LiAlH₄ gives a hydride (Y) containing 21.72% hydrogen along with other products. The compound (Y) reacts with air explosively resulting in boron trioxide. Identify (X) and (Y). Give balanced reactions involved in the formation of (Y) and its reaction with air. Draw the structure of (Y). *(2001 - 5 Marks)*

33. Starting from SiCl₄, prepare the following in steps not exceeding the number given in parentheses (give reactions only):
   (i) Silicon (1)
   (ii) Linear silicone containing methyl groups only (4)
   (iii) Na₂SiO₃ (3) *(2001 - 5 Marks)*

34. Write balanced equations for the reactions of the following compounds with water :
   (i) Al₄C₃
   (ii) CaNCN
   (iii) BF₃
   (iv) NCl₅
   (v) XeF₄ *(2002 - 5 Marks)*

35. How is boron obtained from borax? Give chemical equations with reaction conditions. Write the structure of B₂H₆ and its reaction with HCl. *(2002 - 5 Marks)*

36. Write down reactions involved in the extraction of Pb. What is the oxidation number of lead in litharge? *(2003 - 2 Marks)*

37. Identify the following:
   \[ \text{Na}_₂\text{CO}_₃ \xrightarrow{\text{SO}_₂} \text{A} \xrightarrow{\text{Na}_₂\text{CO}_₃} \text{B} \xrightarrow{\Delta} \text{C} \xrightarrow{\text{I}_₂} \text{D} \]

   Also mention the oxidation state of S in all the compounds.

38. AlF₃ is insoluble in anhydrous HF but it becomes soluble in presence of little amount of KF. Addition of boron trifluoride to the resulting solution causes reprecipitation of AlF₃. Explain with balanced chemical equations. *(2004 - 2 Marks)*

39. How many grams of CaO are required to neutralize 852 gm of P₄O₁₀? Draw structure of P₄O₁₀ molecule. *(2005 - 2 Marks)*

40. Write the structures of (CH₃)₃N and (Me₃Si)₃N. Are they isostuctural? Justify your answer. *(2005 - 2 Marks)*

41. \[ \text{NaBr} + \text{MnO}_₂ \xrightarrow{\text{(A)}} \xrightarrow{\text{Conc. HNO}_₃} \text{(C)} \]

   Identify the missing compounds. Give the equation from A to B and A to C. *(2005 - 4 Marks)*
Match the Following

**DIRECTIONS (Q. 1 to 3):** Each question contains statements given in two columns, which have to be matched. The statements in Column-I are labelled A, B, C and D, while the statements in Column-II are labelled p, q, r, s and t. Any given statement in Column-I can have correct matching with ONE OR MORE statement(s) in Column-II. The appropriate bubbles corresponding to the answers to these questions have to be darkened as illustrated in the following example:
If the correct matches are A-p, s and t; B-q and r; C-p and q; and D-s then the correct darkening of bubbles will look like the given.

1. Match gases under specified conditions listed in Column I with their properties/laws in Column II. Indicate your answer by darkening the appropriate bubbles of the $4 \times 4$ matrix given in the ORS.

**Column I**
(A) Explosive
(B) Artificial gem
(C) Self-reduction
(D) Magnetic material

**Column II**
(p) NaN$_3$
(q) Fe$_2$O$_4$
(r) Cu
(s) Al$_2$O$_3$
(t) Pb(N$_3$)$_2$
(u) Fe$_5$O$_3$
(v) Cu
(w) SiC

2. Match the following:

**Column I**
(A) $\text{Bi}^{3+} \rightarrow \text{(BiO)}^+$
(B) $\text{[AlO}_2\text{]}^\text{-} \rightarrow \text{Al(OH)}_3$
(C) $\text{[SiO}_4\text{]}^{4-} \rightarrow \text{[Si}_2\text{O}_7\text{]}^{6-}$
(D) $\text{[B}_2\text{O}_7\text{]}^{2-} \rightarrow \text{[B(OH)}_3\text{]}$

**Column II**
(p) Heat
(q) Hydrolysis
(r) Acidification
(s) Dilution by water

3. Match each of the diatomic molecules in Column I with its property/properties in Column II.

**Column I**
(A) $\text{B}_2$
(B) $\text{N}_2$
(C) $\text{O}_2$
(D) $\text{O}_2$

**Column II**
(p) Paramagnetic
(q) Undergoes oxidation
(r) Undergoes reduction
(s) Bond order $\geq 2$
(t) Mixing of 's' and 'p' orbital

**DIRECTIONS (for Q. 4):** Following question has matching lists. The codes for the lists have choices (a), (b), (c) and (d) out of which ONLY ONE is correct.

4. The unbalanced chemical reactions given in List I show missing reagent or condition (?) which are provided in List II. Match List I with List II and select the correct answer using the code given below the lists.

**List I**

| P | \( \text{PbO}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{PbSO}_4 + \text{O}_2 + \text{other product} \) |
| Q | \( \text{Na}_2\text{S}_2\text{O}_3 + \text{H}_2\text{O} \rightarrow \text{NaHSO}_4 + \text{other product} \) |
| R | \( \text{N}_2\text{H}_4 \rightarrow \text{N}_2 + \text{other product} \) |
| S | \( \text{XeF}_2 \rightarrow \text{Xe} + \text{other product} \) |

**List II**

1. NO
2. I$_2$
3. Warm
4. Cl$_2$

**Codes:**

<table>
<thead>
<tr>
<th>Code</th>
<th>P</th>
<th>Q</th>
<th>R</th>
<th>S</th>
</tr>
</thead>
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<td>(a)</td>
<td>4</td>
<td>2</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>(b)</td>
<td>3</td>
<td>2</td>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td>(c)</td>
<td>1</td>
<td>4</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>(d)</td>
<td>3</td>
<td>4</td>
<td>2</td>
<td>1</td>
</tr>
</tbody>
</table>
G Comprehension Based Questions

PASSAGE - 1
The noble gases have closed-shell electronic configuration and are monotonic gases under normal conditions. The low boiling points of the lighter noble gases are due to weak dispersion forces between the atoms and the absence of other interatomic interactions.

The direct reaction of xenon with fluorine leads to a series of compounds with oxidation numbers +2, +4 and +6. XeF₄ reacts violently with water to given XeO₃. The compounds of xenon exhibit rich stereochemistry and their geometries can be deduced considering the total number of electron pairs in the valence shell.

1. Argon is used in arc welding because of its (2007)
   (a) low reactivity with metal
   (b) ability to lower the melting point of metal
   (c) flammability
   (d) high calorific value

2. The structure of XeO₃ is (2007)
   (a) linear
   (b) planar
   (c) pyramidal
   (d) T-shaped

3. XeF₄ and XeF₆ are expected to be (2007)
   (a) oxidizing
   (b) reducing
   (c) unreactive
   (d) strongly basic

PASSAGE - 2
There are some deposits of nitrates and phosphates in earth’s crust. Nitrates are more soluble in water. Nitrates are difficult to reduce under the laboratory conditions but microbes do it easily. Ammonia forms large number of complexes with transition metal ions. Hybridization easily explains the ease of sigma donation capability of NH₃ and PH₃. Phosphine is a flammable gas and is prepared from white phosphorus.

4. Among the following, the correct statement is (2008)
   (a) Phosphates have no biological significance in humans
   (b) Between nitrates and phosphates, phosphates are less abundant in earth’s crust
   (c) Between nitrates and phosphates, nitrates are less abundant in earth’s crust
   (d) Oxidation of nitrates is possible in soil

5. Among the following, the correct statement is
   (a) Between NH₃ and PH₃, NH₃ is a better electron donor because the lone pair of electrons occupies spherical s-orbital and is less directional
   (b) Between NH₃ and PH₃, PH₃ is a better electron donor because the lone pair of electrons occupies sp³ orbital and is more directional

6. White phosphorus on reaction with NaOH gives PH₃ as one of the products. This is a
   (a) dimerization reaction
   (b) disproportionation reaction
   (c) condensation reaction
   (d) precipitation reaction

PASSAGE - 3
Bleaching powder and bleach solution are produced on a large scale and used in several household products. The effectiveness of bleach solution is often measured by iodometry. (2012 - II)

7. Bleaching powder contains a salt of an oxoacid as one of its components. The anhydride of that oxoacid is
   (a) Cl₂O
   (b) Cl₂O₇
   (c) ClO₂
   (d) Cl₂O₆

8. 25 mL of household solution was mixed with 30 mL of 0.50 M KI and 10 mL of 4N acetic acid. In the titration of the liberated iodine, 48 mL of 0.25 N Na₂S₂O₃ was used to reach the end point. The molarity of the household bleach solution is
   (a) 0.48 M
   (b) 0.96 M
   (c) 0.24 M
   (d) 0.024 M

PASSAGE - 4
The reactions of Cl₂ gas with cold-dilute and hot-concentrated NaOH in water give sodium salts of two (different) oxoacids of chlorine, P and Q, respectively. The Cl₂ gas reacts with SO₂ gas, in presence of charcoal, to give a product R. R reacts with white phosphorus to give a compound S. On hydrolysis, S gives an oxoacid of phosphorus, T. (JEE Adv. 2013)

9. P and Q, respectively, are the sodium salts of
   (a) Hypochlorous and chloric acids
   (b) Hypochlorus and chlorus acids
   (c) Chloric and perchloric acids
   (d) Chloric and hypochloric acids

10. R, S and T respectively, are
    (a) SO₂Cl₂, PCl₃ and H₃PO₄
    (b) SO₂Cl₂, PCl₃ and H₃PO₃
    (c) SOCl₂, PCl₃ and H₃PO₂
    (d) SOCl₂, PCl₃ and H₃PO₄
**Assertion & Reason Type Questions**

This question contains Statement-1 (Assertion/Statement) and Statement-2 (Reason/Explanation) and has 4 choices (a), (b), (c) and (d) out of which ONLY ONE is correct.

(a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1
(b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1
(c) Statement-1 is True, Statement-2 is False
(d) Statement-1 is False, Statement-2 is True.

1. **Statement-1**: Although PF₅, PCl₅ and PBr₅ are known, the pentahalides of nitrogen have not been observed
   **Statement-2**: Phosphorus has lower electronegativity than nitrogen.
   *(1994 - 2 Marks)*

2. **Statement-1**: F atom has less electron affinity than Cl atom.
   **Statement-2**: Additional electrons are repelled more effectively by 3p electrons in Cl atom than by 2p electrons in F atom.
   *(1998 - 2 Marks)*

3. **Statement-1**: Al(OH)₃ is amphoteric in nature
   **Statement-2**: Al–O and O–H bonds can be broken with equal ease in Al(OH)₃.
   *(1998 - 2 Marks)*

4. **Statement-1**: Between SiCl₄ and CCl₄, only SiCl₄ reacts with water.
   **Statement-2**: SiCl₄ is ionic and CCl₄ is covalent.
   *(2001 S)*

5. **Statement-1**: In water, orthoboric acid behaves as a weak monobasic acid.
   **Statement-2**: In water, orthoboric acid acts as a proton donor.
   *(2007)*

6. **Statement-1**: Boron always forms covalent bond because
   **Statement-2**: The small size of B³⁺ favours formation of covalent bond.
   *(2007)*

7. **Statement-1**: Pb⁴⁺ compounds are stronger oxidising agents than Sn⁴⁺ compounds
   **Statement-2**: The higher oxidation states for the group 14 elements are more stable for the heavier members of the group due to 'inert pair effect'.
   *(2008)*

**Integer Value Correct Type**

1. The coordination number of Al in the crystalline state of AlCl₃ is
   *(2009)*

2. The value of n in the molecular formula BeₙAl₂Si₆O₁₈ is
   *(2010)*

3. Reaction of Br₂ with Na₂CO₃ in aqueous solution gives sodium bromide and sodium bromate with evolution of CO₂ gas. The number of sodium bromide molecules involved in the balanced chemical equation is
   *(2011)*

4. Among the following, the number of compounds that can react with PCl₅ to give POCI₃ is
   O₂, CO₂, SO₂, H₂O, H₂SO₄, P₄O₁₀
   *(2011)*

5. The total number of lone pairs of electrons in N₂O₃ is
   *(JEE Adv. 2015)*

6. Three moles of B₂H₆ are completely reacted with methanol. The number of moles of boron containing product formed is
   *(JEE Adv. 2015)*
1. Alum helps in purifying water by
   (a) forming Si complex with clay particles
   (b) sulphate part which combines with the dirt and removes it
   (c) coagulaing the mud particles
   (d) making mud water soluble.

2. In XeF$_2$, XeF$_4$, XeF$_6$ the number of lone pairs on Xe are respectively
   (a) 2, 3, 1
   (b) 1, 2, 3
   (c) 4, 1, 2
   (d) 3, 2, 1.

3. In case of nitrogen, NCl$_3$ is possible but not NCl$_2$ while in case of phosphorous, PCl$_3$ as well as PCl$_5$ are possible. It is due to
   (a) availability of vacant $d$ orbitals in P but not in N
   (b) lower electronegativity of P than N
   (c) lower tendency of H-bond formation in P than N
   (d) occurrence of P in solid while N in gaseous state at room temperature.

4. Which of the following statements is true?
   (a) HF is less polar than HBr
   (b) absolutely pure water does not contain any ions
   (c) chemical bond formation take place when forces of attraction overcome the forces of repulsion
   (d) in covalency transference of electron takes place.

5. Number of sigma bonds in P$_4$O$_{10}$ is
   (a) 6
   (b) 7
   (c) 17
   (d) 16.

6. Oxidation number of Cl in CaOCl$_2$ (bleaching power) is:
   (a) zero, since it contains Cl$_2$
   (b) $-1$, since it contains Cl$^-$
   (c) $+1$, since it contains ClO$^-$
   (d) $+1$ and $-1$ since it contains ClO$^-$ and Cl$^-$

7. What may be expected to happen when phosphine gas is mixed with chlorine gas?
   (a) PCl$_3$ and HCl are formed and the mixture warms up
   (b) PCl$_3$ and HCl are formed and the mixture cools down
   (c) PH$_3$.Cl$_2$ is formed with warming up
   (d) The mixture only cools down

8. Concentrated hydrochloric acid when kept in open air sometimes produces a cloud of white fumes. The explanation for it is that
   (a) oxygen in air reacts with the emitted HCl gas to form a cloud of chlorine gas
   (b) strong affinity of HCl gas for moisture in air results in forming of droplets of liquid solution which appears like a cloudy smoke
   (c) due to strong affinity for water, concentrated hydrochloric acid pulls moisture of air towards itself. This moisture forms droplets of water and hence the cloud.
   (d) concentrated hydrochloric acid emits strongly smelling HCl gas all the time.

9. Graphite is a soft solid lubricant extremely difficult to melt. The reason for this anomalous behaviour is that graphite
   (a) is an allotropic form of diamond
   (b) has molecules of variable molecular masses like polymers
   (c) has carbon atoms arranged in large plates of rings of strongly bound carbon atoms with weak interplate bonds
   (d) is a non-crystalline substance

10. Glass is a
    (a) super-cooled liquid
    (b) gel
    (c) polymeric mixture
    (d) micro-crystalline solid

11. Which one of the following substances has the highest proton affinity?
    (a) H$_2$S
    (b) NH$_3$
    (c) PH$_3$
    (d) H$_2$O

12. For making good quality mirrors, plates of float glass are used. These are obtained by floating molten glass over a liquid metal which does not solidify before glass. The metal used can be
    (a) tin
    (b) sodium
    (c) magnesium
    (d) mercury
13. Which among the following factors is the most important in making fluorine the strongest oxidizing halogen?
   (a) Hydration enthalpy  
   (b) Ionization enthalpy  
   (c) Electron affinity  
   (d) Bond dissociation energy

14. Which one of the following statement regarding helium is incorrect?  
   (a) It is used to produce and sustain powerful superconducting magnets  
   (b) It is used as a cryogenic agent for carrying out experiments at low temperatures  
   (c) It is used to fill gas balloons instead of hydrogen because it is lighter and non-inflammable  
   (d) It is used in gas-cooled nuclear reactors

15. Bevillium and aluminium exhibit many properties which are similar. But, the two elements differ in
   (a) forming covalent halides  
   (b) forming polymeric hydrides  
   (c) exhibiting maximum covalency in compounds  
   (d) exhibiting amphoteric nature in their oxides

16. Aluminium chloride exists as dimer, Al₂Cl₆ in solid state as well as in solution of non-polar solvents such as benzene. When dissolved in water, it gives
   (a) [Al(OH)₆]³⁻ + 3HCl  
   (b) [Al(H₂O)₆]³⁺ + 3Cl⁻  
   (c) Al³⁺ + 3Cl⁻  
   (d) Al₂O₃ + 6HCl

17. Excess of KI reacts with CuSO₄ solution and then Na₂S₂O₃ solution is added to it. Which of the statements is incorrect for this reaction?
   (a) Na₂S₂O₃ is oxidised  
   (b) Cu₂⁺ is formed  
   (c) Cu₂⁺ is formed  
   (d) Evolved I₂ is reduced

18. The number of hydrogen atom(s) attached to phosphorus atom in hypophosphorous acid is
   (a) three  
   (b) one  
   (c) two  
   (d) zero

19. The correct order of the thermal stability of hydrogen halides (H–X) is
   (a) HI > HCl < HF > HBr  
   (b) HCl < HF < HBr < HI  
   (c) HF > HCl < HBr > HI  
   (d) HI < HBr < HCl < HF

20. Heating an aqueous solution of aluminium chloride to dryness will give
   (a) Al(OH)Cl₂  
   (b) Al₂O₃  
   (c) Al₂Cl₆  
   (d) AlCl₃

21. In silicon dioxide
   (a) there are double bonds between silicon and oxygen atoms  
   (b) silicon atom is bonded to two oxygen atoms  
   (c) each silicon atom is surrounded by two oxygen atoms and each oxygen atom is bonded to two silicon atoms  
   (d) each silicon atom is surrounded by four oxygen atoms and each oxygen atom is bonded to two silicon atoms

22. The structure of diborane (B₂H₆) contains
   (a) four 2c-2e bonds and four 3c-2e bonds  
   (b) two 2c-2e bonds and two 3c-3e bonds  
   (c) two 2c-2e bonds and four 3c-2e bonds  
   (d) four 2c-2e bonds and two 3c-2e bonds

23. Which of the following statements is true?
   (a) HClO₄ is a weaker acid than HClO₃  
   (b) HNO₃ is a stronger acid than HNO₂  
   (c) H₃PO₃ is a stronger acid than H₂SO₃  
   (d) In aqueous medium HF is a stronger acid than HCl

24. The increasing order of the first ionization enthalpies of the elements B, P, S and F (Lowest first) is
   (a) B < P < S < F  
   (b) B < S < P < F  
   (c) F < S < P < B  
   (d) P < S < B < F

25. What products are expected from the disproportionation reaction of hypochlorous acid?
   (a) HCl and Cl₂O  
   (b) HCl and HClO₃  
   (c) HClO₃ and Cl₂O  
   (d) HClO₂ and HClO₄

26. Identify the incorrect statement among the following.
   (a) Br₂ reacts with hot and strong NaOH solution to give NaBr and H₂O.  
   (b) Ozone reacts with SO₂ to give SO₃.  
   (c) Silicon reacts with NaOHₙ to give Na₂SiO₃ and H₂O.  
   (d) Cl₂ reacts with excess of NH₃ to give N₂ and HCl.
27. Regular use of the following fertilizers increases the acidity of soil? [2007]
   (a) Ammonium sulphate
   (b) Potassium nitrate
   (c) Urea
   (d) Superphosphate of lime.

28. Which one of the following is the correct statement? [2008]
   (a) Boric acid is a protonic acid
   (b) Beryllium exhibits coordination number of six
   (c) Chlorides of both beryllium and aluminium have bridged chloride structures in solid phase
   (d) B₂H₆, 2NH₃ is known as ‘inorganic benzene’

29. Which one of the following reactions of xenon compounds is not feasible? [2009]
   (a) 3XeF₄ + 6H₂O → 2Xe + XeOF₃ + 12HF + 1.5O₂
   (b) 2XeF₂ + 2H₂O → 2Xe + 4HF + O₂
   (c) XeF₆ + RbF → Rb[XeF₇]
   (d) XeOF₃ + 6HF → XeF₆ + 3H₂O

30. Which of the following statement is wrong? [2011]
   (a) The stability of hydride increases from NH₃ to BiH₃ in group 15 of the periodic table.
   (b) Nitrogen cannot form dπ − pπ bond.
   (c) Single N − N bond is weaker than the single P − P bond.
   (d) N₂O₄ has two resonance structures.

31. Which of the following statements regarding sulphur is incorrect? [2011]
   (a) S₈ molecule is paramagnetic.
   (b) The vapour at 200°C consists mostly of S₈ rings.
   (c) At 600°C the gas mainly consists of S₂ molecules.
   (d) The oxidation state of sulphur is never less than +4 in its compounds.

32. Boron cannot form which one of the following anions? [2011]
   (a) BF₆³⁻
   (b) BH₄⁻
   (c) B(OH)₄⁻
   (d) BO₂⁻

33. The molecule having smallest bond angle is: [2012]
   (a) NCl₃
   (b) AsCl₃
   (c) SbCl₃
   (d) PCl₃

34. Among the following oxacids, the correct decreasing order of acid strength is: [JEE M 2014]
   (a) HOCl > HClO₂ > HClO₃ > HClO₄
   (b) HClO₄ > HOCl > HClO₂ > HClO₃
   (c) HClO₄ > HClO₃ > HClO₂ > HOCl
   (d) HClO₂ > HClO₄ > HClO₃ > HOCl

35. Which one of the following properties is not shown by NO? [JEE M 2014]
   (a) It is diamagnetic in gaseous state
   (b) It is neutral oxide
   (c) It combines with oxygen to form nitrogen dioxide
   (d) It’s bond order is 2.5

36. The correct statement for the molecule, CsI₃ is: [JEE M 2014]
   (a) It is a covalent molecule.
   (b) It contains Cs⁺ and I₃⁻ ions.
   (c) It contains Cs³⁺ and I⁻ ions.
   (d) It contains Cs⁺, I⁻ and lattice I₂ molecule.

37. Which among the following is the most reactive? [JEE M 2015]
   (a) I₂
   (b) ICl
   (c) Cl₂
   (d) Br₂

38. Assertion: Nitrogen and oxygen are the main components in the atmosphere but these do not react to form oxides of nitrogen.
   Reason: The reaction between nitrogen and oxygen requires high temperature. [JEE M 2015]
   (a) The assertion is incorrect, but the reason is correct
   (b) Both the assertion and reason are incorrect
   (c) Both assertion and reason are correct, and the reason is the correct explanation for the assertion
   (d) Both assertion and reason are correct, but the reason is not the correct explanation for the assertion

39. Which one has the highest boiling point? [JEE M 2015]
   (a) Kr
   (b) Xe
   (c) He
   (d) Ne

40. The pair in which phosphorous atoms have a formal oxidation state of +3 is: [JEE M 2016]
   (a) Orthophosphorous and hypophosphoric acids
   (b) Pyrophosphorous and pyrophosphoric acids
   (c) Orthophosphorous and pyrophosphorous acids
   (d) Pyrophosphorous and hypophosphoric acids

41. The reaction of zinc with dilute and concentrated nitric acid, respectively, produces: [JEE M 2016]
   (a) NO and N₂O
   (b) NO₂ and N₂O
   (c) N₂O and NO₃
   (d) NO₂ and NO
CHAPTER 17
The d- and f-Block Elements and Co-ordination Compounds

Section-A

JEE Advanced / IIT-JEE

A

Fill in the Blanks

1. AgCN dissolves in excess KCN solution to give the complex compound ...........
   (1980)
2. Mn$^{2+}$ can be oxidised to MnO$_4^-$ by ..............
   (SnO$_2$, Pbo$_2$, BaO$_2$) (1981 - 1 Mark)
3. Galvanization of iron denotes coating with ..............
   (1983 - 1 Mark)
4. Silver chloride is sparingly soluble in water because its lattice energy is greater than .......... energy.
   (1987 - 1 Mark)
5. The salts ............. and ............. are isostructural.
   (FeSO$_4$. 7H$_2$O, CuSO$_4$. 5H$_2$O, MnSO$_4$. 4H$_2$O, ZnSO$_4$. 7H$_2$O) (1988 - 1 Mark)
6. The type of magnetism exhibited by [Mn(H$_2$O)$_6$]$^{2+}$ ion is .............
   (1994 - 1 Mark)
7. The IUPAC name of [Co(NH$_3$)$_3$]Cl$_3$ is .............
   (1994 - 1 Mark)
8. When Fe(s) is dissolved in aqueous hydrochloric acid in a closed vessel, the work done is ............
   (1997 - 1 Mark).
9. Silver jewellery items tarnish slowly in the air due to their reaction with .............
   (1997 - 1 Mark)

B
True / False

1. Copper metal reduces Fe$^{2+}$ in an acid medium. (1982 - 1 Mark)
2. Silver fluoride is fairly soluble in water. (1982 - 1 Mark)
3. Silver chloride is more soluble in very concentrated sodium chloride solution than in pure water. (1984 - 1 Mark)
4. Dipositive zinc exhibits paramagnetism due to loss of two electrons from 3d-orbital of neutral atom. (1987 - 1 Mark)
5. Both potassium ferrocyanide and potassium ferricyanide are diamagnetic. (1989 - 1 Mark)
6. Cu$^+$ disproportionates to Cu$^{2+}$ and elemental copper in solution. (1991 - 1 Mark)

C
MCQs with One Correct Answer

1. When same amount of zinc is treated separately with excess of sulphuric acid and excess of sodium hydroxide, the ratio of volume of hydrogen evolved is (1979)
   (a) 1 : 1 (b) 1 : 2 (c) 2 : 1 (d) 9 : 4
2. Which of the following is the weakest base (1980)
   (a) NaOH (b) Ca(OH)$_2$ (c) KOH (d) Zn(OH)$_2$
3. One of the constituent of German silver is (1980)
   (a) Ag (b) Cu (c) Mg (d) Al
   (a) Fe (b) Zn (c) Cu (d) Ag
5. How many unpaired electrons are present in Ni$^{2+}$? (1981 - 1 Mark)
   (a) 0 (b) 2 (c) 4 (d) 8
6. Sodium thiosulphate is used in photography because of its (1981 - 1 Mark)
   (a) reducing behaviour (b) oxidising behaviour (c) complex forming behaviour (d) reaction with light
7. Iron is rendered passive by treatment with concentrated (1982 - 1 Mark)
   (a) H$_2$SO$_4$ (b) H$_3$PO$_4$ (c) HCl (d) HNO$_3$
8. In the metallurgy of iron, when limestone is added to the blast furnace, the calcium ion ends up in (1982 - 1 Mark)
   (a) slag (b) gangue (c) metallic calcium (d) calcium carbonate
9. Zinc-copper couple that can be used as a reducing agent is obtained by : (1984 - 1 Mark)
   (a) mixing zinc dust and copper gauze (b) zinc coated with copper (c) copper coated with zinc (d) zinc and copper wires welded together
10. Amongst the following, the lowest degree of paramagnetism per mole of the compound at 298 K will be shown by (1988 - 1 Mark)
    (a) MnSO$_4$. 4H$_2$O (b) CuSO$_4$. 5H$_2$O (c) FeSO$_4$. 6H$_2$O (d) NiSO$_4$. 6H$_2$O
11. Amongst Ni(CO)₄, [Ni(CN)₄]²⁻ and NiCl₄²⁻

(1991 - 1 Mark)

(a) Ni(CO)₄ and NiCl₂⁻ are diamagnetic and [Ni(CN)₄]²⁻ is paramagnetic
(b) NiCl₄²⁻ and [Ni(CN)₄]²⁻ are diamagnetic and Ni(CO)₄ is paramagnetic
(c) Ni(CO)₄ and [Ni(CN)₄]²⁻ are diamagnetic and NiCl₂⁻ is paramagnetic
(d) Ni(CO)₄ is diamagnetic and NiCl₄²⁻ and [Ni(CN)₄]²⁻ are paramagnetic

12. Which one is solder?

(1995S)

(a) Cu & Pb (b) Zn & Cu (c) Pb & Sn (d) Fe & Zn

13. Which pair gives Cl₂ at room temperature?

(1995S)

(a) HCl(α) + KMnO₄ (b) NaCl + H₂SO₄(α) (c) NaCl + MnO₃ (d) NaCl + HNO₃(α)

14. Which compound is formed when excess of KCN is added to aqueous solution of copper sulphate?

(1996 - 1 Mark)

(a) Cu(CN)₂⁻ (b) K₂[Cu(CN)₄] (c) K₂Cu(CN)₃ (d) K₃Cu(CN)₅

15. Which compound does not dissolve in hot, dilute HNO₃?

(a) HgS (b) PbS (1996 - 1 Mark) (c) CuS (d) CdS

16. An aqueous solution of FeSO₄, Al₂(SO₄)₃ and chrome alum is heated with excess of Na₂O₂ and filtered. The materials obtained are:

(1996 - 1 Mark)

(a) a colourless filtrate and a green residue
(b) a yellow filtrate and a green residue
(c) a yellow filtrate and a brown residue
(d) a green filtrate and a brown residue

17. Ammonium dichromate is used in some fireworks. The green coloured powder blown in the air is

(1997 - 1 Mark)

(a) CrO₃ (b) Cr₂O₃ (c) Cr (d) Cr₂O₃

18. The number of moles of KMnO₄ that will be needed to react with one mole of sulphite ion in acidic solution is

(1997 - 1 Mark)

(a) \( \frac{2}{5} \) (b) \( \frac{3}{5} \) (c) \( \frac{4}{5} \) (d) 1

19. Which of the following is an organometallic compound?

(1997 - 1 Mark)

(a) Lithium methoxide (b) Lithium acetate (c) Lithium dimethylamide (d) Methyl lithium.

20. Which of the following compounds is expected to be coloured?

(1997 - 1 Mark)

(a) Ag₂SO₄ (b) CuF₂ (c) MgF₂ (d) CuCl

21. In the dichromate anion,

(1999 - 2 Marks)

(a) 4 Cr – O bonds are equivalent
(b) 6 Cr – O bonds are equivalent
(c) all Cr – O bonds are equivalent
(d) all Cr – O bonds are nonequivalent

22. The geometry of Ni(CO)₄ and Ni(PPh₃)₂Cl₂ are

(1999 - 2 Marks)

(a) both square planar
(b) tetrahedral and square planar, respectively
(c) both tetrahedral
(d) square planar and tetrahedral, respectively

23. The chemical processes in the production of steel from haematite ore involve

(2000S)

(a) reduction
(b) oxidation
(c) reduction followed by oxidation
(d) oxidation followed by reduction

24. The complex ion which has no ‘d’ electron in the central metal atom is

(2001S)

(a) [MnO₄]⁻ (b) [Co(NH₃)₆]³⁺ (c) [Fe(CN)₆]³⁻ (d) [Cr(H₂O)₆]³⁺

25. Anhydrous ferric chloride is prepared by

(2002S)

(a) heating hydrated ferric chloride at a high temperature in a stream of air
(b) heating metallic iron in a stream of dry chlorine gas
(c) reaction of metallic iron with hydrochloric acid
(d) reaction of metallic iron with nitric acid

26. When MnO₃ is fused with KOH, a coloured compound is formed, the product and its colour is:

(2003S)

(a) K₂MnO₄, purple green (b) KMnO₄, purple (c) Mn₂O₇, brown (d) Mn₃O₄, black

27. In the process of extraction of gold,

(2003S)

Roasted gold ore + CN⁻ + H₂O → [X]²⁻ + OH⁻

[X] + Zn → [Y] + Au

Identify the complexes [X] and [Y]

(a) X = [Au(CN)₄]⁺, Y = [Zn(CN)₄]²⁻
(b) X = [Au(CN)₃]⁻, Y = [Zn(CN)₄]²⁻
(c) X = [Au(CN)₃]⁻, Y = [Zn(CN)₄]⁻
(d) X = [Au(CN)₃]⁻, Y = [Zn(CN)₄]²⁻

28. The species having tetrahedral shape is

(2004S)

(a) [PdCl₄]²⁻ (b) [Ni(CN)₄]²⁻ (c) [Pd(CN)₄]²⁻ (d) [NiCl₄]²⁻

29. The spin magnetic moment of cobalt in the compound Hg₄[Co(SCN)₄] is

(2004S)

(a) \( \sqrt{3} \) (b) \( \sqrt{8} \) (c) \( \sqrt{15} \) (d) \( \sqrt{24} \)
30. The product of oxidation of I\(^-\) with MnO\(_4^+\) in alkaline medium is (2004S)
   (a) IO\(_3^-\)
   (b) I\(_2\)
   (c) IO\(_2^-\)
   (d) IO\(_4^-\)
31. (NH\(_4\))\(_3\)Cr\(_2\)O\(_7\) on heating liberates a gas. The same gas will be obtained by (2004S)
   (a) heating NH\(_4\)NO\(_2\)
   (b) heating NH\(_4\)NO\(_3\)
   (c) treating H\(_2\)O\(_2\) with NaN\(_3\)
   (d) treating Mg\(_3\)N\(_2\) with H\(_2\)O
32. Which pair of compounds is expected to show similar colour in aqueous medium? (2005S)
   (a) FeCl\(_3\) and CuCl\(_2\)
   (b) VOCl\(_3\) and CuCl\(_2\)
   (c) VOCl\(_3\) and FeCl\(_3\)
   (d) FeCl\(_3\) and MnCl\(_2\)
33. Which kind of isomerism is exhibited by octahedral Co(NH\(_3\))\(_3\)Br\(_2\)Cl? (2005S)
   (a) Geometrical and Ionization
   (b) Geometrical and Optical
   (c) Optical and Ionization
   (d) Geometrical only
34. CuSO\(_4\) decolourises on addition of KCN, the product formed is (2006 - 3M, -1)
   (a) Cu\(^{2+}\) get reduced to form [Cu(CN)]\(^{4-}\)
   (b) [Cu(CN)]\(^{3-}\)
   (c) CuCN
   (d) Cu(CN)\(_2\)
35. Among the following metal carboxyls, the C–O bond order is lowest in (2007)
   (a) [Mn(CO)]\(^{3+}\)
   (b) [Fe(CO)]\(^{2-}\)
   (c) [Cr(CO)]\(^3\)
   (d) [V(CO)]\(^4\)
36. Native silver metal forms a water soluble complex with a dilute aqueous solution of NaCN in the presence of (2008)
   (a) nitrogen
   (b) oxygen
   (c) carbon dioxide
   (d) argon
37. Among the following, the coloured compound is (2008)
   (a) CuCl
   (b) K\(_3\) [Cu (CN)]\(_3\)
   (c) CuF\(_3\)
   (d) [Cu(CH\(_3\)CN)]BF\(_4\)
38. The IUPAC name of [Ni(NH\(_3\))\(_4\)] [NiCl\(_4\)] is (2008)
   (a) Tetrachloronickel (II) - tetraamminenickel (II)
   (b) Tetraamminenickel (II) - tetraamminenickel (II)
   (c) Tetraamminenickel (II) - tetraamminenickel (II)
   (d) Tetraamminenickel (II) - tetraamminenickel (II)
39. Both [Ni(CO)]\(_4\) and [Ni(CN)]\(^{2-}\) are diamagnetic. The hybridisations of nickel in these complexes, respectively, are (2008)
   (a) sp\(^3\), sp\(^3\)
   (b) sp\(^3\), dsp\(^2\)
   (c) dsp\(^2\), sp\(^3\)
   (d) dsp\(^2\), sp\(^3\)
40. The spin only magnetic moment value (in Bohr magneton units) of Cr(CO\(_6\)) is (2009)
   (a) 0
   (b) 2.84
   (c) 4.90
   (d) 5.92
41. The ionisation isomer of [Cr(H\(_2\)O\(_4\))[Cl(NO\(_3\))] is (2010)
   (a) [Cr(H\(_2\)O\(_4\))[Cl\(_2\)]
   (b) [Cr(H\(_2\)O\(_4\))[Cl\(_2\)]
   (c) [Cr(H\(_2\)O\(_4\))[Cl(NO\(_3\))]
   (d) [Cr(H\(_2\)O\(_4\))[Cl\(_2\)]
42. The correct structure of ethylenediaminetetraacetic acid (EDTA) is (2010)
   (a) HOOC – H\(_2\)C
   (b) HOOC – H\(_2\)C
   (c) HOOC – H\(_2\)C
   (d) HOOC – H\(_2\)C
43. The complex showing a spin-only magnetic moment of 2.82 B.M. is : (2010)
   (a) Ni(CO\(_4\))
   (b) NiCl\(_4\)\(^3-\)
   (c) Ni(PPh\(_3\))\(_4\)
   (d) Ni(CN\(_4\))\(^2-\)
44. Among the following complexes (K–P)
   K\(_3\) [Fe(CN)]\(_3\) (K), [Co(NH\(_3\))\(_3\)]Cl\(_3\) (L), Na\(_3\) [Co(oxalate)]\(_3\) (M), the [Ni(H\(_2\)O\(_2\))\(_2\)] \(_2\) (N), K\(_2\) [Pt(CN\(_4\))] \(_2\) (O) and [Zn(H\(_2\)O\(_2\))\(_2\)] \(_2\) (P) the diamagnetic complexes are (2011)
   (a) K, L, M, N
   (b) K, M, O, P
   (c) L, M, O, P
   (d) L, M, N, O
45. As per IUPAC nomenclature, the name of the complex [Co(H\(_2\)O\(_4\))[NH\(_3\)]Cl\(_2\)] is : (2012)
   (a) Tetraaquadinicobalt (III) chloride
   (b) Tetraaquadinicobalt (III) chloride
   (c) Diaminetetraaquocobalt (II) chloride
   (d) Diaminetetraaquocobalt (III) chloride
46. The colour of light absorbed by an aqueous solution of CuSO\(_4\) is: (2012)
   (a) orange-red
   (b) blue-green
   (c) yellow
   (d) violet
47. NiCl\(_2\) \(_2\) [P(C\(_2\)H\(_5\))\(_2\)(C\(_6\)H\(_5\))]\(_2\) exhibits temperature depend-ent magnetic behaviour (paramagnetic/diamagnetic). The coordination geometries of Ni\(^{2+}\) in the paramagnetic and diamagnetic states are respectively (2012)
   (a) tetrahedral and tetrahedral
   (b) square planar and square planar
   (c) tetrahedral and square planar
   (d) square planar and tetrahedral
48. Consider the following complex ions, P, Q and R.
P = [FeF₆]³⁻, Q = [V(H₂O)₆]²⁺ and R = [Fe(H₂O)₆]²⁺
The correct order of the complex ions, according to their spin-only magnetic moments (in B.M.) is
(JEE Adv. 2013)
(a) R < Q < P  (b) Q < R < P  
(c) R < P < Q  (d) Q < P < R

49. Among [Ni(CO)₄], [NiCl₂], [Co(NH₃)₄Cl₂]Cl, Na₂[CoF₆], Na₂O₂ and CsO₂, the total number of paramagnetic compounds is (JEE Adv. 2016)
(a) 2  (b) 3  
(c) 4  (d) 5

D  MCQs with One or More Than One Correct

1. Potassium manganate (K₂MnO₄) is formed when (1988 - 1 Mark)
(a) chlorine is passed into aqueous KMnO₄ solution
(b) manganese dioxide is fused with potassium hydroxide in air
(c) formaldehyde reacts with potassium permanganate in presence of a strong alkali
(d) potassium permanganate reacts with conc. sulphuric acid

2. The aqueous solutions of the following salts will be coloured in the case of (1990 - 1 Mark)
(a) Zn(NO₃)₂   (b) LiNO₃
(c) Co(NO₃)₂   (d) CrCl₃
(e) Potash alum

3. Among the following ions which one has the highest paramagnetism? (1993 - 1 Mark)
(a) [Cr(H₂O)₆]³⁺   (b) [Fe(H₂O)₆]²⁺
(c) [Cu(H₂O)₆]²⁺   (d) [Zn(H₂O)₆]²⁺

4. Which of the following alloys contains Cu and Zn? (1993 - 1 Mark)
(a) Bronze  (b) Brass
(c) Gunmetal  (d) Type metal

5. In nitroprusside ion the iron and NO exist as Feᴵᴵ and NO⁺ rather than Feᴵᴵ⁺ and NO. These forms can be differentiated by (1998 - 2 Marks)
(a) estimating the concentration of iron
(b) measuring the concentration of CN⁻
(c) measuring the solid state magnetic moment
(d) thermally decomposing the compound.

6. Addition of high proportions of manganese makes steel useful in making rails of railroads, because manganese
(a) gives hardness to steel  (b) helps the formation of oxides of iron
(c) can remove oxygen and sulphur  (d) can show highest oxidation state of +7.

7. If the bond length of CO bond in carbon monoxide is 1.12Å, then what is the value of CO bond length in Fe(CO)₅? (2006 - 5M, -I)
(a) 1.15Å  (b) 1.128Å
(c) 1.13Å  (d) 1.118Å

8. The compound(s) that exhibit(s) geometrical isomerism is (are) (2009)
(a) [Pt(en)Cl₂]   (b) [Pt(en)₂]Cl₂
(c) [Pt(en)₂Cl₂]   (d) [Pt(NH₃)₂Cl₂]

9. Reduction of the metal centre in aqueous permanganate ion involves (2011)
(a) 3 electrons in neutral medium
(b) 5 electrons in neutral medium
(c) 3 electrons in alkaline medium
(d) 5 electrons in acidic medium

10. The equilibrium 2Cu⁺ ⇌ Cu⁰ + Cuᴵᴵ in aqueous medium at 25°C shifts towards the left in the presence of (2011)
(a) NO₃⁻   (b) Cl⁻
(c) SCN⁻   (d) CN⁻

11. For the given aqueous reactions, which of the statement (s) is (are) true? (2012)

\[ \text{excess KI} + K₃[Fe(CN)₆] \xrightarrow{\text{dilute H}_2\text{SO}_4} \text{brownish-yellow solution} \]
\[ \text{ZnSO}_4 \]
\[ \text{white precipitate} + \text{brownish-yellow filtrate} \]
\[ \text{Na}_2\text{S}_2\text{O}_3 \]
\[ \text{colourless solution} \]

(a) The first reaction is a redox reaction.
(b) White precipitate is Zn₃[Fe(CN)₆]₂⁻.
(c) Addition of filtrate to starch solution gives blue colour.
(d) White precipitate is soluble in NaOH solution.

12. The pair(s) of coordination complexes/ions exhibiting the same kind of isomerism is(are) (JEE Adv. 2013)
(a) [Cr(NH₃)₅Cl]Cl₂ and [Cr(NH₃)₄Cl₂]Cl
(b) [Co(NH₃)₄Cl₂]⁺ and [Pt(NH₃)₂(H₂O)Cl]⁺
(c) [CoBr₂Cl₂]²⁻ and [PtBr₂Cl₂]²⁻
(d) [Pt(NH₃)₃(NO)Cl] and [Pt(NH₃)₂Cl]Br

13. The pair(s) of reagents that yield paramagnetic species is/are (JEE Adv. 2014)
(a) Na and excess of NH₃
(b) K and excess of O₂
(c) Cu and dilute HNO₃
(d) O₂ and 2-ethylanthraquinol
The d- and f-Block Elements and Co-ordination Compounds

14. The correct statement(s) about Cr$^{3+}$ and Mn$^{3+}$ is(are)
   (a) Cr$^{2+}$ is a reducing agent
   (b) Mn$^{3+}$ is an oxidizing agent
   (c) Both Cr$^{2+}$ and Mn$^{3+}$ exhibit d$^4$ electronic configuration
   (d) When Cr$^{2+}$ is used as a reducing agent, the chromium ion attains d$^5$ electronic configuration

15. Fe$^{3+}$ is reduced to Fe$^{2+}$ by using *(JEE Adv. 2015)*
   (a) H$_2$O$_2$ in presence of NaOH
   (b) Na$_2$O$_2$ in water
   (c) H$_2$O$_2$ in presence of H$_2$SO$_4$
   (d) Na$_2$O$_2$ in presence of H$_2$SO$_4$

E  Subjective Problems

1. A certain inorganic compound (A) on heating loses its water of crystallisation. On further heating, a blackish brown powder (B) and two oxides of sulphur (C and D) are obtained. The powder (B) on boiling with hydrochloric acid gives a yellow solution (E). When H$_2$S is passed in (E) a white turbidity (F) and an apple green solution (G) are obtained. The solution (E) on treatment with thioacetate ions gives a blood red coloured compound (H). Identify compounds from (A) to (H). *(1978)*

2. A white amorphous powder (A) on heating yields a colourless, non-combustible gas (B) and a solid (C). The latter compound assumes a yellow colour on heating and changes to white on cooling. ‘C’ dissolves in dilute acid and the resulting solution gives a white precipitate on adding K$_4$Fe(CN)$_6$ solution.
   ‘A’ dissolves in dilute HCl with the evolution of gas, which is identical in all respects with ‘B’. The gas ‘B’ turns lime water milky, but the milkiness disappears with the continuous passage of gas. The solution of ‘A’, as obtained above, gives a white precipitate (D) on the addition of excess of NH$_4$OH and passing H$_2$S. Another portion of the solution gives initially a white precipitate (E) on the addition of sodium hydroxide solution, which dissolves on further addition of the base. Identify the compounds A, B, D, and E. *(1979)*

3. State with balanced equations what happens when
   (i) Silver is treated with hot concentrated sulphuric acid.
   (ii) Ammonium dichromate is heated.
   (iii) Hydrogen sulphide is passed through a solution of potassium permanganate acidified with dilute sulphuric acid. *(1979)*

4. A solution of FeCl$_3$ in water gives a brown precipitate on standing. *(1980)*

5. Complete the following equation (no balancing is needed):
   \[ \text{SO}_2 + \text{MnO}_4^- + \ldots \rightarrow \text{SO}_4^{2-} + \text{Mn}^{2+} + \ldots \]
   *(1981 - 1 Mark)*

6. State with balanced equations what happens when:
   (i) sulphur dioxide gas is bubbled through an aqueous solution of copper sulphate in presence of potassium thiocyanate. *(1982 - 1 Mark)*
   (ii) aqueous solution of ferric sulphate and potassium iodide are mixed. *(1984 - 2 Marks)*
   (iii) aqueous solution of potassium manganate and acid are mixed. *(1984 - 2 Marks)*
   (iv) aqueous solution of potassium chromate and acid are mixed. *(1984 - 2 Marks)*
   (v) potassium permanganate interacts with manganese dioxide in presence of potassium hydroxide; *(1985 - 1 Mark)*
   (vi) potassium ferrocyanide is heated with concentrated sulphuric acid; *(1985 - 1 Mark)*
   (vii) Gold is dissolved in *aqua regia*. *(1987 - 1 Mark)*
   (viii) Write balanced equations for the extraction of silver from silver glance by cyanide process. *(1988 - 1 Mark)*
   (ix) Silver chloride is treated with aqueous sodium cyanide and the product thus formed is allowed to react with zinc in alkaline medium. *(1989 - 1 Mark)*
   (x) Cobalt(II) solution reacts with KNO$_3$ in acetic acid medium. *(1989 - 1 Mark)*
   (xi) Write balanced equations for the extraction of copper from copper pyrites by self-reduction. *(1990 - 2 Marks)*
   (xii) A mixture of potassium dichromate and sodium chloride is heated with concentrated H$_2$SO$_4$. *(1990 - 1 Mark)*
   (xiii) Iron reacts with cold dilute nitric acid. *(1990 - 1 Mark)*
   (xiv) Potassium permanganate is added to a hot solution of manganous sulphate. *(1990 - 1 Mark)*
   (xv) Copper reacts with HNO$_3$ to give NO and NO$_2$ in molar ratio of 2:1. *(1992 - 1 Marks)*
   \[ \text{Cu} + \text{HNO}_3 \rightarrow \ldots + \text{NO} + \text{NO}_2 + \ldots \]
   (xvi) Na$_2$CO$_3$ is added to a solution of copper sulphate. *(1992 - 1 Marks)*
   \[ \text{CuSO}_4 + \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} \rightarrow \ldots + \text{Na}_2\text{SO}_4 + \ldots \]
   (xvii) Potassium dichromate and concentrated hydrochloric acid are heated together. *(1992 - 1 Mark)*
   (xviii) AgBr + Na$_2$S$_2$O$_3$ \rightarrow \ldots + \ldots \ *(1993 - 1 Mark)*
   (xix) (NH$_4$)$_2$S$_2$O$_8$ + H$_2$O + MnSO$_4$ \rightarrow \ldots + \ldots \ *(1993 - 1 Mark)*
   \[ [\text{MnO}_4^-]^2- + \text{H}^+ \rightarrow \ldots + [\text{MnO}_4^-]^\cdot + \text{H}_2\text{O} \]
   *(1994 - 1 Mark)*
(xxi) \( \text{SO}_2 \text{(aq)} + \text{Cr}_2 \text{O}_7^{2-} + 2\text{H}^+ \rightarrow \ldots \ldots \ldots \ldots \ldots \)  
(1994 - 1 Mark)

(xxii) Write a balanced equation for the reaction of argentite with KCN and name the products in solution.  
(1996 - 1 Mark)

(xxiii) Write balanced equations for the reaction of zinc with dilute nitric acid.  
(1997 - 1 Mark)

7. Give balanced equations for extraction of silver from its sulphide ore  
(1982 - 2 Marks)

8. Give reasons for the following :  
(i) Silver bromide is used in photography.  
(1983 - 1 Mark)

(ii) Most transition metal compounds are coloured.  
(1986 - 1 Mark)

(iii) Zinc and not copper is used for the recovery of metallic silver from complex \([\text{Ag(CN)}_2]^-\). Explain.  
(1987 - 1 Mark)

(iv) The colour of mercurous chloride, \(\text{Hg}_2\text{Cl}_2\), changes from white to black when treated with ammonia.  
(1988 - 1 Mark)

(1992 - 1 Mark)

(vi) \(\text{CrO}_3\) is an acid anhydride.  
(1999 - 2 Marks)

9. State the conditions under which the following preparation is carried out.  
Potassium permanganate from manganese hydroxide.  
Give the necessary equations which need not be balanced.  
(1983 - 1 Mark)

10. What happens when :  
(i) aqueous ammonia is added dropwise to a solution of copper sulphate till it is in excess.  
(1985 - 1 Mark)

(ii) \(\text{CrCl}_3\) solution is treated with sodium hydroxide and then with hydrogen peroxide.  
(1985 - 1 Mark)

11. Mention the products formed when zinc oxide is treated with excess of sodium hydroxide solution.  
(1986 - 1 Mark)

12. What is the actual reducing agent of haematite in blast furnace?  
(1987 - 1 Mark)

13. The acidic, aqueous solution of ferrous ion forms a brown complex in the presence of \text{NO}_3\text{-}, by the following two steps.  
Complete and balance the equations :  
(1993 - 2 Marks)

\[
\begin{align*}
\text{[Fe(H}_2\text{O)}_6]\text{H}^+ + \text{NO}_3^- + \text{H}^+ & \rightarrow \ldots \ldots + \text{[Fe(H}_2\text{O)}_6]\text{H}^+ + \text{H}_2\text{O} \\
\text{[Fe(H}_2\text{O)}_6]\text{H}^+ + \ldots \ldots & \rightarrow \ldots \ldots + \text{H}_2\text{O}
\end{align*}
\]

14. Identify the complexes which are expected to be coloured.  
Explain  
(1994 - 2 Marks)

(i) \([\text{Ti(NO)}_3]_4\)  
(ii) \([\text{Cu(NCCCH}_3)_4]^-\text{BF}_4^-\)  
(iii) \([\text{Cr(NH}_3)_6]^{3+}\text{Cl}^-\)  
(iv) \(\text{K}_3\text{[VF}_6]\)

15. Write down the IUPAC names of the following compounds:  
(i) \([\text{Co(NH}_3)_5\text{ONO}]\text{Cl}_2\)  
(1995 - 1 Mark)

(ii) \(\text{K}_3\text{[Cr(CN)}_6]\)  
(1995 - 1 Mark)

(iii) \([\text{Cr(NH}_3)_5\text{CO}_3]\text{Cl}\)  
(1996 - 1 Mark)

16. Compare qualitatively the first and second ionisation potentials of copper and zinc. Explain the observation.  
(1996 - 2 Marks)

17. Write the formulae of the following complexes:  
(i) Pentamminechlorocobalt(III)  
(1997 - 1 Mark)

(ii) Lithium tetrahydroaluminate(III)  
(1997 - 1 Mark)

18. When the ore haematite is burnt in air with coke around 2000°C along with lime, the process not only produces steel but also produces a silicate slag that is useful in making building materials such as cement. Discuss the same and show through balanced chemical equations.  
(1998 - 4 Marks)

19. Work out the following using chemical equations  
(1998 - 2 Marks)

In moist air copper corrodes to produce a green layer on the surface.

20. A, B, and C are three complexes of chromium (III) with the empirical formula \(\text{H}_2\text{O}_6\text{Cl}_2\text{Cr}\). All the three complexes have water and chloride ion as ligands. Complex A does not react with concentrated \(\text{H}_2\text{SO}_4\) whereas complexes B and C lose 6.75% and 13.5% of their original mass, respectively, on treatment with concentrated \(\text{H}_2\text{SO}_4\). Identify A, B and C.  
(1999 - 6 Marks)

21. Write the chemical reaction associated with the 'brown ring test'.  
(2000 - 2 Marks)

22. Draw the structures of \([\text{Co(NH}_3}_6]\)\(^{3+}\), \([\text{Ni(CN)}_4]\)\(^{-}\) and \([\text{Ni(CO)}_4]\). Write the hybridisation of atomic orbitals of the transition metal in each case.  
(2000 - 4 Marks)

23. (i) Write the chemical reactions involved in the extraction of metallic silver from argentite.  
(ii) Write the balanced chemical equation for developing photographic films.  
(2000 - 4 Marks)

24. A metal complex having composition \(\text{Cr(NH}_3)_2\text{Cl}_2\text{Br}\) has been isolated in two forms (A) and (B). The form (A) reacts with \(\text{AgNO}_3\) to give a white precipitate readily soluble in dilute aqueous ammonia, whereas (B) gives a pale yellow precipitate soluble in concentrated ammonia. Write the
The d- and f-Block Elements and Co-ordination Compounds

formula of (A) and (B) and state the hybridization of chromium in each. Calculate their magnetic moments (spin only value).

(2001 - 5 Marks)

25. Deduce the structure of [NiCl₂]²⁻ and [Ni(CN)₆]²⁻ considering the hybridization of the metal ion. Calculate the magnetic moment (spin only) of the species.

(2002 - 5 Marks)

26. Write the IUPAC nomenclature of the given complex along with its hybridisation and structure.

K₂[Cr(NO)(NH₃)₄] (CN)₄, µ = 1.73 BM (2003 - 4 Marks)

27. Nickel chloride, when treated with dimethylglyoxime in presence of ammonium hydroxide, a bright red precipitate is obtained. Answer the following.

(a) Draw the structure of the complex showing H-bonds
(b) Give oxidation state of nickel and its hybridisation
(c) Predict the magnetic behaviour of the complex

(2004 - 4 Marks)

28. Some reactions of two ores, A₁ and A₂ of the metal M are given below.

(2004 - 4 Marks)

\[ \text{[A₁]} \xrightarrow{\text{calcination}} \text{[C]} \downarrow +\text{CO}_2 + \text{H}_2\text{O} \]
\[ \text{KI/HCl} \rightarrow \text{[D]} \downarrow +\text{I}_2 \]

29. \[ \text{Fe}^{3+} \xrightarrow{\text{SCN}^-} \text{(A)} \xrightarrow{\text{Blood red colouration}} \text{(B)} \text{excess} \xrightarrow{\text{excess}} \text{colourless} \]

What are (A) and (B)? Give IUPAC name of (A). Find the spin only magnetic moment of (B).

(2005 - 4 Marks)

30. Write the chemical reaction involved in developing of a black and white photographic film. An aqueous Na₂S₂O₃ solution is acidified to give a milky white turbidity. Identify the product and write the balanced half chemical reaction for it.

(2005 - 4 Marks)

31. \[ \text{MCl}_4 \xrightarrow{\text{Zn}} \text{Purple colour compound; M = Transition metal} \]

\[ \text{MCl}_4 \xrightarrow{\text{moist air}} \text{(A)} \xrightarrow{\text{(B)}} \text{white fumes} \]

Identify (A), (B) and MCl₄. Also explain colour difference between MCl₄ and (A).

(2005 - 4 Marks)

**F** Match the Following

DIRECTIONS (Q. No. 1 and 2): Each question contains statements given in two columns, which have to be matched. The statements in Column-I are labelled A, B, C and D, while the statements in Column-II are labelled p, q, r, s and t. Any given statement in Column-I can have correct matching with ONE OR MORE statement(s) in Column-II. The appropriate bubbles corresponding to the answers to these questions have to be darkened as illustrated in the following example:

If the correct matches are A-p, s and t; B-q and r; C-p and q; and D-s then the correct darkening of bubbles will look like the given.

1. Match the complexes in Column I with their properties listed in Column II.

<table>
<thead>
<tr>
<th>Column I</th>
<th>Column II</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A) [Co(NH₃)₆(H₂O)₂]Cl₂</td>
<td>(p) geometrical isomers</td>
</tr>
<tr>
<td>(B) [Pt(NH₃)₂Cl₂]</td>
<td>(q) paramagnetic</td>
</tr>
<tr>
<td>(C) [Co(H₂O)₆]Cl₃</td>
<td>(r) diamagnetic</td>
</tr>
<tr>
<td>(D) [Ni(H₂O)₆]Cl₂</td>
<td>(s) metal ion with +2 oxidation state</td>
</tr>
</tbody>
</table>

(2007)

2. Match each of the reactions given in Column I with the corresponding product(s) given in Column II.

<table>
<thead>
<tr>
<th>Column I</th>
<th>Column II</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A) Cu + dil HNO₃</td>
<td>(p) NO</td>
</tr>
<tr>
<td>(B) Cu + conc HNO₃</td>
<td>(q) NO₂</td>
</tr>
<tr>
<td>(C) Zn + dil HNO₃</td>
<td>(r) N₂O</td>
</tr>
<tr>
<td>(D) Zn + conc HNO₃</td>
<td>(s) Cu(NO₃)₂</td>
</tr>
<tr>
<td></td>
<td>(t) Zn(NO₃)₂</td>
</tr>
</tbody>
</table>

(2009)
3. Match each coordination compound in List-I with an appropriate pair of characteristics from List-II and select the correct answer using the code given below the lists.

\{en = H₂NCH₂CH₂NH₂; atomic numbers: Ti = 22, Cr = 24, Co = 27, Pt = 78\}

**List-I**
- P. [Cr(NH₃₄Cl₂)Cl]
- Q. [Ti(H₂O)₅Cl](NO₃)₂
- R. [Pt(en)(NH₃)Cl]NO₃
- S. [Co(NH₃₄(NO₃)₂]NO₃

**List-II**
1. Paramagnetic and exhibits ionisation isomerism
2. Diamagnetic and exhibits cis-trans isomerism
3. Paramagnetic and exhibits cis-trans isomerism
4. Diamagnetic and exhibits ionisation isomerism

**Code:**

<table>
<thead>
<tr>
<th></th>
<th>P</th>
<th>Q</th>
<th>R</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>4</td>
<td>2</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>(b)</td>
<td>3</td>
<td>1</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>(c)</td>
<td>2</td>
<td>1</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>(d)</td>
<td>1</td>
<td>3</td>
<td>4</td>
<td>2</td>
</tr>
</tbody>
</table>

**G Comprehension Based Questions**

**PASSAGE 1**

The coordination number of Ni²⁺ is 4.

NiCl₂ + KCN (excess) → A (cyano complex)

NiCl₂ + Conc. HCl (excess) → B (chloro complex)

1. The IUPAC name of A and B are \(2006 - 5 M, -2\)
   - (a) Potassium tetracyanonicelate (II), potassium tetrachloronicelate (II)
   - (b) Tetracyanonicelate (II), tetrachloronicelate (II)
   - (c) Tetracyanonicelate (II), tetrachloronicelate (II)
   - (d) Potassium tetracyanonicelate (II), potassium tetrachloronicelate (II)

2. Predict the magnetic nature of A and B \(2006 - 5 M, -2\)
   - (a) Both are diamagnetic
   - (b) A is diamagnetic and B is paramagnetic with one unpaired electron
   - (c) A is diamagnetic and B is paramagnetic with two unpaired electrons
   - (d) Both are paramagnetic

3. The hybridization of A and B are \(2006 - 5 M, -2\)
   - (a) \(sp^2, sp^3\)
   - (b) \(sp^2, sp^3\)
   - (c) \(sp^2, sp^2\)
   - (d) \(sp^2d^2, d^2sp^3\)

**PASSAGE 2**

Copper is the most noble of the first row transition metals and occurs in small deposits in several countries. Ores of copper include chalcanthite (CuSO₄·5H₂O), atacamite (Cu₂Cl(OH)₂), cuprite (Cu₂O), copper glance (Cu₂S) and malachite (Cu₂(OH)₂CO₃). However, 80% of the world copper production comes from the ore chalcopyrite (CuFeS₂). The extraction of copper from chalcopyrite involves partial roasting, removal of iron and self-reduction.

4. Partial roasting of chalcopyrite produces
   - (a) \(CuS\) and FeO
   - (b) \(CuO\) and FeO
   - (c) CuS and Fe₂O₃
   - (d) \(CuO\) and Fe₂O₃

5. Iron is removed from chalcopyrite as
   - (a) FeO
   - (b) FeS
   - (c) Fe₂O₃
   - (d) FeSiO₃

6. In self-reduction, the reducing species is
   - (a) S
   - (b) \(O^{2-}\)
   - (c) \(S^{2-}\)
   - (d) \(SO₂\)

**PASSAGE 3**

When a metal rod M is dipped into an aqueous colourless concentrated solution of compound N, the solution turns light blue. Addition of aqueous NaCl to the blue solution gives a white precipitate O. Addition of aqueous NH₃ dissolves O and gives an intense blue solution.

7. The metal rod M is
   - (a) Fe
   - (b) Cu
   - (c) Ni
   - (d) CO

8. The compound N is
   - (a) AgNO₃
   - (b) Zn(NO₃)₂
   - (c) Al(NO₃)₃
   - (d) Pb(NO₃)₂

9. The final solution contains
   - (a) \([\text{Pb(NH}_3)_4]^{2+}\) and \([\text{CoCl}_4]^{2-}\)
   - (b) \([\text{Al(NH}_3)_4]^{3+}\) and \([\text{Cu(NH}_3)_4]^{2+}\)
   - (c) \([\text{Ag(NH}_3)_2]^{+}\) and \([\text{Cu(NH}_3)_4]^{2+}\)
   - (d) \([\text{Ag(NH}_3)_2]^{+}\) and \([\text{Ni(NH}_3)_6]^{2+}\)
Assertion & Reason Type Questions

1. **Statement-1**: To a solution of potassium chromate if a strong acid is added it changes its colour from yellow to orange.
   **Statement-2**: The colour change is due to the oxidation of potassium chromate.
   (1988 - 2 Marks)

2. **Statement-1**: Zn$^{2+}$ is diamagnetic.
   **Statement-2**: Two electrons are lost from 4s orbital to form Zn$^{2+}$.
   (1998 - 2 Marks)

3. **Statement-1**: The geometrical isomers of the complex [M(NH$_3$)$_4$Cl$_2$] are optically inactive.
   **Statement-2**: Both geometrical isomers of the complex [M(NH$_3$)$_4$Cl$_2$] possess axis of symmetry.
   (2008 - 2 Marks)

4. **Statement-1**: [Fe(H$_2$O)$_5$NO]SO$_4$ is paramagnetic.
   **Statement-2**: The Fe in [Fe(H$_2$O)$_5$NO]SO$_4$ has three unpaired electrons.
   (2008)

Integer Value Correct Type

1. The number of water molecule(s) directly bonded to the metal centre in CuSO$_4$.5H$_2$O is
   (2009 - 4 Marks)

2. The oxidation number of Mn in the product of alkaline oxidative fusion of MnO$_2$ is
   (2009 - 4 Marks)

Section-B

1. A square planar complex is formed by hybridisation of which atomic orbitals?
   [2002]
   (a) $s, p_x, p_y, d_{yz}$
   (b) $s, p_x, p_y, d_{x^2-y^2}$
   (c) $s, p_x, p_y, d_z^2$
   (d) $s, p_y, p_z, d_{xy}$

2. The type of isomerism present in nitropentammine chromium (III) chloride is
   [2002]
   (a) optical
   (b) linkage
   (c) ionization
   (d) polymerisation

3. CH$_3$ – Mg – Br is an organo metallic compound due to
   [2002]
   (a) Mg – Br bond
   (b) C – Mg bond
   (c) C – Br bond
   (d) C – H bond

4. Most common oxidation states of Ce (cerium) are
   (a) +2, +3
   (b) +2, +4
   (c) +3, +4
   (d) +3, +5

5. Arrange Ce$^{3+}$, La$^{3+}$, Pr$^{3+}$ and Yb$^{3+}$ in increasing order of their ionic radii.
   [2002]
   (a) Yb$^{3+}$ < Pr$^{3+}$ < Ce$^{3+}$ < La$^{3+}$
   (b) Ce$^{3+}$ < Yb$^{3+}$ < Pr$^{3+}$ < La$^{3+}$
   (c) Yb$^{3+}$ < Pr$^{3+}$ < La$^{3+}$ < Ce$^{3+}$
   (d) Pr$^{3+}$ < La$^{3+}$ < Ce$^{3+}$ < Yb$^{3+}$

6. Which of the following ions has the maximum magnetic moment?
   [2002]
   (a) Mn$^{2+}$
   (b) Fe$^{2+}$
   (c) Ti$^{2+}$
   (d) Cr$^{2+}$

7. The most stable ion is
   [2002]
   (a) [Fe(OH)$_3$]$^{3-}$
   (b) [Fe(Cl)$_6$]$^{3-}$
   (c) [Fe(CN)$_6$]$^{3-}$
   (d) [Fe(H$_2$O)$_6$]$^{3+}$
8. When KMnO₄ acts as an oxidising agent and ultimately forms [MnO₄]²⁻, MnO₂, Mn₂O₃, Mn³⁺ then the number of electrons transferred in each case respectively is
   (a) 4, 3, 1, 5  (b) 1, 5, 3, 7  [2002]
   (c) 1, 3, 4, 5  (d) 3, 5, 7, 1.

9. The radius of La³⁺ (Atomic number of La = 57) is 1.06 Å. Which one of the following given values will be closest to the radius of Lu³⁺ (Atomic number of Lu = 71)?
   (a) 1.40 Å  (b) 1.06 Å  [2003]
   (c) 0.85 Å  (d) 1.60 Å

10. Ammonia forms the complex ion [Cu(NH₃)₄]²⁺ with copper ions in alkaline solutions but not in acidic solutions. What is the reason for it?  [2003]
    (a) In acidic solutions protons coordinate with ammonia molecules forming NH₄⁺ ions and NH₃ molecules are not available
    (b) In alkaline solutions insoluble Cu(OH)₂ is precipitated which is soluble in excess of any alkal
    (c) Copper hydroxide is an amphoteric substance
    (d) In acidic solutions hydration protects copper ions

11. One mole of the complex compound Co(NH₃)₆Cl₃, gives 3 moles of ions on dissolution in water. One mole of the same complex reacts with two moles of AgNO₃ solution to yield two moles of AgCl (s). The structure of the complex is
    (a) [Co(NH₃)₆Cl₃] 2 NH₃  [2003]
    (b) [Co(NH₃)₆Cl₃] CI : NH₃
    (c) [Co(NH₃)₆Cl₂] Cl₂ : NH₃
    (d) [Co(NH₃)₅Cl]Cl₂

12. In the coordination compound, K₄[Ni(CN)₄], the oxidation state of nickel is  [2003]
    (a) 0  (b) +1
    (c) +2  (d) −1

13. A red solid is insoluble in water. However it becomes soluble if some KI is added to water. Heating the red solid in a test tube results in liberation of some violet coloured fumes and droplets of a metal appear on the cooler parts of the test tube. The red solid is  [2003]
    (a) HgI₂  (b) HgO
    (c) Pb₂O₄  (d) (NH₄)₂Cr₂O₇

14. A reduction in atomic size with increase in atomic number is a characteristic of elements of  [2003]
    (a) d-block  (b) f-block
    (c) radioactive series  (d) high atomic masses

15. What would happen when a solution of potassium chromate is treated with an excess of dilute nitric acid?  [2003]
    (a) Cr₂O₇²⁻ and H₂O are formed
    (b) CrO₄²⁻ is reduced to +3 state of Cr
    (c) CrO₄²⁻ is oxidized to +7 state of Cr
    (d) Cr³⁺ and Cr₂O₇²⁻ are formed

16. Which one of the following nitrates will leave behind a metal on strong heating?  [2003]
    (a) Copper nitrate  (b) Manganese nitrate
    (c) Silver nitrate  (d) Ferric nitrate

17. Of the following outer electronic configurations of atoms, the highest oxidation state is achieved by which one of them?  [2004]
    (a) (n−1)d³ ns²  (b) (n−1)d⁵ ns¹
    (c) (n−1)d⁸ ns²  (d) (n−1)d⁵ ns²

18. The soldiers of Napolean army while at Alps during freezing winter suffered a serious problem as regards to the tin buttons of their uniforms. White metallic tin buttons got converted to grey power. This transformation is related to  [2004]
    (a) a change in the partial pressure of oxygen in the air
    (b) a change in the crystalline structure of tin
    (c) an interaction with nitrogen of the air at very low temperature
    (d) an interaction with water vapour contained in the humid air

19. Among the properties (a) reducing (b) oxidising (c) complexing, the set of properties shown by CN⁻ ion towards metal species is  [2004]
    (a) c, a  (b) b, c
    (c) a, b  (d) a, b, c

20. The coordination number of a central metal atom in a complex is determined by  [2004]
    (a) the number of ligands around a metal ion bonded by sigma and pi-bonds both
    (b) the number of ligands around a metal ion bonded by pi-bonds
    (c) the number of ligands around a metal ion bonded by sigma bonds
    (d) the number of only anionic ligands bonded to the metal ion.

21. Which one of the following complexes is an outer orbital complex?  [2004]
    (a) [Co(NH₃)₆]³⁺  (b) [Mn(CN)₆]⁴⁻
    (c) [Fe(CN)₆]⁴⁻  (d) [Ni(NH₃)₆]²⁺
    (Atomic nos.: Mn = 25; Fe = 26; Co = 27; Ni = 28)

22. Coordination compounds have great importance in biological systems. In this context which of the following statements is incorrect?  [2004]
    (a) Cyanocobalamin is B₁₂ and contains cobalt
    (b) Haemoglobin is the red pigment of blood and contains iron
    (c) Chlorophylls are green pigments in plants and contain calcium
    (d) Carboxypeptidase - A is an enzyme and contains zinc
23. Cerium (Z = 58) is an important member of the lanthanoids. Which of the following statements about cerium is incorrect? [2004]
   (a) The +4 oxidation state of cerium is not known in solutions
   (b) The +3 oxidation state of cerium is more stable than the +4 oxidation state
   (c) The common oxidation states of cerium are +3 and +4
   (d) Cerium (IV) acts as an oxidizing agent

24. Which one of the following has largest number of isomers?
   (a) [Ir(PR₃)₂H(CO)]²⁺ [2004]
   (b) [Co(NH₃)₅Cl]²⁺
   (c) [Ru(NH₃)₄Cl₂]⁺
   (d) [Co(en)₂Cl₂]⁺ (R = alkyl group, en = ethylenediamine)

25. The correct order of magnetic moments (spin only values in B.M.) among is [2004]
   (a) [Fe(CN)₆]⁴⁻ > [MnCl₄]²⁻ > [CoCl₄]²⁻
   (b) [MnCl₄]²⁻ > [Fe(CN)₆]⁴⁻ > [CoCl₄]²⁻
   (c) [MnCl₄]²⁻ > [CoCl₄]²⁻ > [Fe(CN)₆]⁴⁻
   (d) [Fe(CN)₆]⁴⁻ > [CoCl₄]²⁻ > [MnCl₄]²⁻

26. The oxidation state Cr in [Cr(NH₃)₄Cl₂]⁺ is [2005]
   (a) 0 (b) +1
   (c) +2 (d) +3

27. Heating mixture of Cu₂O and Cu₂S will give [2005]
   (a) Cu₂SO₃ (b) CuO + CuS
   (c) Cu + SO₃ (d) Cu + SO₂

28. The oxidation state of chromium in the final product formed by the reaction between KI and acidified potassium dichromate solution is: [2005]
   (a) +3 (b) +2
   (c) +6 (d) +4

29. Calomel (Hg₂Cl₂) on reaction with ammonium hydroxide gives [2005]
   (a) HgO (b) Hg₂O
   (c) NH₂⁻ – Hg – Hg – Cl (d) HgNH₂Cl

30. The lanthanide contraction is responsible for the fact that [2005]
   (a) Zr and Zn have the same oxidation state
   (b) Zr and Hf have about the same radius
   (c) Zr and Nb have similar oxidation state
   (d) Zr and Y have about the same radius

31. The IUPAC name of the coordination compound K₃[Fe(CN)₆] is [2005]
   (a) Tripotassium hexacyanoferrate (II)
   (b) Potassium hexacyanoferrate (II)
   (c) Potassium hexacyanoferrate (III)
   (d) Potassium hexacyanoferrate (II)

32. Which of the following compounds shows optical isomerism? [2005]
   (a) [Co(CN)₆]³⁻ (b) [Cr(C₂O₄)₃]³⁻
   (c) [ZnCl₄]²⁻ (d) [Cu(NH₃)₄]²⁺

33. Which one of the following cyanide complexes would exhibit the lowest value of paramagnetic behaviour? [2005]
   (a) [Co(CN)₆]³⁻ (b) [Fe(CN)₅]⁻
   (c) [Mn(CN)₆]³⁻ (d) [Cr(CN)₆]³⁻

   (At Nos : Cr = 24, Mn = 25, Fe = 26, Co = 27)

34. The value of the ‘spin only’ magnetic moment for one of the following configurations is 2.84 BM. The correct one is [2005]
   (a) d⁵ (in strong ligand field)
   (b) d⁶ (in weak as well as in strong fields)
   (c) d⁴ (in weak ligand fields)
   (d) d⁴ (in strong ligand fields)

35. Which of the following factors may be regarded as the main cause of lanthanide contraction? [2005]
   (a) Greater shielding of 5d electrons by 4f electrons
   (b) Poorer shielding of 5d electrons by 4f electrons
   (c) Effective shielding of one of 4f electrons by another in the subshell
   (d) Poor shielding of one of 4f electron by another in the subshell

36. The IUPAC name for the complex [Co(NO₂)(NH₃)₃Cl]₂ is: [2006]
   (a) pentaammine nitrito-N-cobalt(II) chloride
   (b) pentaammine nitrito-N-cobalt(III) chloride
   (c) nitrito-N-pentaamminecobalt(III) chloride
   (d) nitrito-N-pentaamminecobalt(II) chloride

37. A metal, M forms chlorides in its +2 and +4 oxidation states. Which of the following statements about these chlorides is correct? [2006]
   (a) MCl₂ is more ionic than MCl₄
   (b) MCl₂ is more easily hydrolysed than MCl₄
   (c) MCl₂ is more volatile than MCl₄
   (d) MCl₂ is more soluble in anhydrous ethanol than MCl₄
38. Nickel (Z = 28) combines with a uninegative monodentate ligand X⁻ to form a paramagnetic complex [NiX₄]²⁻. The number of unpaired electron(s) in the nickel and geometry of this complex ion are, respectively: [2006]
(a) one, square planar   (b) two, square planar
(c) one, tetrahedral   (d) two, tetrahedral

39. In Fe(CO)₅, the Fe – C bond possesses [2006]
(a) ionic character   (b) σ-character only
(c) π-character   (d) both σ and π characters

40. Lanthanoid contraction is caused due to [2006]
(a) the same effective nuclear charge from Ce to Lu
(b) the imperfect shielding on outer electrons by 4f electrons from the nuclear charge
(c) the appreciable shielding on outer electrons by 4f electrons from the nuclear charge
(d) the appreciable shielding on outer electrons by 5d electrons from the nuclear charge

41. How many EDTA (ethylenediaminetetraacetic acid) molecules are required to make an octahedral complex with a Ca²⁺ ion? [2006]
(a) One   (b) Two
(c) Six   (d) Three

42. The "spin-only" magnetic moment [in units of Bohr magneton, (μₐ)] of Ni²⁺ in aqueous solution would be (At. No. Ni = 28) [2006]
(a) 6   (b) 1.73
(c) 2.84   (d) 4.90

43. The stability of dihalides of Si, Ge, Sn and Pb increases steadily in the sequence [2007]
(a) PbX₂ << SnX₂ << GeX₂ << SiX₂
(b) GeX₂ << SiX₂ << SnX₂ << PbX₂
(c) SiX₂ << GeX₂ << PbX₂ << SnX₂
(d) SiX₂ << GeX₂ << SnX₂ << PbX₂

44. Identify the incorrect statement among the following:
(a) 4f and 5f orbitals are equally shielded. [2007]
(b) d-Block elements show irregular and erratic chemical properties among themselves.
(c) La and Lu have partially filled d-orbitals and no other partially filled orbitals.
(d) The chemistry of various lanthanoids is very similar.

45. Which of the following has a square planar geometry? [2007]
(a) [PtCl₄]²⁻   (b) [CoCl₄]²⁻
(c) [FeCl₄]²⁻   (d) [NiCl₄]²⁻
(At. nos.: Fe = 26, Co = 27, Ni = 28, Pt = 78)

46. The actinoids exhibit more number of oxidation states in general than the lanthanoids. This is because [2007]
(a) the 5f orbitals extend further from the nucleus than the 4f orbitals
(b) the 5f orbitals are more buried than the 4f orbitals
(c) there is a similarity between 4f and 5f orbitals in their angular part of the wave function
(d) the actinoids are more reactive than the lanthanoids.

47. The coordination number and the oxidation state of the element ‘E’ in the complex [2008]
[E(en)₂(C₂O₄)₂]NO₂ where (en) is ethylene diamine are, respectively,
(a) 6 and 2   (b) 4 and 2
(c) 4 and 3   (d) 6 and 3

48. Larger number of oxidation states are exhibited by the actinoids than those by the lanthanoids, the main reason being [2008]
(a) 4f orbitals more diffused than the 5f orbitals
(b) less energy difference between 5f and 6d than between 4f and 5d orbitals
(c) more energy difference between 5f and 6d than between 4f and 5d orbitals
(d) more reactive nature of the actinoids than the lanthanoids

49. In which of the following complexes of the Co (at. no. 27), will the magnitude of Δ₆ be the highest? [2008]
(a) [Co(CN)₆]³⁻   (b) [Co(C₂O₄)₃]³⁻
(c) [Co(H₂O)₆]³⁺   (d) [Co(NH₃)₆]³⁺

50. Amount of oxalic acid present in a solution can be determined by its titration with KMnO₄ solution in the presence of H₂SO₄. The titration gives unsatisfactory result when carried out in the presence of HCl, because HCl
(a) gets oxidised by oxalic acid to chlorine [2008]
(b) furnishes H⁺ ions in addition to those from oxalic acid
(c) reduces permanganate to Mn²⁺
(d) Oxidises oxalic acid to carbon dioxide and water

51. Which of the following has an optical isomer? [2009]
(a) [Co(en)(NH₃)₂]²⁺   (b) [Co(H₂O)₄(en)]³⁺
(c) [Co(en)₂(NH₃)₂]³⁺   (d) [Co(NH₃)₃Cl]⁺

52. In context with the transition elements, which of the following statements is incorrect? [2009]
(a) In the highest oxidation states, the transition metal show basic character and form cationic complex.
(b) In the highest oxidation states of the first five transition elements (Sc to Mn), all the 4s and 3d electrons are used for bonding.

53. Which of the following pairs represent linkage isomers? [2009]
(a) [Pd(PPh₃)₂(NCS)₂] and [Pd(PPh₃)₂(SCN)₂]
(b) [Co(NH₃)₅NO]SO₄ and [Co(NH₃)₅SO₄]NO₃
(c) [PtCl₅(NH₃)₄] Br₂ and [PtBr₂(NH₃)₄]Cl₂
(d) [Cu(NH₃)₄]₂[PtCl₄] and [Pt(NH₃)₄][CuCl₄]
54. Knowing that the chemistry of lanthanoids (Ln) is dominated by its +3 oxidation state, which of the following statements is incorrect? [2009]
   (a) The ionic size of Ln (III) decreases in general with increasing atomic number.
   (b) Ln (III) compounds are generally colourless.
   (c) Ln (III) hydroxides are mainly basic in character.
   (d) Because of the large size of the Ln (III) ions the bonding in its compounds is predominantly ionic in character.

55. A solution containing 2.675 g of CoCl₃ 6 NH₃ (molar mass = 267.5 g mol⁻¹) is passed through a cation exchanger. The chloride ions obtained in solution were treated with excess of AgNO₃ to give 4.78 g of AgCl (molar mass = 143.5 g mol⁻¹). The formula of the complex is [2010]
   (a) [Co(NH₃)₆]Cl₃  (b) [CoCl₂(NH₃)₄]Cl  (c) [CoCl₃(NH₃)₂]Cl  (d) [CoCl(NH₃)₃]Cl₂

56. Which one of the following has an optical isomer? [2010]
   (a) [Zn(en)(NH₃)₂]²⁺  (b) [Co(en)₃]³⁺  (c) [Co(H₂O)₆(en)]³⁺  (d) [Zn(en)₂]²⁺
   (en = ethylenediamine)

57. Which of the following facts about the complex [Cr(NH₃)₆]Cl₃ is wrong? [2011]
   (a) The complex involves d²sp³ hybridisation and is octahedral in shape.
   (b) The complex is paramagnetic.
   (c) The complex is an outer orbital complex.
   (d) The complex gives white precipitate with silver nitrate solution.

58. In context of the lanthanoids, which of the following statements is not correct? [2011]
   (a) There is a gradual decrease in the radii of the members with increasing atomic number in the series.
   (b) All the members exhibit +3 oxidation state.
   (c) Because of similar properties the separation of lanthanoids is not easy.
   (d) Availability of 4f electrons results in the formation of compounds in +4 state for all the members of the series.

59. The magnetic moment (spin only) of [NiCl₄]²⁻ is: [2011]
   (a) 1.82 BM  (b) 5.46 BM  (c) 2.82 BM  (d) 1.41 BM

60. The outer electron configuration of Gd (Atomic No.: 64) is: [2011]
   (a) 4f⁷ 5d⁶ 6s²  (b) 4f⁷ 5d⁶ 6s²  (c) 4f⁴ 5d⁴ 6s²  (d) 4f⁷ 5d⁴ 6s²

61. Which among the following will be named as dibromodibis (ethylene diamine) chromium (III) bromide? [2012]
   (a) [Cr(en)₂]Br₃  (b) [Cr(en)₂Br₂]Br  (c) [Cr(en)Br₄]⁻  (d) [Cr(en)Br₃]Br

62. Iron exhibits +2 and +3 oxidation states. Which of the following statements about iron is incorrect? [2012]
   (a) Ferrous oxide is more basic in nature than the ferric oxide.
   (b) Ferrous compounds are relatively more ionic than the corresponding ferric compounds.
   (c) Ferrous compounds are less volatile than the corresponding ferric compounds.
   (d) Ferrous compounds are more easily hydrolysed than the corresponding ferric compounds.

63. Which of the following complex species is not expected to exhibit optical isomerism? [JEE M 2013]
   (a) [Co(en)₃]³⁺  (b) [Co(en)₂Cl₂]⁺  (c) [Co(NH₃)₂Cl₂]⁻  (d) [Co(en)(NH₃)₂Cl₂]⁺

64. Which of the following arrangements does not represent the correct order of the property stated against it? [JEE M 2013]
   (a) V²⁺ < Cr²⁺ < Mn²⁺ < Fe²⁺: paramagnetic behaviour
   (b) Ni²⁺ < Co²⁺ < Fe²⁺ < Mn²⁺: ionic size
   (c) Co³⁺ < Fe³⁺ < Cr³⁺ < Sc³⁺: stability in aqueous solution
   (d) Sc < Ti < Cr < Mn: number of oxidation states

65. Four successive members of the first row transition elements are listed below with atomic numbers. Which one of them is expected to have the highest E¹⁰ M³⁺ / M²⁺ value? [JEE M 2013]
   (a) Cr (Z = 24)  (b) Mn (Z = 25)  (c) Fe (Z = 26)  (d) Co (Z = 27)

66. The octahedral complex of a metal ion M³⁺ with four monodentate ligands L₁, L₂, L₃ and L₄ absorb wavelengths in the region of red, green, yellow and blue, respectively. The increasing order of ligand strength of the four ligands is: [JEE M 2014]
   (a) L₄ < L₃ < L₂ < L₁  (b) L₁ < L₃ < L₂ < L₄  (c) L₃ < L₂ < L₄ < L₁  (d) L₁ < L₂ < L₄ < L₃
67. Which series of reactions correctly represents chemical reactions related to iron and its compound? [JEE M 2014]

(a) \[ \text{Fe} \xrightarrow{\text{dil. H}_2\text{SO}_4} \text{FeSO}_4 \xrightarrow{\text{H}_2\text{SO}_4, \text{O}_2} \text{Fe}_2(\text{SO}_4)_3 \xrightarrow{\text{heat}} \text{Fe} \]

(b) \[ \text{Fe} \xrightarrow{\text{O}_2, \text{heat}} \text{FeO} \xrightarrow{\text{dil. H}_2\text{SO}_4} \text{FeSO}_4 \xrightarrow{\text{heat}} \text{Fe} \]

(c) \[ \text{Fe} \xrightarrow{\text{Cl}_2, \text{heat, air}} \text{FeCl}_3 \xrightarrow{\text{heat, air}} \text{FeCl}_2 \xrightarrow{\text{Zn}} \text{Fe} \]

(d) \[ \text{Fe} \xrightarrow{\text{O}_2, \text{heat}} \text{Fe}_3\text{O}_4 \xrightarrow{\text{CO, 600°C}} \text{FeO} \xrightarrow{\text{CO, 700°C}} \text{Fe} \]

68. Which of the following compounds is not colored yellow? [JEE M 2015]

(a) \( \text{(NH}_4\text{)}_2[\text{As(}\text{Mo}_3\text{O}_10\text{)}_4] \)

(b) \( \text{BaCrO}_4 \)

(c) \( \text{Zn}_2[\text{Fe(CN)}_6] \)

(d) \( \text{K}_3[\text{Co(NO}_2)_6] \)

69. Match the catalysts to the correct processes: [JEE M 2015]

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A) ( \text{TiCl}_4 )</td>
<td>(i) Wacker process</td>
</tr>
<tr>
<td>(B) ( \text{PdCl}_2 )</td>
<td>(ii) Ziegler - Natta polymerization</td>
</tr>
<tr>
<td>(C) ( \text{CuCl}_2 )</td>
<td>(iii) Contact process</td>
</tr>
<tr>
<td>(D) ( \text{V}_2\text{O}_5 )</td>
<td>(iv) Deacon’s process</td>
</tr>
</tbody>
</table>

(a) (A) - (ii), (B) - (iii), (C) - (iv), (D) - (i)

(b) (A) - (iii), (B) - (i), (C) - (ii), (D) - (iv)

(c) (A) - (iii), (B) - (i), (C) - (iv), (D) - (i)

(d) (A) - (ii), (B) - (i), (C) - (iv), (D) - (iii)

70. The number of geometric isomers that can exist for square planar complex \( [\text{Pt} \ (\text{Cl}) \ (\text{py}) \ (\text{NH}_3) \ (\text{NH}_2\text{OH})]^{+} \) is \( \text{(py=pyridine)} \): [JEE M 2015]

(a) 4 \quad (b) 6

(c) 2 \quad (d) 3

71. The color of \( \text{KMnO}_4 \) is due to:

(a) \( \text{L} \rightarrow \text{M} \) charge transfer transition

(b) \( \sigma - \sigma^* \) transition

(c) \( \text{M} \rightarrow \text{L} \) charge transfer transition

(d) \( d - d \) transition

72. Which of the following compounds is metallic and ferromagnetic? [JEE M 2016]

(a) \( \text{VO}_2 \)

(b) \( \text{MnO}_2 \)

(c) \( \text{TiO}_2 \)

(d) \( \text{CrO}_2 \)

73. Which one of the following complexes shows optical isomerism? [JEE M 2016]

(a) \( \text{trans}[\text{Co(en)}_2\text{Cl}_2]\text{Cl} \)

(b) \( [\text{Co(NH}_3)_4\text{Cl}]\text{Cl} \)

(c) \( [\text{Co(NH}_3)_3\text{Cl}_2] \)

(d) \( cia[\text{Co(en)}_2\text{Cl}_2]\text{Cl} \)

(en = ethylenediamine)

74. The pair having the same magnetic moment is:

[At. No.: \( \text{Cr} = 24 \), \( \text{Mn} = 25 \), \( \text{Fe} = 26 \), \( \text{Co} = 27 \)] [JEE M 2016]

(a) \( [\text{Mn(H}_2\text{O})_6]^{2+} \) and \( [\text{Cr(H}_2\text{O})_6]^{2+} \)

(b) \( [\text{CoCl}_4]^{2-} \) and \( [\text{Fe(H}_2\text{O})_6]^{2+} \)

(c) \( [\text{Cr(H}_2\text{O})_6]^{3+} \) and \( [\text{CoCl}_4]^{2-} \)

(d) \( [\text{Cr(H}_2\text{O})_6]^{3+} \) and \( [\text{Fe(H}_2\text{O})_6]^{2+} \)
CHAPTER 18
Haloalkanes and Haloarenes

Section-A

JEE Advanced/ IIT-JEE

A Fill in the Blanks

1. The halogen which is most reactive in the halogenation of alkanes under sunlight is ............... (chlorine, bromine, iodine) (1981 - 1 Mark)
2. The compound prepared by the action of magnesium on dry ethyl bromide in ether is known as .............. reagent. (1982 - 1 Mark)
4. Vinyl chloride on reaction with dimethyl copper gives ............... . (1997 - 1 Mark)

B True / False

1. m-Chlorobromobenzene is an isomer of m-bromochlorobenzene. (1985 - ½ Mark)
2. The reaction of vinyl chloride with hydrogen iodide to give 1-chloro-1-iodoethane is an example of anti-Markovnikov’s rule. (1989 - 2 Marks)

C MCQs with One Correct Answer

1. Chlorobenzene can be prepared by reacting aniline with:
(a) hydrochloric acid (1984 - 1 Mark)
(b) cuprous chloride
(c) chlorine in presence of anhydrous aluminium chloride
(d) nitrous acid followed by heating with cuprous chloride
2. The reaction of toluene with chlorine in presence of ferric chloride gives predominantly:
(a) benzyl chloride (1986 - 1 Mark)
(b) m-chlorotoluene
(c) benzyl chloride
(d) α- and p-chlorotoluene
3. The reaction conditions leading to the best yields of C₂H₅Cl are:
(a) C₂H₆ (excess) + Cl₂ \rightarrow \text{uv light} \quad (1986 - 1 Mark)
(b) C₂H₆ + Cl₂ \rightarrow \text{dark, room temperature}
(c) C₂H₆ + Cl₂ (excess) \rightarrow \text{uv light}
(d) C₂H₆ + Cl₂ \rightarrow \text{uv light}

4. n-Propyl bromide on treatment with ethanolic potassium hydroxide produces (1987 - 1 Mark)
   (a) Propane (b) Propene
   (c) Propyne (d) Propanol

5. The number of structural and configurational isomers of a bromo compound, C₅H₅Br, formed by the addition of HBr to 2-pentene respectively are (1988 - 1 Mark)
   (a) 1 and 2 (b) 2 and 4
   (c) 4 and 2 (d) 2 and 1

6. 1-Chlorobutane on reaction with alcoholic potash gives (1991 - 1 Mark)
   (a) 1-butene (b) 1-butanol
   (c) 2-butene (d) 2-butanol

7. The chief reaction product of reaction between n-butane and bromine at 130°C is: (1995S)
   (a) CH₃CH₂CH₂CH₂Br
   (b) CH₃CH₂CHBr
   (c) CH₃ – CH₂CHBr
   (d) CH₃CH₂CB₂

8. Isobutyl magnesium bromide with dry ether and ethyl alcohol gives: (1995S)
   (a) CH₃CHCH₂OH & CH₃CH₂MgBr
   (b) CH₃CHCH₃ & MgBr(OC₂H₅)
   (c) CH₃CH₂CH = CH₂ & Mg(OH)Br
   (d) CH₃CHCH₃ & CH₃CH₂OMgBr

9. (CH₃)₂CMgCl on reaction with D₂O produces: (1997 - 1 Mark)
   (a) (CH₃)₂CD (b) (CH₃)₂OD
   (c) (CD₃)₂CD (d) (CD₃)₂OD.
10. A solution of (+)-2-chloro-2-phenylethane in toluene racemises slowly in the presence of small amount of SbCl₅ due to the formation of (1999 - 2 Marks)
(a) carbanion  (b) carbene  
(c) free-radical  (d) carboxylation

11. Identify the set of reagent / reaction conditions 'X' and 'Y' in the following set of transformations (2002S)
CH₃ - CH₂ - CH₂Br → \[X\] → CH₃ - CH - CH₃  
Br
(a) X = dilute aqueous NaOH, 20°C; Y = HBr/acidic acid, 20°C 
(b) X = concentrated alcoholic NaOH, 80°C; Y = HBr/acidic acid, 20°C 
(c) X = dilute aqueous NaOH, 20°C; Y = Br₂/CHCl₃, 0°C 
(d) X = concentrated alcoholic NaOH, 80°C; Y = Br₂/CHCl₃, 0°C

12. \[\text{CH₃} \quad \text{OH} \quad \text{H⁺} \quad \text{Br₂,CCl₄} \quad \text{C₄H₄Br₂} \]

How many structures for F are possible? (2003S)
(a) 2  (b) 5  
(c) 6  (d) 3

13. What would be the product formed when 1-bromo-3-chlorocyclobutane reacts with two equivalents of metallic sodium in ether? (2005S)
(a) (b) 
(c) (d)

14. When phenyl magnesium bromide reacts with tert-butanol, the product would be (2005S)
(a) Benzene  (b) Phenol  
(c) ter-butylbenzene  (d) ter-butyl phenyl ether

15. The reagent(s) for the following conversion, is/are (2007)
Br
(a) alcoholic KOH  (b) alcoholic KOH followed by NaN₃ 
(c) aqueous KOH followed by NaN₃  (d) Zn/CH₃OH

16. The major product of the following reaction is – (2008)

\[\text{Me} \quad \text{Br} \quad \text{F} \quad \text{Ph} \quad \text{S} \quad \text{Na} \quad \text{dimethylformamide} \]

\[\text{Me} \quad \text{SPh} \quad \text{F} \quad \text{NO₂} \quad \text{Br} \quad \text{Me} \quad \text{SPh} \quad \text{NO₂} \]

(a) (b) 

D) MCQs with One or More Than One Correct

1. Aryl halides are less reactive towards nucleophilic substitution reaction as compared to alkyl halides due to: (1990 - 1 Mark)
   (a) The formation of less stable carbonium ion  
   (b) Resonance stabilization  
   (c) Longer carbon-halogen bond  
   (d) The inductive effect  
   (e) sp² hybridized carbon attached to the halogen.

2. Benzyl chloride (C₆H₅CH₂Cl) can be prepared from toluene by chlorination with (1998 - 2 Marks)
   (a) SO₂Cl₂  (b) SOCl₂  
   (c) Cl₂  (d) NaOCl

E) Subjective Problems

1. (a) Show by chemical equations only, how you would prepare the following from the indicated starting materials. Specify the reagents in each step of the synthesis. (1981 - ½ Mark)
   (i) Hexachlorehthane, C₂Cl₆, from calcium carbide.  
   (ii) Chloroform from carbon disulphide.

   (b) Give one chemical test which would distinguish between C₆H₅OH from CHCl₃. (1979)

2. Write the structural formula of the major product in each of the following cases: (1992 - 1 Mark)
   (i) chloroform reacts with aniline in the presence of excess alkali  
   (ii) bromoethane reacts with one-half of the molar quantity of silver carbonate.  

   (iii) (CH₃)₂C – CH₂CH₃  

   (iv) CH₂CH₂CH₂Cl  

   (v) C₆H₅ – CH₂ – CH – CH₃  

   (vi) Me  

   (vii) C₆H₅CH₂CHClC₆H₅  

   (viii) C₆H₅ – C – CH₂Br  

   (1993 - 1 Mark)

(vi) Me  

(1997 - 1 Mark)

(1998 - 2 Marks)

(1990 - 1 Mark)
3. Give reasons for the following:
   (i) 7-Bromo-1, 3, 5-cycloheptatriene exists as ionic compound, while 5-bromo-1, 3-cyclopentadiene does not ionise even in presence of Ag⁺ ion. Explain.
   (2004 - 2 Marks)
   (ii) \[ \text{Br} \quad \text{a} \quad \text{aq C₂H₅OH} \rightarrow \text{Acidic solution} \]
   \[ \text{Br} \quad \text{aq C₂H₅OH} \rightarrow \text{Neutral solution. Explain.} \] (2005 - 1 Mark)

4. State the conditions under which the following preparation are carried out. Give the necessary equations which need not be balanced:
   (i) Lead tetraethyl from sodium-lead alloy
   (1983 - 1 Mark)
   (ii) Methyl chloride from aluminium carbide
   (1983 - 1 Mark)

5. Write the structure of all the possible isomers of dichloroethene. Which of them will have zero dipole moment?
   (1985 - 2 Marks)

6. What happens when excess chlorine is passed through boiling toluene in the presence of sunlight? (1987 - 1 Mark)

7. What effect should the following resonance of vinyl chloride have on its dipole moment?
   (1987 - 1 Mark)
   \[ \text{CH}_2 = \text{CH} - \text{Cl} \rightleftharpoons \text{CH}_2^- - \text{CH}_2 = \text{Cl}^+ \]

8. An organic compound X, on analysis gives 24.24 per cent carbon and 4.04 per cent hydrogen. Further, sodium extract of 1.0 g of X gives 2.90 g of silver chloride with acidified silver nitrate solution. The compound X may be represented by two isomeric structures, Y and Z. Y on treatment with aqueous potassium hydroxide solution gives a dihydroxy compound while Z on similar treatment gives ethanol. Find out the molecular formula of X and give the structures of Y and Z.
   (1989 - 4 Marks)

9. Draw the stereochemical structures of the products in the following reaction:
   (1994 - 4 Marks)
   \[ \text{Br} \quad \text{H} \quad \text{NaOH} \quad \text{Sn}_2 \rightarrow \]

10. An alkyl halide, X, of formula C₅H₁₀Cl on treatment with potassium tertiary butoxide gives two isomeric alkenes Y and Z (C₅H₁₂). Both alkenes on hydrogenation give 2, 3-dimethylbutane. Predict the structures of X, Y and Z.
   (1996 - 3 Marks)

11. How will you prepare m-bromiodobenzene from benzene (in not more than 5-7 steps)?
   (1996 - 2 Marks)

12. Cyclobutyl bromide on treatment with magnesium in dry ether forms an organometallic (A). The organometallic reacts with ethanol to give an alcohol (B) after mild acidification. Prolonged treatment of alcohol (B) with an equivalent amount of HBr gives 1-bromo-1-methycyclopentane (C). Write the structures of (A), (B) and explain how (C) is obtained from (B).
   (2001 - 5 Marks)

**H**

Assertion & Reason Type Questions

1. Read the following Statement-1 (Assertion) and Statement-2 (Reason) and answer as per the options given below:
   Statement-1: Bromobenzene upon reaction with Br₂/Fe gives 1,4-dibromobenzene as the major product. (2008)
   Statement-2: In bromobenzene, the inductive effect of the bromo group is more dominant than the mesomeric effect in directing the incoming electrophile.
   (a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
   (b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.
   (c) Statement-1 is True, Statement-2 is False
   (d) Statement-1 is False, Statement-2 is True

**I**

Integer Value Correct Type

1. The total number of alkenes possible by dehydrobromination of 3-bromo-3-cyclopentylhexane using alcoholic KOH is _______ (2011)

2. In the following monobromination reaction, the number of possible chiral products is _______. (JEE Adv: 2016)
   \[ \text{Br}_2 \text{(1.0 mole)} \rightarrow \text{S}_n_2 \rightarrow \text{enantiomerically pure} \]

**Section-B**

JEE Main / AIEEE

1. Bottles containing C₅H₁₀I and C₅H₈CH₃I lost their original labels. They were labelled A and B for testing. A and B were separately taken in test tubes and boiled with NaOH solution. The end solution in each tube was made acidic with dilute HNO₃ and then some AgNO₃ solution was added. Substance B gave a yellow precipitate. Which one of the following statements is true for this experiment? (2003)
   (a) A and C₅H₈CH₃I
   (b) B and C₅H₈I
   (c) Addition of HNO₃ was unnecessary
   (d) A was C₅H₁₀I

2. The compound formed on heating chlorobenzene with chloral in the presence of concentrated sulphuric acid, is
   (a) freon
   (b) DDT
   (c) gammexene
   (d) hexachloroethane

3. Tertiary alkyl halides are practically inert to substitution by \text{S}_{n_2} \text{ mechanism because it is:} (2005)
   (a) steric hindrance
   (b) inductive effect
   (c) instability
   (d) insolubility

4. Alkyl halides react with dialkyl copper reagents to give
   (a) alkenyl halides
   (b) alkanes
   (c) alkyl copper halides
   (d) alkenes
5. Elimination of bromine from 2-bromobutane results in the formation of – [2005]
   (a) Predominantly 2-butyne
   (b) Predominantly 1-buten
   (c) Predominantly 2-buten
   (d) equimolar mixture of 1 and 2-buten

6. Phenyl magnesium bromide reacts with methanol to give
   (a) a mixture of toluene and Mg(OH)Br [2006]
   (b) a mixture of phenol and Mg(Me)Br
   (c) a mixture of anisole and Mg(OH)Br
   (d) a mixture of benzene and Mg(OMe)Br

7. Fluorobenzene (C₆H₅F) can be synthesized in the laboratory [2006]
   (a) by direct fluorination of benzene with F₂ gas
   (b) by reacting bromobenzene with NaF solution
   (c) by heating phenol with HF and KF
   (d) from aniline by diazotisation followed by heating the diazonium salt with HBF₄

8. Reaction of trans 2-phenyl-1-bromocyclopentane on reaction with alcoholic KOH produces [2006]
   (a) 1-phenylecyclopentene
   (b) 3-phenylecyclopentene
   (c) 4-phenylecyclopentene
   (d) 2-phenylecyclopentene

9. The structure of the major product formed in the following reaction [2006]

10. Which of the following is the correct order of decreasing S₄,2 reactivity? [2007]
    (a) R,XC > R,CX > RCH,X
    (b) RCH,X > R,XC > R,CX
    (c) R,CX > RCH,X > RCH₂X
    (d) R₂X > R₂CHX > RCH₂X
    (X is a halogen)

11. The organic chloro compound, which shows complete sterochemical inversion during a S₄,2 reaction, is [2008]
    (a) (CH₃)₂CHCl
    (b) (CH₃)₃CCl
    (c) (CH₃)₂CHCl
    (d) CH₃Cl

12. Consider the following bromides:

!(A) Me - Br - CH₂ - Br
!(B) Me - Br - CH₂ - Me
!(C) Me - Br

The correct order of S₄,1 reactivity is [2010]
(a) B > C > A
(b) B > A > C
(c) C > B > A
(d) A > B > C

13. How many chiral compounds are possible on monochlorination of 2-methyl butane? [2012]
   (a) 8
   (b) 2
   (c) 4
   (d) 6

14. What is DDT among the following? [2012]
   (a) Greenhouse
gas
   (b) A fertilizer
   (c) Biodegradable pollutant
   (d) Non-biodegradable pollutant

15. Compound (A), C₈H₇Br, gives a white precipitate when warmed with alcoholic AgNO₃. Oxidation of (A) gives an acid (B), C₈H₆O₄. (B) easily forms anhydride on heating. Identify the compound (A). [JEE M 2013]

![Chemical Structures]

16. In S₄,2 reactions, the correct order of reactivity for the following compounds: [JEE M 2014]
    CH₃Cl, CH₃CH₂Cl, (CH₃)₂CHCl and (CH₃)₃CCl is:
    (a) CH₃Cl > (CH₃)₂CHCl > CH₃CH₂Cl > (CH₃)₃CCl
    (b) CH₃Cl > CH₃CH₂Cl > (CH₃)₂CHCl > (CH₃)₃CCl
    (c) CH₃CH₂Cl > CH₃Cl > (CH₃)₂CHCl > (CH₃)₃CCl
    (d) (CH₃)₂CHCl > CH₃CH₂Cl > CH₃Cl > (CH₃)₃CCl

17. The major organic compound formed by the reaction of 1, 1, 1-trichloroethane with silver powder is: [JEE M 2014]
    (a) Acetylene
    (b) Ethene
    (c) 2-Butyne
    (d) 2-Butene

18. The synthesis of alkyl fluorides is best accomplished by: [JEE M 2015]
    (a) Finkelstein reaction
    (b) Swarts reaction
    (c) Free radical fluorination
    (d) Sandmeyer's reaction
CHAPTER 19
Alcohols, Phenols and Ethers

Section-A

JEE Advanced/ IIT-JEE

A Fill in the Blanks

1. Ethanol vapour is passed over heated copper and the product is treated with aqueous NaOH. The final product is ............... (1983 - 1 Mark)
2. The acidity of phenol is due to the ............... of its anion. (1984 - 1 Mark)
3. Formation of phenol from chlorobenzene is an example of ............... aromatic substitution. (1989 - 1 Mark)
4. Phenol is acidic because of resonance stabilization of its conjugate base, namely ............... (1990 - 1 Mark)
5. Aliphatic ethers are purified by shaking with a solution of ferrous salt to remove ............... which are formed on prolonged standing in contact with air. (1992 - 1 Mark)
6. Glycerine contains one ............... hydroxy group. (1997 - 1 Mark)

B True / False

1. Sodium ethoxide is prepared by reacting ethanol with aqueous sodium hydroxide. (1986 - 1 Mark)

C MCQs with One Correct Answer

1. Ethyl alcohol is heated with conc H₂SO₄ the product formed is (1980)
   (a) H₃C – C – OC₂H₅  (b) C₂H₅OH
   (c) C₂H₅OH  (d) C₂H₂
2. Which of the following is basic (1980)
   (a) CH₃ – CH₂ – OH  (b) OH – CH₂ – CH₂ – OH
   (c) H – O – O – H  (d) H₃C – C – OH
3. The compound which reacts fastest with Lucas reagent at room temperature is (1981 - 1 Mark)
   (a) butan-1-ol  (b) butan-2-ol
   (c) 2-methylpropan-1-ol  (d) 2-methylpropan-2-ol
4. A compound that gives a positive iodoform test is (1982 - 1 Mark)
   (a) 1-pentanol  (b) 2-pentanone
   (c) 3-pentanone  (d) pentanal
5. Diethyl ether on heating with conc. H₂SO₄ gives two moles of (1983 - 1 Mark)
   (a) ethanol  (b) iodoform
   (c) ethyl iodide  (d) methyl iodide
6. An industrial method of preparation of methanol is: (1984 - 1 Mark)
   (a) catalytic reduction of carbon monoxide in presence of ZnO–Cr₂O₃
   (b) by reacting methane with steam at 900°C with a nickel catalyst
   (c) by reducing formaldehyde with lithium aluminium hydride
   (d) by reacting formaldehyde with aqueous sodium hydroxide solution
7. When phenol is treated with excess bromine water, it gives: (1984 - 1 Mark)
   (a) m-Bromophenol  (b) o- and p-Bromophenol
   (c) 2, 4-Dibromophenol  (d) 2, 4, 6-Tribromophenol
8. HBr reacts fastest with: (1986 - 1 Mark)
   (a) 2-methylpropan-2-ol  (b) propan-1-ol
   (c) propan-2-ol  (d) 2-methylpropan-1-ol
9. Which of the following compounds is oxidised to prepare methyl ethyl ketone? (1987 - 1 Mark)
   (a) 2-Propanol  (b) 1-Butanol
   (c) 2-Butanol  (d) t-Butyl alcohol
10. Phenol reacts with bromine in carbon disulphide at low temperature to give (1988 - 1 Mark)
    (a) m-bromophenol  (b) o- and p-bromophenol
    (c) p-bromophenol  (d) 2, 4, 6-tribromophenol
11. Chlorination of toluene in the presence of light and heat followed by treatment with aqueous NaOH gives (1990 - 1 Mark)
    (a) o-Cresol  (b) p-Cresol
    (c) 2, 4-Dihydroxytoluene  (d) Benzoic acid
12. When phenol is reacted with CHCl₃ and NaOH followed by acidification, salicylaldehyde is obtained. Which of the following species are involved in the above mentioned reaction as intermediate? (1995S)
    (a)  (b)  
    (c)  (d)
13. The compound that will react most readily with NaOH to form methanol is (2000S)
   (a) (CH₃)₄N⁺I⁻          (b) CH₃OCH₃
   (c) (CH₃)₃S⁺I⁻          (d) (CH₃)₂CCl

14. 1-Propanol and 2-propanol can be best distinguished by (2001S)
   (a) oxidation with alkaline KMnO₄ followed by reaction with Fehling solution
   (b) oxidation with acidic dichromate followed by reaction with Fehling solution
   (c) oxidation by heating with copper followed by reaction with Fehling solution
   (d) oxidation with concentrated H₂SO₄ followed by reaction with Fehling solution

15. \[ \text{OH} + \text{C}_2\text{H}_5\text{I} \xrightarrow{\text{OC}_2\text{H}_5 \text{, Anhydrous (C}_2\text{H}_5\text{OH)}} ? \] (2003S)
   (a) C₆H₅OC₂H₅          (b) C₂H₅OC₂H₅
   (c) C₆H₅OC₆H₅          (d) C₆H₅I

16. The product of acid catalyzed hydration of 2-phenylpropene is (2004S)
   (a) 3-phenyl-2-propanol   (b) 1-phenyl-2-propanol
   (c) 2-phenyl-2-propanol   (d) 2-phenyl-1-propanol

17. The best method to prepare cyclohexene from cyclohexanol is by using (2005S)
   (a) Conc. HCl + ZnCl₂      (b) Conc. H₂PO₄
   (c) HBr                   (d) Conc. HCl

18. The increasing order of boiling points of the below mentioned alcohols is (2006 - 3M, -1)
   (I) 1,2-dihydroxybenzene  (II) 1,3-dihydroxybenzene
   (III) 1,4-dihydroxybenzene (IV) Hydroxybenzene
   (a) 1<II<IV<III          (b) 1<II<III<IV
   (c) IV<II<1<III         (d) IV<1<II<III

19. In the reaction \[ \text{OCH₃} \xrightarrow{\text{HBr}} \] the products are (2010)
   (a)  \[ \text{OCH₃} \text{and H₂} \]
   (b)  \[ \text{Br and CH₃Br} \]
   (c)  \[ \text{Br and CH₃OH} \]
   (d)  \[ \text{OH and CH₃Br} \]

20. For the identification of β-naphthol using dye test, it is necessary to use (JEE Adv. 2014)
   (a) Dichloromethane solution of β-naphthol
   (b) Acidic solution of β-naphthol
   (c) Neutral solution of β-naphthol
   (d) Alkaline solution of β-naphthol

21. The acidic hydrolysis of ether (X) shown below is fastest when (JEE Adv. 2014)
   \[ \text{OR} \xrightarrow{\text{Acid}} \text{OH} + \text{ROH} \]
   (a) One phenyl group is replaced by a methyl group
   (b) One phenyl group is replaced by a para-methoxyphenyl group
   (c) Two phenyl groups are replaced by two para-methoxyphenyl groups
   (d) No structural change is made to X

D MCQs with One or More Than One Correct

1. The reaction of \[ \text{CH}_3\text{CH} = \text{CH} \xrightarrow{\text{HBr}} \] with HBr gives (1998 - 2 Marks)
   (a) \[ \text{CH}_3\text{CHBrCH}_2\text{OH} \]
   (b) \[ \text{CH}_3\text{CH}_2\text{CHBrOH} \]
   (c) \[ \text{CH}_3\text{CHBrCH}_2\text{Br} \]
   (d) \[ \text{CH}_3\text{CH}_2\text{CHBr-Br} \]

2. The ether \[ \text{O} \xrightarrow{\text{CH}_2} \text{CH} \text{ when treated with HI produces} \] (1999 - 3 Marks)
   (a) \[ \text{CH}_2\text{I} \]
   (b) \[ \text{CH}_3\text{OH} \]
   (c) \[ \text{CH}_3\text{Br} \]
   (d) \[ \text{CH}_3\text{OH} \]
3. In the reaction \[ \text{NaOH(aq)/Br}_2 \rightarrow \text{the intermediate} \] \[ \text{(2010)} \]

(a) \[ \begin{array}{c}
\text{O}^\ominus \\
\text{Br}
\end{array} \]

(b) \[ \begin{array}{c}
\text{O}^\ominus \\
\text{Br}
\end{array} \]

(c) \[ \begin{array}{c}
\text{O}^\ominus \\
\text{Br}
\end{array} \]

(d) \[ \begin{array}{c}
\text{O}^\ominus \\
\text{Br}
\end{array} \]

4. The major product(s) of the following reaction is(are) \[ \text{(JEE Adv. 2013)} \]

\[ \text{aqueous Br}_2(3.0 \text{ equivalents}) \rightarrow ? \]

(a) \[ \text{P} \]

(b) \[ \text{Q} \]

(c) \[ \text{R} \]

(d) \[ \text{S} \]

5. The correct combination of names for isomeric alcohols with molecular formula \( \text{C}_4\text{H}_{10}\text{O} \) is(are) \[ \text{(JEE Adv. 2014)} \]

(a) Tert-butanol and 2-methylpropan-2-ol

(b) Tert-butanol and 1, 1-dimethylethan-1-ol

(c) n-butanol and butan-1-ol

(d) Isobutyl alcohol and 2-methylpropan-1-ol

6. The reactivity of compound \( Z \) with different halogens under appropriate conditions is given below: \[ \text{(JEE Adv. 2014)} \]

\[ \begin{array}{c}
\text{mono halo substituted} \\
\text{derivative when } \text{X}_2 = \text{I}_2 \\
\end{array} \]

\[ \begin{array}{c}
\text{di halo substituted} \\
\text{derivative when } \text{X}_2 = \text{Br}_2 \\
\end{array} \]

\[ \begin{array}{c}
\text{tri halo substituted} \\
\text{derivative when } \text{X}_2 = \text{Cl}_2 \\
\end{array} \]

The observed pattern of electrophilic substitution can be explained by:

(a) The steric effect of the halogen

(b) The steric effect of the tert-butyl group

(c) The electronic effect of the phenolic group

(d) The electronic effect of the tert-butyl group

7. The major product \( U \) in the following reactions is \[ \text{(JEE Adv. 2015)} \]

\[ \begin{array}{c}
\text{CH}_3=\text{CH-CH}_3 \text{H}^+ \\
\text{high pressure, heat} \\
\rightarrow T \\
\end{array} \]

\[ \begin{array}{c}
\text{radical, initiator, } \text{O}_2
\end{array} \]

E. Subjective Problems

1. An organic liquid (A), containing C, H and O with boiling point: \( 78^\circ \text{C} \), and possessing a rather pleasant odour, on heating with concentrated sulphuric acid gives a gaseous product (B) – with the empirical formula, \( \text{CH}_2 \). ‘B’ decolourises bromine water as well as alkaline KMnO\(_4\) solution and takes up one mole of \( \text{H}_2 \) (per mole of ‘B’) in the presence of finely divided nickel at high temperature. Identify the substances ‘A’ and ‘B’. \[ \text{(1979)} \]
2. A compound (X) containing C, H and O is unreactive towards sodium. It does not add bromine. It also does not react with Schiff’s reagent. On refluxing with an excess of hydroiodic acid, (X) yields only one organic product (Y). On hydrolysis, (Y) yields a new compound (Z) which can be converted into (Y) by reaction with red phosphorus and iodine. The compound (Z) on oxidation with potassium permanganate gives a carboxylic acid. The equivalent weight of this acid is 60. What are the compounds (X), (Y) and (Z)? Write chemical equations leading to the conversion of (X) to (Y). (1981 - 3 Marks)

3. Outline the reaction sequence for the conversion of
   (i) 1-propanol from 2-propanol (in three steps) (1982 - 1 Mark)
   (ii) ethyl alcohol to vinyl acetate. (in not more than 6 steps) (1986 - 3 Marks)
   (iii) phenol to acetophenone (1989 - 1½ Marks)
   (iv) Aspirin (2003 - 2 Marks)

4. State with balanced equations what happens when:
   (i) acetic anhydride reacts with phenol in presence of a base. (1982 - 1 Mark)
   (ii) Ethylene glycol is obtained by the reaction of ethylene with potassium permanganate. (1991 - 1 Mark)

5. Give reasons for the following:
   (i) Sodium metal can be used for drying diethyl ether but not ethanol. (1982 - 1 Mark)
   (ii) Phenol is an acid but it does not react with sodium bicarbonate. (1987 - 1 Mark)
   (iii) Acid catalysed dehydration of t-butanol is faster than that of n-butanol. (1998 - 2 Marks)

6. An alcohol A, when heated with conc. H₂SO₄ gives an alkene B. When B is bubbled through bromine water and the product obtained is dehydrohalogenated with excess of sodium amide, a new compound C is obtained. The compound C gives D when treated with warm dilute H₂SO₄ in presence of Hg₂SO₄. D can also be obtained either by oxidizing A with KMnO₄ or from acetic acid through its calcium salt. Identify A, B, C and D. (1983 - 4 Marks)

7. A compound of molecular formula C₄H₆O₂ is insoluble in water and dilute sodium bicarbonate but dissolves in dilute aqueous sodium hydroxide. On treatment with bromine water, it readily gives a precipitate of C₅H₅OBr₂. Write down the structure of the compound. (1985 - 2 Marks)

8. Give a chemical test/suggest a reagent to distinguish between methanol and ethanol. (1985 - 1 Mark)

9. Complete the following with appropriate structures:
   (i)  
   (ii)  
   (1986 - 1 Mark)

10. Compound ‘X’ (molecular formula, C₅H₅O) does not react appreciably with Lucas reagent at room temperature but gives a precipitate with ammonical silver nitrate. With excess of MeMgBr, 0.42 g of ‘X’ gives 224 ml of CH₄ at STP. Treatment of ‘X’ with H₂ in presence of Pt catalyst followed by boiling with excess H₂, gives n-pentane. Suggest structure for ‘X’ and write the equation involved. (1992 - 1 Mark)

11. When t-butanol and n-butanol are separately treated with a few drops of dilute KMnO₄, in one case only the purple colour disappears and a brown precipitate is formed. Which of the two alcohols gives the above reaction and what is the brown precipitate? (1994 - 2 Marks)

12. When phenol is reacted with CHCl₃ and NaOH followed by acidification, salicylaldehyde is obtained. Which of the following species are involved in the above mentioned reaction as intermediates? (1995 - 2 Marks)

13. 3,3-Dimethylbutan-2-ol loses a molecule of water in the presence of concentrated sulphuric acid to give tetramethylethylene as a major product. Suggest a suitable mechanism. (1996 - 2 Marks)

14. A compound D (C₅H₆O) upon treatment with alkaline solution of iodine gives a yellow precipitate. The filtrate on acidification gives a white solid E (C₅H₅O₂). Write the structures of D and E and explain the formation of E. (1996 - 2 Marks)

15. An optically active alcohol A (C₅H₆O) absorbs two moles of hydrogen per mole of A upon catalytic hydrogenation and gives a product B. The compound B is resistant to oxidation by CrO₃ and does not show any optical activity. Deduce the structures of A and B. (1996 - 2 Marks)

16. Predict the structures of the intermediates/products in the following reaction sequence:

   (1996 - 2 Marks)
17. 2, 2-Dimethyloxirane can be cleaved by acid (H⁺). Write mechanism.  
(1997 - 2 Marks)

18. Which of the following is the correct method for synthesising methyl-t-butyl ether and why?

(i) (CH₃)₂CBr + NaOMe →  
(1997 - 2 Marks)

(ii) CH₃Br + NaO-t-Bu →  
(1997 - 2 Marks)

19. Write the intermediate steps for each of the following reaction.  
(1998 - 1 Mark)

20. Explain briefly the formation of the products giving the structures of the intermediates.  
(1999 - 3 Marks)

21. A biologically active compound, bombykol (C₁₈H₃₀O) is obtained from a natural source. The structure of the compound is determined by the following reactions.  
(2002 - 5 Marks)

(a) On hydrogenation, bombykol gives a compound A, C₁₈H₃₂O, which reacts with acetic anhydride to give an ester;

(b) Bombykol also reacts with acetic anhydride to give another ester, which on oxidative ozonolysis (O₃/H₂O₂) gives a mixture of butanoic acid, oxalic acid and 10-acetoxydecanoic acid.

Determine the number of double bonds in bombykol. Write the structures of compound A and bombykol. How many geometrical isomers are possible for bombykol?

22. An organic compound (P) of molecular formula C₄H₉O is treated with dil. H₂SO₄ to give two compounds (Q) and (R) both of which respond iodoform test. The rate of reaction of (P) with dil. H₂SO₄ is 10¹⁰ faster than the reaction of ethylene with dil. H₂SO₄. Identify the organic compounds, (P), (Q) and (R) and explain the extra reactivity of (P).  
(2004 - 4 Marks)

23. Identify (X) and (Y) in the following reaction sequence.  
(2005 - 2 Marks)

F Match the Following

Following question has matching lists. The codes for the lists have choices (a), (b), (c) and (d) out of which ONLY ONE is correct.

1. Match the chemical conversions in List I with the appropriate reagents in List II and select the correct answer using the code given below the lists:  
(JEE Adv. 2013)

**List I**

- P
- Q
- R
- S

**List II**

- 1. (i) Hg(OAc)₂, (ii) NaBH₄
- 2. NaOEt
- 3. Et-Br
- 4. (i) BH₃, (ii) H₂O₂/NaOH

**Codes:**

<table>
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<th></th>
<th>P</th>
<th>Q</th>
<th>R</th>
<th>S</th>
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</tr>
<tr>
<td>(b)</td>
<td>3</td>
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<td>4</td>
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<tr>
<td>(d)</td>
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G Comprehension Based Questions

PASSAGE-I

Riemer-Tiemann reaction introduces an aldehyde group, on to the aromatic ring of phenol, ortho to the hydroxyl group. This reaction involves electrophilic aromatic substitution. This is a general method for the synthesis of substituted salicylaldehyde as depicted below.
1. Which one of the following reagents is used in the above reaction? (2007)
   (a) aq. NaOH + CH₃Cl  (b) aq. NaOH + CH₂Cl₂
   (c) aq. NaOH + CHCl₃  (d) aq. NaOH + CCl₄

2. The electrophile in the reaction is (2007)
   (a) :CHCl  (b) :CHCl₂
   (c) :CCl₂  (d) :CCl₃

3. The structure of the intermediate I is (2007)

4. Compound H is formed by the reaction of (2008)
   (a) \( \text{PhCO} + \text{PhMgBr} \)
   (b) \( \text{PhCO} + \text{PhCH₂MgBr} \)
   (c) \( \text{PhCO} + \text{PhCH₂MgBr} \)
   (d) \( \text{PhCO} + \text{PhMgBr} \)

PASSAGE - 2
A tertiary alcohol H upon acid catalysed dehydration gives a product I. Ozonolysis of I leads to compounds J and K. Compound J upon reaction with KOH gives benzyl alcohol and compound L, whereas K on reaction with KOH gives only M.

5. The structure of compound I is (2008)
   (a) \( \text{Ph} - \text{CH} = \text{CH} - \text{Ph} \)
   (b) \( \text{H} \)
   (c) \( \text{H} \)
   (d) \( \text{H} \)

6. The structure of compounds J, K and L respectively, are – (2008)
   (a) PhCOCH₃, PhCH₂COC₂H₅ and PhCH₂COO⁻K⁺
   (b) PhCHO, PhCH₂CHO and PhCOO⁻K⁺
   (c) PhCOCH₃, PhCH₂CHO and CH₃COO⁻K⁺
   (d) PhCHO, PhCOCH₃ and PhCOO⁻K⁺

Assertion & Reason Type Questions

1. Read the following statement and explanation and answer as per the options given below: (1988 - 2 Marks)
   Statement (S) : Solubility of n-alcohols in water decreases with increase in molecular weight.
   Explanation (E) : The relative proportion of the hydrocarbon part in alcohols increases with increasing molecular weight which permits enhanced hydrogen bonding with water.
   (a) Both (S) and (E) are correct and (E) is the correct explanation of (S).
   (b) Both (S) and (E) are correct but (E) is not the correct explanation of (S).
   (c) (S) is correct but (E) is wrong.
   (d) (S) is wrong but (E) is correct.

Integer Value Correct Type

1. The number of resonance structures for N is (JEE Adv. 2015)

2. The number of hydroxyl group(s) in Q is (JEE Adv. 2015)
1. During dehydration of alcohols to alkenes by heating with conc. H₂SO₄, the initiation step is (a) formation of carboxylation (b) elimination of water (c) formation of an ester (d) protonation of alcohol molecule

2. Among the following compounds which can be dehydrated very easily is  
\[
\begin{align*}
\text{CH}_3 \\
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 \\
\text{OH} \\
\text{OH} \\
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} \\
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \\
\end{align*}
\]
(a) CH₃CH₂CCH₂CH₃  (b) CH₃CH₂CH₂CH₂OH  (c) CH₃CH₂CH₂CH₂CH₂OH  (d) CH₃CH₂CH₂CH₂CH₂OH

3. The best reagent to convert pent-3-en-2-ol into pent-3-in-2-one is  
(a) Pyridinium chloro-chromate  (b) Chromic anhydride in glacial acetic acid  (c) Acidic dichromate  (d) Acidic permanganate

4. p-cresol reacts with chloroform in alkaline medium to give the compound A which adds hydrogen cyanide to form, the compound B. The latter on acidic hydrolysis gives chiral carboxylic acid. The structure of the carboxylic acid is  
\[
\begin{align*}
\text{OH} \\
\text{CH}_3 \\
\text{CH}_3\text{CH}_2\text{COOH} \\
\text{OH} \\
\text{CH}_3\text{OH} \\
\text{CH}_3\text{OH} \text{COOH} \\
\text{CH}_3\text{OH} \text{COOH} \\
\end{align*}
\]
(a) (b) (c) (d)

5. HBr reacts with CH₂ = CH – OCH₃ under anhydrous conditions at room temperature to give  
\[
\begin{align*}
\text{BrCH}_2\text{–CH}_2\text{–OCH}_3 \\
\text{H}_2\text{C–CHBr–OCH}_3 \\
\text{CH}_3\text{CHO and CH}_3\text{Br} \\
\text{BrCH}_2\text{CHO and CH}_3\text{OH} \\
\end{align*}
\]
(a) BrCH₂–CH₂–OCH₃  (b) H₂C–CHBr–OCH₃  (c) CH₃CHO and CH₃Br  (d) BrCH₂CHO and CH₃OH

6. Among the following the one that gives positive iodoform test upon reaction with I₂ and NaOH is  
\[
\begin{align*}
\text{CH}_3 \\
\text{CH}_3\text{CH} – \text{CHCH}_2\text{OH} \\
\text{PhCHOHCH}_3 \\
\text{CH}_3\text{CH}_2\text{OH(CH)CH}_2\text{CH}_3 \\
\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \\
\end{align*}
\]
(a)  (b)  (c)  (d)

7. The structure of the compound that gives a tribromo derivative on treatment with bromine water is  
\[
\begin{align*}
\text{CH}_3 \\
\text{OH} \\
\text{CH}_3 \\
\text{OH} \\
\text{CH}_3 \\
\text{OH} \\
\end{align*}
\]
(a)  (b)  (c)  (d)

8. The electrophile involved in the above reaction is  
\[
\text{OH} \\
\text{CHCl}_3 + \text{NaOH} \rightarrow \text{O}^\cdot\text{Na}^+ \\
\text{CHO}
\]
(a) trichloromethyl anion (Cl₃C⁻)  (b) formyl cation (CHO⁻)  (c) dichloromethyl cation (Cl₂C⁻)  (d) dichlorocarbene (CCl₂)

9. In the following sequence of reactions,  
\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{OH} & \xrightarrow{\text{P} + \text{I}_2} \text{A} & \xrightarrow{\text{Mg} \text{ ether}} \text{B} & \xrightarrow{\text{HCHO}} \text{C} & \xrightarrow{\text{H}_2\text{O}} \text{D} \\
\end{align*}
\]
the compound D is  
(a) propanal  (b) butanal  (c) n-butyl alcohol  (d) n-propyl alcohol

10. Phenol, when it first reacts with concentrated sulphuric acid and then with concentrated nitric acid, gives  
\[
\begin{align*}
\text{2, 4, 6-trinitrobenzene} \\
\text{o-nitrophenol} \\
\text{p-nitrophenol} \\
\text{nitrobenzene} \\
\end{align*}
\]
(a)  (b)  (c)  (d)
11. The major product obtained on interaction of phenol with sodium hydroxide and carbon dioxide is\[2009\]
   (a) salicylaldehyde  (b) salicylic acid  
   (c) phthalic acid  (d) benzoic acid

12. From amongst the following alcohols the one that would react fastest with conc. HCl and anhydrous ZnCl₂, is\[2010\]
   (a) 2-Butanol  (b) 2-Methylpropan-2-ol  
   (c) 2-Methylpropanol  (d) 1-Butanol

13. The main product of the following reaction is \[\text{C}_6\text{H}_5\text{CH}_2\text{CH(OH)CH(CH}_3)_2\text{H}_3\text{SO}_4\rightarrow?\] \[2010\]
   (a) \[
   \begin{array}{c}
   \text{H} \\
   \text{C} \\
   \text{C} \\
   \text{H} \\
   \text{CH}_3
   \end{array}
   \]
   (b) \[
   \begin{array}{c}
   \text{C}_6\text{H}_5\text{CH}_2 \\
   \text{C} \\
   \text{C} \\
   \text{CH}_3
   \end{array}
   \]
   (c) \[
   \begin{array}{c}
   \text{H}_2\text{C} \\
   \text{C} \\
   \text{C} \\
   \text{CH}_2
   \end{array}
   \]
   (d) \[
   \begin{array}{c}
   \text{C}_6\text{H}_5 \\
   \text{C} \\
   \text{C} \\
   \text{H}
   \end{array}
   \]

14. Phenol is heated with a solution of mixture of KBr and KBrO₃. The major product obtained in the above reaction is:\[2011\]
   (a) 2-Bromophenol  (b) 3-Bromophenol  
   (c) 4-Bromophenol  (d) 2, 4, 6-Tribromophenol

15. Arrange the following compounds in order of decreasing acidity:\[JEE M 2013\]
   (I)  
   (II)  
   (III)  
   (IV)  
   (a) II > IV > I > III  (b) 1 > II > III > IV  
   (c) III > I > II > IV  (d) IV > III > I > II

16. An unknown alcohol is treated with the “Lucas reagent” to determine whether the alcohol is primary, secondary or tertiary. Which alcohol reacts fastest and by what mechanism:\[JEE M 2013\]
   (a) secondary alcohol by S_N1  
   (b) tertiary alcohol by S_N1  
   (c) secondary alcohol by S_N2  
   (d) tertiary alcohol by S_N2

17. Sodium phenoxyde when heated with CO₂ under pressure at 125°C yields a product which on acetylation produces C.
   \[
   \begin{array}{c}
   \text{O} \\
   \text{Na} \\
   \text{C} \\
   \text{O} \\
   \text{C}
   \end{array}
   \]
   \[
   \begin{array}{c}
   \text{O} \\
   \text{CO}_2
   \end{array}
   \]
   \[
   \begin{array}{c}
   \text{H} \\
   \text{Acy}_{2}\text{O}
   \end{array}
   \]
   \[
   \begin{array}{c}
   \text{H} \\
   \text{Acy}_{2}\text{O}
   \end{array}
   \]
   The major product C would be \[\text{JEE M 2014}\]

18. Thiol group is present in:\[JEE M 2016\]
   (a) Cysteine  (b) Methionine  
   (c) Cytosine  (d) Cystine

19. The product of the reaction given below is:\[JEE M 2016\]
   \[
   \begin{array}{c}
   \text{O} \\
   \text{R}
   \end{array}
   \]
   \[
   \begin{array}{c}
   \text{N} \\
   \text{S} \\
   \text{OH}
   \end{array}
   \]
   \[
   \begin{array}{c}
   \text{C} \\
   \text{O}
   \end{array}
   \]
   X

20. 2-chloro-2-methylpentane on reaction with sodium methoxide in methanol yields:\[JEE M 2016\]
   (1) \[
   \begin{array}{c}
   \text{C}_2\text{H}_5\text{CH}_2 \\
   \text{OCH}_3
   \end{array}
   \]
   (2) \[
   \begin{array}{c}
   \text{C}_2\text{H}_5\text{CH}_3 \\
   \text{C} \\
   \text{H}_3
   \end{array}
   \]
   (3) \[
   \begin{array}{c}
   \text{C}_2\text{H}_5\text{CH} = \text{C} \\
   \text{CH}_3
   \end{array}
   \]
   \[
   \begin{array}{c}
   \text{CH}_3
   \end{array}
   \]
   \[
   \begin{array}{c}
   \text{CH}_3
   \end{array}
   \]
   \[
   \begin{array}{c}
   \text{CH}_3
   \end{array}
   \]
   (a) (3) only  (b) (a) and (b)  
   (c) All of these  (d) (a) and (c)
Chapter 20: Aldehydes, Ketones and Carboxylic Acids

Section-A

JEE Advanced/ IIT-JEE

A Fill in the Blanks

1. Formic acid when heated with conc. H₂SO₄ produces \( \text{(H₂SO₄ produces)} \) \( \text{(1983 - 1 Mark)} \)
   (a) \( \text{trimethylacetaldehyde} \) (b) \( \text{acetaldehyde} \) (c) \( \text{benzaldehyde} \) (d) \( \text{formaldehyde} \)

2. Fehling’s solution ‘A’ consists of an aqueous solution of copper sulphate, while Fehling’s solution ‘B’ consists of an alkaline solution of \( \text{(1990 - 1 Mark)} \)
   (a) acetone (b) ethanol (c) diethyl ketone (d) isopropyl alcohol

3. The structure of the intermediate product, formed by the oxidation of toluene with \( \text{CrO₃} \) and acetic anhydride, whose hydrolysis gives benzaldehyde is \( \text{(1992 - 1 Mark)} \)

4. The structure of the enol form of \( \text{CH₃-CO-CH₂-CO-CH₃} \) with intramolecular hydrogen bonding is \( \text{(1993 - 1 Mark)} \)

B True / False

1. Benzaaldehyde undergoes aldol condensation in an alkaline medium. \( \text{(1982 - 1 Mark)} \)

2. Hydrolysis of an ester in presence of a dilute acid is known as saponification. \( \text{(1983 - 1 Mark)} \)

3. The yield of ketone when a secondary alcohol is oxidized is more than the yield of aldehyde when a primary alcohol is oxidized. \( \text{(1983 - 1 Mark)} \)

4. The reaction of methyl magnesium iodide with acetone followed by hydrolysis gives secondary butanol. \( \text{(1987 - 1 Mark)} \)

5. The boiling point of propionic acid is less than that of \( \text{n} \)-butyl alcohol, an alcohol of comparable molecular weight. \( \text{(1991 - 1 Mark)} \)

C MCQs with One Correct Answer

1. The reagent with which both acetaldehyde and acetone react easily is \( \text{(1981 - 1 Mark)} \)
   (a) Fehling’s reagent (b) Grignard reagent (c) Schiff’s reagent (d) Tollens’ reagent

2. When acetaldehyde is heated with Fehling’s solution it gives a precipitate of \( \text{(1983 - 1 Mark)} \)
   (a) Cu (b) CuO (c) \( \text{Cu}_2\text{O} \) (d) \( \text{Cu + Cu}_2\text{O} + \text{CuO} \)

3. The Cannizzaro reaction is not given by \( \text{(1983 - 1 Mark)} \)
   (a) \( \text{trimethylacetaldehyde} \) (b) \( \text{acetaldehyde} \) (c) \( \text{benzaldehyde} \) (d) \( \text{formaldehyde} \)

4. The compound that will not give iodoform on treatment with alkali and iodine is \( \text{(1985 - 1 Mark)} \)
   (a) acetone (b) ethanol (c) diethyl ketone (d) isopropyl alcohol

5. Polarisation of electrons in acrolein may be written as \( \text{(1988 - 1 Mark)} \)
   (a) \( \delta^- \text{CH}_2 = \text{CH} - \text{CH} = \delta^+ \) (b) \( \delta^- \text{CH}_2 = \text{CH} - \text{CH} = \delta^+ \)
   (c) \( \delta^- \text{CH}_2 = \text{CH} - \text{CH} = \delta^- \) (d) \( \delta^- \text{CH}_2 = \text{CH} - \text{CH} = \delta^- \)

6. The enolic form of acetone contains \( \text{(1990 - 1 Mark)} \)
   (a) 9 sigma bonds, 1 pi-bond and 2 lone pairs (b) 8 sigma bonds, 2 pi-bonds and 2 lone pairs (c) 10 sigma bonds, 1 pi-bond and 1 lone pair (d) 9 sigma bonds, 2 pi-bonds and 1 lone pair

7. \( m \)-Chlorobenzaldehyde on reaction with conc. KOH at room temperature gives \( \text{(1991 - 1 Mark)} \)
   (a) potassium \( m \)-chlorobenzoate and \( m \)-hydroxybenzaldehyde (b) \( m \)-hydroxybenzaldehyde and \( m \)-chlorobenzyl alcohol (c) \( m \)-chlorobenzyl alcohol and \( m \)-hydroxybenzyl alcohol (d) potassium \( m \)-chlorobenzoate and \( m \)-chlorobenzyl alcohol

8. Hydrogenation of benzoic acid in the presence of Pd on BaSO₄ gives \( \text{(1992 - 1 Mark)} \)
   (a) Benzylic alcohol (b) Benzylicdehyde (c) Benzoic acid (d) Phenol

9. The organic product formed in the reaction \( \text{(1995S)} \)
   \( \text{C}_6\text{H}_5\text{COOH} \xrightarrow{\text{LiAlH}_4} \text{II H}_2\text{O}^- \)
   (a) \( \text{C}_6\text{H}_5\text{CH}_2\text{OH} \) (b) \( \text{C}_6\text{H}_5\text{COOH} \text{& CH}_4 \) (c) \( \text{C}_6\text{H}_5\text{CH}_3 \text{& CH}_3\text{OH} \) (d) \( \text{C}_6\text{H}_5\text{CH}_3 \text{& CH}_4 \)

10. The reaction products of \( \text{C}_6\text{H}_5\text{OCH}_3 + \text{H}_2 \) \( \xrightarrow{\text{A}} \) is \( \text{(1995S)} \)
    (a) \( \text{C}_6\text{H}_5\text{OH} + \text{CH}_3\text{I} \) (b) \( \text{C}_6\text{H}_5\text{I} + \text{CH}_3\text{OH} \) (c) \( \text{C}_6\text{H}_5\text{CH}_3 + \text{HOI} \) (d) \( \text{C}_6\text{H}_6 + \text{CH}_3\text{OH} \)
11. In the Cannizzaro reaction given below, \( \textbf{(1996 - 1 Mark)} \)

\[
2 \text{PhCHO} \xrightarrow{\text{-OH}} \text{PhCH}_2\text{OH} + \text{PhCO}_2^-,
\]

the slowest step is

(a) the attack of -OH at the carbonyl group,
(b) the transfer of hydride to the carbonyl group,
(c) the abstraction of proton from the carboxylic acid,
(d) the deprotonation of PhCH$_2$OH.

12. When propionic acid is treated with aqueous sodium bicarbonate, CO$_2$ is liberated. The 'C' of CO$_2$ comes from \( \textbf{(1999 - 2 Marks)} \)

(a) methyl group  
(b) carboxylic acid group  
(c) methylene group  
(d) bicarbonate

13. The enol form of acetone, after treatment with D$_2$O, gives. \( \textbf{(1999 - 2 Marks)} \)

(a) $\text{CH}_3-\text{C}\equiv\text{CD}_2$  
(b) $\text{CD}_3-\text{C}\equiv\text{CD}_3$

14. Which one of the following will most readily be dehydrated in acidic condition? \( \textbf{(2000S)} \)

(a) \[
\begin{array}{c}
\text{O} \\
\text{H}
\end{array}
\]

(b) \[
\begin{array}{c}
\text{O} \\
\text{H}
\end{array}
\]

(c) \[
\begin{array}{c}
\text{O} \\
\text{H}
\end{array}
\]

(d) \[
\begin{array}{c}
\text{O} \\
\text{H}
\end{array}
\]

15. Benzoyl chloride is prepared from benzoic acid by \( \textbf{(2000S)} \)

(a) \( \text{Cl}_2, h\nu \)  
(b) \( \text{SO}_2\text{Cl}_2 \)  
(c) \( \text{SOCl}_2 \)  
(d) \( \text{Cl}_2, \text{H}_2\text{O} \)

16. The appropriate reagent for the following transformation is \( \textbf{(2000S)} \)

(a) $\text{Zn(Hg), HCl}$  
(b) $\text{NH}_2\text{NH}_2, \text{OH}^-$  
(c) $\text{H}_2\text{Ni}$  
(d) $\text{NaBH}_4$

17. A mixture of benzaldehyde and formaldehyde on heating with aqueous NaOH solution gives \( \textbf{(2001S)} \)

(a) benzyl alcohol and sodium formate  
(b) sodium benzoate and methyl alcohol  
(c) sodium benzoate and sodium formate  
(d) benzyl alcohol and methyl alcohol

18. The product of acid hydrolysis of P and Q can be distinguished by \( \textbf{(2003S)} \)

\[
P = \text{H}_2\text{C} = \text{C} = \text{COCH}_3, \quad Q = \text{H}_3\text{C} = \text{C} = \text{COCH}_3
\]

(a) Lucas Reagent  
(b) 2,4-DNP  
(c) Fehling's Solution  
(d) NaHSO$_3$

19. Major product is : \( \textbf{(2003S)} \)

20. Ethyl ester $\xrightarrow{\text{CH}_3\text{MgBr excess}}$ P. The product P will be \( \textbf{(2003S)} \)

(a) \[
\begin{array}{c}
\text{H}_3\text{C} \\
\text{H}_3\text{C}
\end{array}
\]

(b) \[
\begin{array}{c}
\text{H}_3\text{C} \\
\text{H}_3\text{C}
\end{array}
\]

(c) \[
\begin{array}{c}
\text{H}_3\text{C} \\
\text{H}_3\text{C}
\end{array}
\]

(d) \[
\begin{array}{c}
\text{H}_3\text{C} \\
\text{H}_3\text{C}
\end{array}
\]
21. An enantiomerically pure acid is treated with a racemic mixture of an alcohol having one chiral carbon. The ester formed will be (2003S)
   (a) Optically active mixture (b) Pure enantiomer
   (c) Meso compound (d) Racemic mixture

22. The correct order of reactivity of PhMgBr with (2004S)
   Ph – C – Ph
   CH₃ – C – H
   CH₃ – C – CH₃ is
   (I) (II) (III)
   (a) (I) > (II) > (III) (b) (III) > (II) > (I)
   (c) (II) > (III) > (I) (d) (I) > (III) > (II)

23. How will you convert butan-2-one to propanoic acid? (2005S)
   (a) Tollen’s reagent (b) Fehling’s solution
   (c) NaOH/I₂/H⁺ (d) NaOH/Nal/H⁺

24. MeO\[\text{ph} \text{CHO} + (X)\] 
   \[\xrightarrow{\text{CH₃COONa H⁺}}\] \[\text{CH} = \text{CHOH}\]
   The compound (X) is (2005S)
   (a) CH₃COOH (b) BrCH₂–COOH
   (c) (CH₃CO)₂O (d) CHO – COOH

25. 4-Methylbenzenesulphonic acid reacts with sodium acetate to give (2005S)
   \[\text{CH₃SO₃Na} \quad \text{CH₃COOH} \quad \text{COONa} \quad \text{SO₃} \quad \text{CH₃} \quad \text{CH₃} \quad \text{SO₂} - \text{O} - \text{COCH₃} \quad \text{NaOH} \]
   (a) (b) (c) (d)

26. In the following reaction sequence, the correct structures of E, F and G are
   \[\text{Ph} \quad \text{OH} \xrightarrow{\text{Heat}} [E] \xrightarrow{\text{I₂ NaOH}} [F] + [G] \]
   [* implies ¹³C labelled carbon] (2008)
   (a) E = Ph \[\text{O} \quad \text{CH₃} \]
   (b) F = Ph \[\text{O} \quad \text{Na} \quad \text{G = CH₃} \]
   (c) (d)

27. The correct acidity order of the following is (2009S)
   \[\text{OH} \quad \text{OH} \quad \text{COOH} \quad \text{COOH} \]
   (I) (II) (III) (IV)
   (a) (II) > (IV) > (II) > (I) (b) (IV) > (III) > (I) > (II)
   (c) (II) > (III) > (IV) > (I) (d) (I) > (III) > (IV) > (I)

28. In the reaction
   \[\text{H₃C} - \text{phenyl} - \text{NH₂} \xrightarrow{1. \text{NaOH/Br₂}} \text{T} \]
   \[\xrightarrow{2. \text{aryl} - \text{COCl}}\]
   the structure of the product T is: (2010)
   (a) \[\text{H₃C} - \text{phenyl} - \text{O} - \text{COO}\]
   (b) \[\text{aryl} - \text{NH} - \text{C} - \text{phenyl} - \text{CH₃}\]
   (c) \[\text{H₃C} - \text{phenyl} - \text{NH} - \text{C} - \text{phenyl}\]
   (d) \[\text{H₃C} - \text{phenyl} - \text{NH} - \text{C} - \text{phenyl}\]
29. The compounds P, Q and S were separately subjected to nitration using HNO₃/H₂SO₄ mixture. The major product formed in each case respectively, is:

(a) ![Diagram of compound A]
(b) ![Diagram of compound B]
(c) ![Diagram of compound C]
(d) ![Diagram of compound D]

30. The major product of the following reaction is:

![Reaction Diagram]

(a) a hemiacetal
(b) an acetal
(c) an ether
(d) an ester

31. The carboxyl functional group (−COOH) is present in:

(a) picric acid
(b) barbituric acid
(c) ascorbic acid
(d) aspirin

32. The major product H of the given reaction sequence is:

CH₃—CH₂—CO—CH₃ → G → H

(a) CH₃—CH═C—COOH
(b) CH₃—CH═C—CN
(c) CH₃—CH₂—C—COOH
(d) CH₃—CH—C—CO—NH₂

33. The compound that undergoes decarboxylation most readily under mild condition is:

(a) ![Diagram of compound A]
(b) ![Diagram of compound B]
(c) ![Diagram of compound C]
(d) ![Diagram of compound D]

34. The compound that does NOT liberate CO₂, on treatment with aqueous sodium bicarbonate solution, is:

(a) Benzoic acid
(b) Benzenesulphonic acid
(c) Salicylic acid
(d) Carbolic acid (Phenol)

35. The major product in the following reaction is:

![Reaction Diagram]

(a) ![Diagram of compound A]
(b) ![Diagram of compound B]
(c) ![Diagram of compound C]
(d) ![Diagram of compound D]
36. The correct order of acidity for the following compounds is

(a) I > II > III > IV (b) III > I > II > IV (c) III > IV > II > I (d) I > III > IV > II

(JEE Adv. 2016)

37. The major product of the following reaction sequence is

(i) HCHO (excess) / NaOH, heat
(ii) HCHO/H⁺ (catalytic amount)

(a) (b) (c) (d)

(JEE Adv. 2016)

6. A new carbon-carbon bond formation is possible in
   (a) Cannizzaro reaction (1998 - 2 Marks)
   (b) Friedel–Craft alkylation
   (c) Clemmensen reduction
   (d) Reimer–Tiemann reaction

7. Which of the following will react with water?
   (1998 - 2 Marks)
   (a) CHCl₃ (b) Cl₂CCHO (c) CCl₄ (d) ClCH₂CH₂Cl

8. Which of the following will undergo aldol condensation?
   (1998 - 2 Marks)
   (a) acetaldehyde (b) propanaldehyde (c) benzaldehyde (d) trideuterocetaldehyde

9. Which of the following reactants on reaction with conc. NaOH followed by acidification gives following lactone as the product?
   (2006 - 5M, -1)

10. \[ \text{ + Cl–CH₂CH₂CH₃} \]
    \[ \text{AlCl₃} \rightarrow \text{P} \]
    \[ (i) O₂ /Δ \rightarrow Q + \text{Phenol} \]

The major products P and Q are
   (2006 - 5M, -1)

   (a) (b) (c) (d)

11. The smallest ketone and its next homologue are reacted with NH₂OH to form oxime
    (2006 - 5M, -1)
    (a) Two different oximes are formed
    (b) Three different oximes are formed
    (c) Two oximes formed are optically active
    (d) All oximes formed are optically active
12. Identify the binary mixture(s) that can be separated into individual compounds, by differential extraction as shown in the given scheme.

\[ \text{NaOH (aq)} \rightarrow \text{Compound 1} + \text{Compound 2} \]

(a) \( \text{C}_4\text{H}_8\text{OH} \) and \( \text{C}_6\text{H}_5\text{COOH} \)
(b) \( \text{C}_6\text{H}_5\text{COOH} \) and \( \text{C}_6\text{H}_5\text{CH}_2\text{OH} \)
(c) \( \text{C}_6\text{H}_5\text{CH}_2\text{OH} \) and \( \text{C}_6\text{H}_5\text{OH} \)
(d) \( \text{C}_6\text{H}_5\text{CH}_2\text{OH} \) and \( \text{C}_6\text{H}_5\text{COOH} \)

13. With reference to the scheme given below, which of the given statement(s) about T, U, V and W is (are) correct?

\[ \text{\chem{C=O}} \xrightarrow{\text{LiAlH}_4} \text{\chem{O=O}} \]

(a) T is soluble in hot aqueous NaOH
(b) U is optically active
(c) Molecular formula of W is \( \text{C}_{10}\text{H}_{18}\text{O}_4 \)
(d) V gives effervescence on treatment with aqueous NaHCO\(_3\)

14. In the following reaction, the product(s) formed is(are)

\[ \text{OH} \rightarrow \text{CHCl}_3 \xrightarrow{\text{OH}^-} \]

(a) P (major)
(b) Q (minor)
(c) R (minor)
(d) S (major)

15. After completion of the reactions (I and II), the organic compound(s) in the reaction mixtures is(are)

\[ \text{Br}_2 \text{ (1.0 mol)} \rightarrow \text{aqueous NaOH} \]

(a) Reaction I: P and Reaction II: P
(b) Reaction I: U, acetone and Reaction II: Q, acetone
(c) Reaction I: T, U, acetone and Reaction II: P
(d) Reaction I: R, acetone and Reaction II: S, acetone

16. The major product of the following reaction is

\[ \text{\chem{\text{O=C=O}}} \xrightarrow{i. \text{KOH, H}_2\text{O}} \xrightarrow{\text{ii. H}^+\text{ heat}} \]

(a) \( \text{(a)} \)
(b) \( \text{(b)} \)
(c) \( \text{(c)} \)
(d) \( \text{(d)} \)

17. Positive Tollens’s test is observed for

\[ \text{H=O} \]

(a) \( \text{(a)} \)
(b) \( \text{(b)} \)
(c) \( \text{(c)} \)
(d) \( \text{(d)} \)
18. The correct statement(s) about the following reaction sequence is(are)

\[ \text{Cumene(C}_9\text{H}_{12}) \xrightarrow{(i) \text{O}_2, (ii) H_3O^+} \text{P} \xrightarrow{\text{CHCl}_3/\text{NaOH}} \text{Q (major)} + \text{R (minor)} \xrightarrow{\text{NaOH}, \text{Ph}_2\text{CBr}_2} \text{S}\]

(a) R is steam volatile
(b) Q gives dark violet coloration with 1% aqueous FeCl$_3$ solution
(c) S gives yellow precipitate with 2, 4-dinitrophenylhydrazine
(d) S gives dark violet coloration with 1% aqueous FeCl$_3$ solution

19. Reagent(s) which can be used to bring about the following transformation is (are)

\[ \text{LiAlH}_4 \text{ in (C}_2\text{H}_5\text{)_2O} \quad \text{or} \quad \text{BH}_3 \text{ in THF} \quad \text{or} \quad \text{NaBH}_4 \text{ in C}_2\text{H}_5\text{OH} \quad \text{or} \quad \text{Raney Ni/H}_2 \text{ in THF}\]

E Subjective Problems

1. Write the structural formula of the main organic product formed when:

(i) Methanal reacts with ammonia

(ii) Ethyl acetate is treated with double the molar quantity of ethyl magnesium bromide and the reaction mixture poured into water.

(iii) Benzene

(iv) Propanal

(v) H$_2$CO

(vi) C$_6$H$_5$COOH + CH$_3$MgI \rightarrow ? + ?

(vii) C$_6$H$_5$CH$_2$CO$_2$CH$_3$ \(\xrightarrow{(i) \text{CH}_3\text{MgBr (excess)}}\) \(\xrightarrow{(ii) \text{H}^+}\)

(viii) CH$_3$ - CH$_2$ - COOH

(ix) C$_6$H$_5$ - CHO + CH$_3$ - COOC$_2$H$_5$ \(\xrightarrow{\text{NaOC}_2\text{H}_5 \text{in absolute} C_2\text{H}_5\text{OH and heat}}\)

(x) o-HOOC - C$_6$H$_4$ - CH$_2$ - C$_6$H$_5$

\[ \xrightarrow{\text{SOCl}_2} \text{G} \xrightarrow{\text{anhydrous AlCl}_3} \text{H} \xrightarrow{\text{Zn-} \text{Hg}, \text{HCl}} \text{I} \xrightarrow{\text{1995 - 2 Marks}} \]

(xi) Complete the following reaction with appropriate structure.

\[ \xrightarrow{\text{CH}_3\text{CH}_2\text{H}_2\text{C}=\text{O}, 1.\text{KCN/H}_2\text{SO}_4, 2.\text{LiAlH}_4} \text{D} \xrightarrow{\text{2000 - 1 Mark}} \]

(xii) \[\xrightarrow{\text{1997 - 1 Mark}} \]

(xiii) \[\xrightarrow{\text{1997 - 1 Mark}} \]

(xiv) \[\xrightarrow{\text{1997 - 1 Mark}} \]

(xv) \[\xrightarrow{\text{1997 - 1 Mark}} \]

(xvi) \[\xrightarrow{\text{1997 - 1 Mark}} \]

(xvii) \[\xrightarrow{\text{2000 - 2 Marks}} \]

(xviii) \[\xrightarrow{\text{2000 - 1 Mark}} \]

(xix) Write the structures of the products A and B.

\[ \xrightarrow{1. \text{alcoholic KOH (excess)} \xrightarrow{2. \text{H}^+}} \]

(2000 - 2 Marks)

(xx) Identify A, B, C and give their structures.

\[ \xrightarrow{\text{B}_5, \text{NaOH}} \xrightarrow{\text{H}^+, \Delta} \]

(2000 - 3 Marks)
2. Write the chemical equation to show what happens when ethyl acetate is treated with sodium ethoxde in ethanol and the reaction mixture is acidified.  
(1981 - 2 Marks)

3. Outline the reaction sequence for the conversion of
(i) methanal to ethanol (the number of steps should not be more than three).  
(1981 - 2 Marks)
(ii) acetylene to acetone  
(1985 - 1 Mark)
(iii) acetic acid to tertiary-butyl alcohol.  
(1989 - 1½ Marks)
(iv) Ethanal to 2-hydroxy-3-butoenoic acid.  
(1990 - 2 Marks)
(v) Ethanoic acid to a mixture of methanoic acid and diphenyl ketone.  
(1990 - 2 Marks)
(vi) Carry out the following transformation in not more than three steps.  
(1999 - 3 Marks)
\[
\text{CH}_3 - \text{CH}_2 - \text{C} = \text{C} - \text{H} \rightarrow \text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{C} = \text{C} - \text{CH}_3
\]

4. Outline the accepted mechanism of the following reaction. Show the various steps including the charged intermediates.  
(1981 - 3 Marks)

\[
\begin{align*}
\text{O} \\
\text{O} \\
+ \text{CH}_3 - \text{C} - \text{Cl} & \xrightarrow{\text{AlCl}_3} \\
\text{CH}_3 - \text{C} - \text{CH}_3 + \text{HCl}
\end{align*}
\]

5. An alkene (A) on ozonolysis yields acetone and an aldehyde. The aldehyde is easily oxidized to an acid (B). When B is treated with bromine in presence of phosphorus, it yields a compound (C) which on hydrolysis gives a hydroxy acid (D). This acid can also be obtained from acetone by reaction with hydrogen cyanide followed by hydrolysis. Identify the compounds A, B, C and D.  
(1982 - 2 Marks)

6. Give reasons for the following:
(i) Acetic acid can be halogenated in the presence of red P and Cl₂ but formic acid cannot be halogenated in the same way.  
(1983 - 1 Mark)
(ii) Formic acid is a stronger acid than acetic acid;  
(1985 - 1 Mark)
(iii) Suggest a reason for the large difference between the boiling points of butanol and butanal, although they have almost the same solubility in water.  
(1985 - 2 Marks)
(iv) Hydrazones of aldehydes and ketones are not prepared in highly acidic medium.  
(1986 - 1 Mark)
(v) Iodoform is obtained by the reaction of acetone with hypoidote but not with iodide ion.  
(1991 - 1 Mark)
(vi) In acylium ion, the structure R – C⁺ = O⁺ is more stable than R – C⁺ = O⁻.  
(1994 - 1 Mark)
(vii) Although phenoxide ion has more number of resonating structures than benzoate ion, benzoic acid is a stronger acid than phenol. Why?  
(1997 - 2 Marks)
(viii) Explain why o-hydroxybenzaldehyde is a liquid at room temperature while p-hydroxybenzaldehyde is a high melting solid.  
(1999 - 2 Marks)

7. State the conditions under which the following preparation are carried out. Give the necessary equations which need not be balanced.
(i) Ethanol from acetylene  
(1983 - 1 Mark)
(ii) Acetic acid from methyl iodide  
(1983 - 1 Mark)

8. What happens when p-xylene is reacted with concentrated sulphuric acid and the resultant product is fused with KOH.  
(1984 - 2 Marks)

9. Write down the reactions involved in the preparation of the following using the reagents indicated against it in parenthesis:
Propionic anhydride from propionaldehyde  
\[\text{AgNO}_3/\text{NH}_4\text{OH, P}_2\text{O}_5.\]  
(1984 - 2 Marks)

10. Give a chemical test/suggest a reagent to distinguish between acetalddehyde from acetone.  
(1987 - 1 Mark)

11. Arrange the following in increasing ease of hydrolysis
\[\text{CH}_3\text{COOC}_2\text{H}_5, \text{CH}_3\text{COCl}, (\text{CH}_3\text{CO})_2\text{O}, \text{CH}_3\text{CONH}_2.\]  
(1986 - 1 Mark)

12. A white precipitate was formed slowly when silver nitrate was added to a compound (A) with molecular formula C₆H₁₂Cl. Compound (A) on treatment with hot alcoholic potassium hydroxide gave a mixture of two isomeric alkenes (B) and (C), having formula C₆H₁₂. The mixture of (B) and (C), on ozonolysis, furnished four compounds:
(i) CH₃CHO;  
(ii) C₂H₅CHO;  
(iii) CH₃COCH₃ and (iv) H₂C – CH – CHO \[\xrightarrow{\text{CH}_3}\]  
(1986 - 4 Marks)

What are the structures of (A), (B) and (C)?

13. A liquid (X), having a molecular formula C₆H₁₂O₂ is hydrolysed with water in the presence of an acid to give a carboxylic acid (Y) and an alcohol (Z). Oxidation of (Z) with chromic acid gives (Y). What are the structures of (X), (Y) and (Z)?  
(1986 - 3 Marks)

14. Complete the following with appropriate structures:
(i) (CH₃CO)₂O \[\xrightarrow{\text{C}_2\text{H}_5\text{OH}}\] CH₃COOH + ?  
(1986 - 1 Mark)
(ii) ? \[\xrightarrow{\text{NaOH}}\] \[\text{CH} = \text{CH} – \text{CHO}\]  
(1986 - 1 Mark)

15. An unknown compound of carbon, hydrogen and oxygen contains 69.77% carbon and 11.63% hydrogen and has a molecular weight of 86. It does not reduce Fehling solution, but forms a bisulphite addition compound and gives a positive iodoform test. What are the possible structures for the unknown compound?  
(1987 - 5 Marks)

16. An organic compound (A) on treatment with acetic acid in the presence of sulphuric acid produces an ester (B), (A) on mild oxidation gives (C), (C) with 50% potassium hydroxide followed by acidification with dilute hydrochloric acid generates (A) and (D), (D) with phosphorus pentachloride followed by reaction with ammonia gives (E), (E) on dehydration produces hydrocyanic acid. Identify the compounds A, B, C, D and E.  
(1987 - 5 Marks)
17. Complete the following reactions:

(i) \( \text{H}_2\text{C} – \text{CHO} \xrightarrow{\text{CH}_3\text{MgBr}} \text{H}_2\text{C} – \text{C}-\text{CH}_3 \xrightarrow{\ell} \text{OH} \xrightarrow{\ell} \text{H}_3\text{C} – \text{C}-\text{CH}_3 \)  

(1988 - 1 Marks)

(ii) \( \text{CH}_3\text{COOH} \xrightarrow{\ell} \text{ClCH}_2\text{COOH} \) excess ammonia  

(1988 - 1 Marks)

(iii) \( \text{SO}_3\text{H} \xrightarrow{\text{acid catalyst}} \text{OH} \xrightarrow{\ell} \text{CHCl}_3/\text{NaOH} \)  

(1988 - 1 Marks)

(iv) \( \text{ } \xrightarrow{\text{base catalyst}} \text{ } \xrightarrow{\ell} \text{ } \)  

(1988 - 1 Marks)

18. A hydrocarbon \( A \) (molecular formula \( C_5H_{10} \)) yields 2-methylbutane on catalytic hydrogenation. \( A \) adds \( \text{HBr} \) (in accordance with Markownikoff’s rule) to form a compound \( B \) which on reaction with silver hydroxide forms an alcohol \( C, C_6H_7\text{O} \). Alcohol \( C \) on oxidation gives a ketone \( D \). Deduc the structures of \( A, B, C \) and \( D \) and show the reactions involved.  

(1988 - 5 Marks)

19. A ketone ‘A’ which undergoes haloform reaction gives compound \( B \) on reduction. \( B \) on heating with sulphuric acid gives compound \( C \), which forms monooxoenucleate \( D \). \( D \) on hydrolysis in presence of zinc dust gives only acetaldehyde. Identify \( A, B \) and \( C \). Write down the reactions involved.  

(1989 - 4 Marks)

20. The sodium salt of a carboxylic acid, \( A \), was produced by passing a gas, \( B \), into an aqueous solution of caustic alkali at an elevated temperature and pressure. \( A \), on heating in presence of sodium hydroxide followed by treatment with sulphuric acid gave a dibasic acid, \( C \). A sample of 0.4 g of acid \( C \), on combustion gave 0.08 g of water and 0.39 g of carbon dioxide. The silver salt of the acid \( C \) weighing 1.0 g on ignition yielded 0.71 g of silver as residue. Identify \( A, B \) and \( C \).  

(1990 - 5 Marks)

21. Compound \( A \) (\( C_6H_{12}O_2 \)) on reduction with LiAlH\(_4\) yielded two compounds \( B \) and \( C \). The compound \( B \) on oxidation gave \( D \), which on treatment with aqueous alkali and subsequent heating furnished \( E \). The latter on catalytic hydrogenation gave \( G \). The compound \( D \) was oxidised further to give \( F \) which was found to be a monobasic acid (molecular weight = 60.0). Deduce the structures of \( A, B, C, D \) and \( E \).  

(1990 - 4 Marks)

22. An organic compound containing \( C, H \) and \( O \) exists in two isomeric forms \( A \) and \( B \). An amount of 0.108 g of one of the isomers gives on combustion 0.308 g of \( \text{CO}_2 \) and 0.072 g of \( \text{H}_2\text{O} \). \( A \) is insoluble in \( \text{NaOH} \) and \( \text{NaHCO}_3 \) while \( B \) is soluble in \( \text{NaOH} \). \( A \) reacts with conc. \( \text{H}_2\text{SO}_4 \) to give compounds \( C \) and \( D \). \( C \) can be separated from \( D \) by ethanolic \( \text{AgNO}_3 \) solution and \( D \) is soluble in \( \text{NaOH} \). \( B \) reacts readily with bromine water to give compound \( E \) of molecular formula, \( \text{C}_6\text{H}_5\text{OBr}_3 \). Identify, \( A, B, C, D \) and \( E \) with justification and give their structures.  

(1991 - 6 Marks)

23. (i) \( \text{C}_8\text{H}_5\text{COOH} \xrightarrow{\text{PCL}_5} \text{C} \)  

(1991 - 2 Marks)

(ii) \( \text{H}_2\text{C} – \text{CH}=\text{CH}_2 \xrightarrow{\ell} \text{F} \)  

(1991 - 2 Marks)

Identify \( C, D \) and \( E \).

24. Compound ‘\( X \)’, containing chlorine on treatment with strong ammonia gives a solid ‘\( Y \)’ which is free from chlorine. ‘\( Y \)’ analysed as \( C = 49.31\% \), \( H = 9.59\% \) and \( N = 19.18\% \) and reacts with \( \text{Br}_2 \) and caustic soda to give a basic compound ‘\( Z \)’. ‘\( Z \)’ reacts with \( \text{HNO}_2 \) to give ethanol. Suggest structures for ‘\( X \)’, ‘\( Y \)’ and ‘\( Z \)’.  

(1992 - 1 Mark)

25. An organic compound ‘\( A \)’ on treatment with ethyl alcohol gives a carboxylic acid ‘\( B \)’ and compound ‘\( C \)’. Hydrolysis of ‘\( C \)’ under acidic conditions gives ‘\( B \)’ and ‘\( D \)’. Oxidation of ‘\( D \)’ with \( \text{KMnO}_4 \) also gives ‘\( B \)’. ‘\( B \)’ on heating with \( \text{Ca(OH)}_2 \) gives ‘\( E \)’ (molecular formula, \( \text{C}_6\text{H}_5\text{O} \)). ‘\( E \)’ does not give Tollent’s test and does not induce Feuling’s solution but forms a 2,4-dinitrophenylhydrazone. Identify ‘\( A \)’, ‘\( B \)’, ‘\( C \)’, ‘\( D \)’ and ‘\( E \)’.  

(1992 - 3 Marks)

26. Arrange the following in increasing order of expected enol content  

(1992 - 1 Mark)

\( \text{CH}_3\text{COCH}_2\text{CHO}, \text{CH}_3\text{COCH}_3, \text{CH}_3\text{CHO}, \text{CH}_3\text{COCH}_2\text{COCH}_3 \)

27. In the following reactions identify the compounds \( A, B \) and \( D \).  

(1994 - 1 \times 4 = 4 Marks)

\[
\begin{align*}
P\text{Cl}_5 & \quad + \quad \text{SO}_2 & \quad \rightarrow & \quad \text{A} & \quad + & \quad \text{B} \\
\text{A} & \quad + \quad \text{CH}_3\text{COOH} & \quad \rightarrow & \quad \text{C} & \quad + & \quad \text{SO}_2 & + & \text{HCl} \\
2\text{C} & \quad + \quad (\text{CH}_3)_2\text{Cd} & \quad \rightarrow & \quad 2\text{D} & \quad + & \quad \text{CdCl}_2
\end{align*}
\]

28. When gas \( A \) is passed through dry KOH at low temperature, a deep red coloured compound \( B \) and a gas \( C \) are obtained. The gas \( A \), on reaction with but-2-ene, followed by treatment with \( \text{Zn/H}_2\text{O} \) yields acetaldehyde. Identify \( A, B \) and \( C \).  

(1994 - 3 Marks)

29. An organic compound \( A, \text{C}_8\text{H}_6 \), on treatment with dilute sulphuric acid containing mercuric sulphate gives a compound \( B \), which can also be obtained from a reaction of benzene with an acid chloride in the presence of anhydrous aluminium chloride. The compound \( B \), when treated with iodine in aqueous KOH, yields \( C \) and a yellow compound \( D \). Identify \( A, B, C \) and \( D \) with justification. Show how \( B \) is formed from \( A \).  

(1994 - 3 Marks)

30. Which of the following carboxylic acids undergoes decarboxylation easily? Explain briefly.  

(1995 - 2 Marks)

\( \text{(i) C}_6\text{H}_5\text{CO} – \text{CH}_2 – \text{COOH} \)  

\( \text{(ii) C}_6\text{H}_5\text{CO} – \text{COOH} \)  

\( \text{(iii) C}_6\text{H}_5 – \text{CH} – \text{COOH} \)  

\( \text{(iv) C}_6\text{H}_5 – \text{CH} – \text{COOH} \)  

\( \text{OH} \)  

\( \text{NH}_2 \)
31. Suggest appropriate structures for the missing compounds. (The number of carbon atoms remains the same throughout the reactions.)

\[
\text{dil. KMnO}_4 \rightarrow \text{A} \rightarrow \text{B} \rightarrow \text{C}
\]

(1996 - 3 Marks)

32. An ester A (C₄H₅O₂), on treatment with excess methyl magnesium chloride followed by acidification, gives an alcohol B as the sole organic product. Alcohol B, on oxidation with NaOCl followed by acidification, gives acetic acid. Deduce the structures of A and B. Show the reactions involved.

(1998 - 6 Marks)

33. An aldehyde A (C₁₁H₂₂O₂), which does not undergo self aldol condensation, gives benzaldehyde and two moles of B on ozonolysis. Compound B, on oxidation with silver ion gives oxalic acid. Identify the compounds A and B.

(1998 - 2 Marks)

34. Write the intermediate steps for the following reaction.

\[
\text{C₆H₅CH(OH)C=CH} \xrightarrow{\text{H}_3\text{O}^+} \text{C₆H₅CH=CHCHO}
\]

(1998 - 2 + 2 Marks)

35. Complete the following reaction with appropriate structures of products/reagents:

\[
\text{[Cl]} \rightarrow \text{[D]}
\]

(i) LiAlH₄

(ii) \( \text{H}^+ \), Heat

(1998 - 2 + 2 Marks)

36. Complete the following reaction with appropriate reagents:

\[
\text{[H]} \rightarrow \text{[D]}
\]

(i) \( \text{Mg/ether} \)

(ii) \( \text{X/} \text{H}_3\text{O}^+ \)

(1999 - 3 Marks)

37. Explain briefly the formation of the products giving the structures of the intermediates.

\[
\text{NaOEt} \rightarrow \text{Br}
\]

(i) \( \text{NaH}_2\text{O} \)

(ii) \( \text{CH}_3\text{CHO} \)

(1999 - 5 Marks)

38. An organic compound A, C₆H₅O₂, on reaction with CH₃MgBr followed by acid treatment gives compound B. The compound B on ozonolysis gives compound C, which in presence of a base gives 1-acetylcylopetene D. The compound B on reaction with HBr gives compound E. Write the structures of A, B, C and E. Show how D is formed from C.

(2000 - 5 Marks)

39. An organic compound A, C₆H₅O₃, in dry benzene in the presence of anhydrous AlCl₃ gives compound B. The compound B on treatment with PCl₅, followed by reaction with H₂/Pd (BaSO₄) gives compound C, which on reaction with hydrazine gives a cyclic compound D (C₈H₁₀N₂). Identify A, B, C and D. Explain the formation of D from C.

(2000 - 5 Marks)

40. Identify (A), (B), (C), (D) and (E) in the following schemes and write their structures:

\[
\text{Br} \xrightarrow{\text{CCl}_4} \rightarrow \text{[A]} \xrightarrow{\text{NaNH}_2} \rightarrow \text{[B]}
\]

\[
\text{HgSO}_4 / \text{H}_2\text{SO}_4 \rightarrow \text{[C]} \xrightarrow{\text{NH}_2\text{NHCONH}_2} \rightarrow \text{[D]}
\]

\[
\text{[C]} \xrightarrow{\text{NaOD} / \text{D}_2\text{O} \text{(excess)}} \rightarrow \text{[E]}
\]

(2001 - 5 Marks)

41. Identify (X), (Y) and (Z) in the following synthetic scheme and write their structures.

\[
\text{Ba}^+\text{CO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{(X) gas} \quad \text{[C\* denotes C}^{14}\text{]}
\]

\[
\text{CH}_2 = \text{CH} \xrightarrow{(\text{i}) \text{Mg/ether} \quad \text{H}_3\text{O}^+} \rightarrow \text{(Y)} \xrightarrow{\text{LiAlH}_4} \rightarrow \text{(Z)}
\]

(2001 - 5 Marks)

Explain the formation of labelled formaldehyde (H₂C*O) as one of the products when compound (Z) is treated with HBr and subsequently ozonolysed. Mark the C* carbon in the entire scheme.

42. Five isomeric para-disubstituted aromatic compounds A to E with molecular formula C₈H₈O₂ were given for identification. Based on the following observations, give structures of the compounds.

(2002 - 5 Marks)

(i) Both A and B form a silver mirror with Tollens’ reagent; also B gives a positive test with FeCl₃ solution.

(ii) C gives positive iodoform test.

(iii) D is readily extracted in aqueous NaHCO₃ solution.

(iv) E on acid hydrolysis gives 1,4-dihydroxybenzene.

43. Identify X, Y and Z in the following synthetic scheme and write their structures.

\[
\text{CH}_3\text{CH}_2\text{C} = \text{C} \xrightarrow{(\text{i}) \text{NaNH}_2 \quad \text{H}_3\text{O}^+} \rightarrow \text{X}
\]

\[
\text{H}_2 / \text{Pd-BaSO}_4 \rightarrow \text{Y} \rightarrow \text{alkaline KMnO}_4 \rightarrow \text{Z}
\]

Is the compound Z optically active? Justify your answer.

(2002 - 5 Marks)

44. A racemic mixture of (±) 2-phenylpropanoic acid on esterification with (+) 2-butanol gives two esters. Mention the stereochemistry of the two esters produced.

(2003 - 2 Marks)


(2003 - 2 Marks)

46. A monomer of a polymer on ozonolysis gives two moles of CH₂O and one mole of CH₃COCHO. Write the structure of monomer and write all – ‘cis’ configuration of polymer chain.

(2005 - 2 Marks)
**F Match the Following**

**DIRECTIONS (Q. No. 1):** Each question contains statements given in two columns, which have to be matched. The statements in Column-I are labelled A, B, C and D, while the statements in Column-II are labelled p, q, r, s and t. Any given statement in Column-I can have correct matching with ONE OR MORE statement(s) in Column-II. The appropriate bubbles corresponding to the answers to these questions have to be darkened as illustrated in the following example:

If the correct matches are A-p, s and t; B-q and r; C-p and q; and D-s then the correct darkening of bubbles will look like the given.

<table>
<thead>
<tr>
<th>Column I</th>
<th>Column II</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A) $\text{H}_2\text{N} - \text{NH}_3\text{Cl}$</td>
<td>(p) sodium fusion extract of the compound gives Prussian blue colour with FeSO$_4$</td>
</tr>
<tr>
<td>(B) $\text{HO--NH}_2\text{Cl}$</td>
<td>(q) gives positive FeCl$_3$ test</td>
</tr>
<tr>
<td>(C) $\text{HO--NH}_2\text{Cl}$</td>
<td>(r) gives white precipitate with AgNO$_3$</td>
</tr>
<tr>
<td>(D) $\text{O}_2\text{N--NH}_2\text{Br}$</td>
<td>(s) reacts with aldehydes to form the corresponding hydrazone derivative</td>
</tr>
</tbody>
</table>

**DIRECTIONS (Q. No. 2):** Following question has matching lists. The codes for the list have choices (a), (b), (c) and (d) out of which ONLY ONE is correct.

2. Different possible **thermal** decomposition pathways for peroxesters are shown below. Match each pathway from List-I with an appropriate structure from List-II and select the correct answer using the code given below the lists. *(JEE Adv. 2014)*

![Peroxyster](image)

**List-I**

| P. Pathway P |
| Q. Pathway Q |
| R. Pathway R |
| S. Pathway S |

**List-II**

| 1. $\text{C}_6\text{H}_5\text{CH}_2\text{O} \overset{\text{O}}{\text{O}} \text{O} \overset{\text{CH}_3}{\text{CH}_3}$ |
| 2. $\text{C}_6\text{H}_5\text{O} \overset{\text{O}}{\text{O}} \text{O} \overset{\text{CH}_3}{\text{CH}_3}$ |
| 3. $\text{C}_6\text{H}_5\text{CH}_2\text{O} \overset{\text{O}}{\text{O}} \overset{\text{CH}_3}{\text{CH}_3} \overset{\text{CH}_3}{\text{CH}_2\text{C}_6\text{H}_5}$ |
| 4. $\text{C}_6\text{H}_5\text{O} \overset{\text{O}}{\text{O}} \overset{\text{CH}_3}{\text{CH}_3} \overset{\text{C}_6\text{H}_5}{\text{C}_6\text{H}_5}$ |

**Code:**

<table>
<thead>
<tr>
<th>Code:</th>
<th>P</th>
<th>Q</th>
<th>R</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>1</td>
<td>3</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>(b)</td>
<td>2</td>
<td>4</td>
<td>3</td>
<td>1</td>
</tr>
</tbody>
</table>
G Comprehension Based Questions

PASSAGE-1

In the following reaction sequence, product I, J and L are formed. K represents a reagent. (2008)

\[
\text{Hex - 3 - ynal} \xrightarrow{1. \text{NaBH}_4, 2. \text{PbO}} I \xrightarrow{1. \text{Mg/ether}, 2. \text{CO}_2, 3. \text{H}_2\text{O}} J \xrightarrow{\text{H}_2, \text{Pd/C}} L
\]

1. The structure of the product I is:
   (a) \[\text{Me} \quad \text{Br}\]
   (b) \[\text{Me} \quad \text{Br} \quad \text{Br}\]
   (c) \[\text{Me} \quad \text{Br} \quad \text{Br}\]
   (d) \[\text{Me} \quad \text{Br} \quad \text{Br}\]

2. The structures of compound J and K, respectively, are:
   (a) \[\text{Me} \quad \text{COOH and SOCl}_2\]
   (b) \[\text{Me} \quad \text{OH and SOCl}_2\]
   (c) \[\text{Me} \quad \text{COOH}\]
   (d) \[\text{Me} \quad \text{COOH} \quad \text{and CH}_2\text{SO}_2\text{Cl}\]

3. The structure of product L is:
   (a) \[\text{Me} \quad \text{CHO}\]
   (b) \[\text{Me} \quad \text{CHO}\]
   (c) \[\text{Me} \quad \text{CHO}\]
   (d) \[\text{Me} \quad \text{CHO}\]

PASSAGE-2

A carbonyl compound P, which gives positive iodoform test, undergoes reaction with MeMgBr followed by dehydration to give an olefin Q. Ozonolysis of Q leads to a dicarbonyl compound R, which undergoes intramolecular aldol reaction to give predominantly S. (2009)

\[
P \xrightarrow{1. \text{MeMgBr, } 2. \text{H}^+, \text{H}_2\text{O}, 3. \text{H}_2\text{SO}_4, \Delta} Q \xrightarrow{1. \text{O}_3, 2. \text{Zn}, \text{H}_2\text{O}} R \xrightarrow{1. \text{OH}^-, 2. \Delta} S
\]

4. The structure of the carbonyl compound P is:
   (a) \[\text{Me} \quad \text{O}\]
   (b) \[\text{Me} \quad \text{O}\]
   (c) \[\text{Et} \quad \text{O}\]
   (d) \[\text{Me} \quad \text{O}\]

5. The structures of the products Q and R, respectively, are:
   (a) \[\text{Me} \quad \text{Me} \quad \text{H} \quad \text{COMe}\]
   (b) \[\text{Me} \quad \text{Me} \quad \text{H} \quad \text{Me}\]
   (c) \[\text{Me} \quad \text{Me} \quad \text{Et} \quad \text{Me}\]
   (d) \[\text{Me} \quad \text{Me} \quad \text{Et} \quad \text{Et}\]

6. The structure of the product S is:
   (a) \[\text{Me} \quad \text{O}\]
   (b) \[\text{Me} \quad \text{O}\]
   (c) \[\text{Me} \quad \text{O}\]
   (d) \[\text{Me} \quad \text{O}\]

PASSAGE-3

Two aliphatic aldehydes P and Q react in the presence of aqueous K$_2$CO$_3$ to give compound R, which upon treatment with HCN provides compound S. On acidification and heating, S gives the product shown below. (2010)

\[
\text{H}_3\text{C} \quad \text{OH}
\]

\[
\text{H}_3\text{C} \quad \text{O}
\]
7. The compounds P and Q respectively are:

(a)  
(b)  
(c)  
(d)  

8. The compound R is:

(a)  
(b)  
(c)  
(d)  

9. The compound S is:

(a)  
(b)  
(c)  
(d)  

10. The compound I is

(A)  
(B)  
(C)  
(D)  

11. The compound K is

(a)  
(b)  
(c)  
(d)  

12. Compounds formed from P and Q are, respectively
(a) Optically active S and optically active pair (T, U)
(b) Optically inactive S and optically inactive pair (T, U)
(c) Optically active pair (T, U) and optically active S
(d) Optically inactive pair (T, U) and optically inactive S
13. In the following reaction sequences V and W are respectively

\[ Q \xrightarrow{H/Na\Delta} V \]

\[ \text{V} + \text{AlCl}_3 \text{(anhydrous)} \rightarrow 1. \text{Zn-Hg/HCl} \]

\[ \text{2. } \text{H}_3\text{PO}_4 \rightarrow \text{W} \]

(a) \[ \begin{array}{c}
\text{O} \\
\text{O}
\end{array} \]

(b) \[ \begin{array}{c}
\text{CH}_2\text{OH} \\
\text{CH}_2\text{OH}
\end{array} \]

(c) \[ \begin{array}{c}
\text{O} \\
\text{O}
\end{array} \]

(d) \[ \begin{array}{c}
\text{HOH}_2\text{C} \\
\text{CH}_2\text{OH}
\end{array} \]

**PASSAGE-6**

In the following reactions

\[ \text{C}_6\text{H}_5 \xrightarrow{\text{Pd-BaSO}_4} \text{H}_2 \xrightarrow{(i) \text{B}_3\text{H}_6, (ii) \text{H}_2\text{O}, \text{NaOH, H}_2\text{O}} \text{X} \]

\[ \text{H}_2\text{O} \xrightarrow{\text{HgSO}_4, \text{H}_2\text{SO}_4} \text{C}_6\text{H}_5\text{H}_2 \xrightarrow{(i) \text{E}_{\text{NH}_{3}, \text{H}_2\text{O}, (ii) H}^+, \text{heat}} \text{Y} \]

14. Compound X is

(a) \[ \begin{array}{c}
\text{O} \\
\text{CH}_3
\end{array} \]

(b) \[ \begin{array}{c}
\text{O} \\
\text{CH}_3
\end{array} \]

(c) \[ \begin{array}{c}
\text{OH} \\
\text{CH}_3
\end{array} \]

(d) \[ \begin{array}{c}
\text{OH} \\
\text{CHO}
\end{array} \]

15. The major compound Y is

\[ (\text{JEE Adv. 2015}) \]

(a) \[ \begin{array}{c}
\text{CH}_3
\end{array} \]

(b) \[ \begin{array}{c}
\text{CH}_3
\end{array} \]

(c) \[ \begin{array}{c}
\text{CH}_3
\end{array} \]

(d) \[ \begin{array}{c}
\text{CH}_3
\end{array} \]

** Assertion & Reason Type Questions **

Each of this question contains STATEMENT-1 (Assertion/Statement) and STATEMENT-2 (Reason/Explanation) and has 4 choices (a), (b), (c) and (d) out of which ONLY ONE is correct.

(a) Statement-1 is True, Statement-2 is False, Statement-2 is a correct explanation for Statement-1

(b) Statement-1 is True, Statement-2 is True, Statement-2 is NOT a correct explanation for Statement-1

(c) Statement-1 is True, Statement-2 is False

(d) Statement-1 is False, Statement-2 is True.

1. **Statement-1**: Acetate ion is more basic than the methoxide ion.
   **Statement-2**: The acetate ion is resonance stabilized
   \[(1994 - 2 \text{ Marks})\]

2. **Statement-1**: Acetic acid does not undergo haloform reaction.
   **Statement-2**: Acetic acid has no alpha hydrogens.
   \[(1998 - 2 \text{ Marks})\]

3. **Statement-1**: Dimethyl sulphide is commonly used for the reduction of an ozonide of an alkene to get the carbonyl compounds.
   **Statement-2**: It reduces the ozonide giving water soluble dimethyl sulphoxide and excess of it evaporates.
   \[(2001S)\]

4. **Statement-1**: p-Hydroxybenzoic acid has a lower boiling point than o-hydroxybenzoic acid.
   **Statement-2**: o-Hydroxybenzoic acid has intramolecular hydrogen bonding.
   \[(2007)\]

** Integer Value Correct Type **

1. In the scheme given below, the total number of intramolecular aldol condensation products formed from 'Y' is

\[ \begin{array}{c}
\text{1. O}_3 \\
\text{2. Zn, H}_2\text{O}
\end{array} \]

\[ \begin{array}{c}
\text{1. NaOH (aq)} \\
\text{2. heat}
\end{array} \]

\[(2010)\]
2. Amongst the following, the total number of compounds soluble in aqueous NaOH is

![Chemical structures]

(2010)

3. The total number of carboxylic acid groups in the product P is

![Chemical structure]

(2010)

4. Consider all possible isomeric ketones, including stereoisomers of MW = 100. All these isomers are independently reacted with NaBH₄ (NOTE: stereoisomers are also reacted separately). The total number of ketones that give a racemic product(s) is/are (JEE Adv. 2014)

5. Among the following, the number of reaction(s) that produce(s) benzaldehyde is (JEE Adv. 2015)

I. ![Chemical structure] → Anhydrous AlCl₃/CuCl
II. ![Chemical structure] → H₂O 100°C
III. ![Chemical structure] → H₂ Pd-BaSO₄
IV. ![Chemical structure] → DIBAL-H Toluene, -78°C

---

**Section - B**

1. CH₃CH₂COOH → Cl₂ red[P] → A → alc.KOH → B. What is B?
   - (a) CH₃CH₂COCI
   - (b) CH₃CH₂CHO [2002]
   - (c) CH₂=CHCOOH
   - (d) CH₂=CH₂COOH

2. On vigorous oxidation by permanganate solution. (CH₃)₂C=CH - CH₂ - CHO gives [2002]
   - (a) CH₃CH₂CH₂COOH
   - (b) CH₃CH₂CHO
   - (c) CH₃CH₂CH₂OH
   - (d) CH₃CH₂CHO

3. Picric acid is: [2002]
   - (a) ![Chemical structure]
   - (b) ![Chemical structure]

4. When CH₂ = CH — COOH is reduced with LiAlH₄, the compound obtained will be [2003]
   - (a) CH₃—CH=CH₂
   - (b) CH₃—CH₂—CH₂—CH=CH₂
   - (c) CH₃—CH₂—CH₂—CHO
   - (d) CH₃—CH₂—CH₂—COOH

5. On mixing ethyl acetate with aqueous sodium chloride, the composition of the resultant solution is [2004]
   - (a) CH₃COCl + CH₃COOH + CH₃CH₂OH + NaCl
   - (b) CH₃COONa + CH₃COOH
   - (c) CH₃COOC₂H₅ + NaCl
   - (d) CH₃Cl + CH₃COONa

6. Acetyl bromide reacts with excess of CH₃Mgl followed by treatment with a saturated solution of NH₄Cl gives [2004]
   - (a) 2-methyl-2-propanol
   - (b) acetamide
   - (c) acetone
   - (d) acetyl iodide

7. Which one of the following is reduced with zinc and hydrochloric acid to give the corresponding hydrocarbon?
   - (a) Acetamide
   - (b) Acetic acid [2004]
   - (c) Ethyl acetate
   - (d) Butan-2-one

8. Which one of the following undergoes reaction with 50% sodium hydroxide solution to give the corresponding alcohol and acid? [2004]
   - (a) Butanal
   - (b) Benzaldehyde
   - (c) Phenol
   - (d) Benzoic acid
9. Among the following acids which has the lowest pKₐ value? [2005]
   (a) CH₃CH₂COOH  (b) (CH₃)₂CH – COOH
   (c) HCOOH       (d) CH₃COOH

10. Reaction of cyclohexanone with dimethylamine in the presence of catalytic amount of an acid forms a compound if water during the reaction is continuously removed. The compound formed is generally known as [2005]
    (a) an amine   (b) an imine
    (c) an anemine (d) a Schiff’s base

11. The increasing order of the rate of HCN addition to compound A – D is [2006]
    (A) HCHO        (B) CH₂COCH₃
    (C) PhCOCH₃     (D) PhCOPh
    (a) D < C < B < A (b) C < D < B < A
    (c) A < B < C < D (d) D < B < C < A

12. The correct order of increasing acid strength of the compounds [2006]
    (A) CH₃CO₂H    (B) MeOCH₂CO₂H
    (C) CF₃CO₂H    (D) MeH₂CO₂H
    is
    (a) D < A < B < C (b) A < D < B < C
    (c) B < D < A < C (d) D < A < C < B

13. A liquid was mixed with ethanol and a drop of concentrated H₂SO₄ was added. A compound with a fruity smell was formed. The liquid was: [2009]
    (a) HCHO        (b) CH₂COCH₃
    (c) CH₃COOH     (d) CH₂OH

14. Which of the following on heating with aqueous KOH produces acetaldehyde? [2009]
    (a) CH₃CH₂Cl  (b) CH₂ClCH₂Cl
    (c) CH₂CH₂Cl₂ (d) CH₃COCl

15. In Cannizzaro reaction given below

\[ 2\text{PhCHO} + \text{OH}^- \rightarrow \text{PhCH₂OH} + \text{PhCO}_2\text{O} \]

the slowest step is: [2009]
   (a) the transfer of hydride to the carbonyl group
   (b) the abstraction of proton from the carboxylic group
   (c) the deprotonation of Ph CH₂OH
   (d) the attack of OH at the carboxyl group

16. Which of the following reagents may be used to distinguish between phenol and benzoic acid? [2011]
    (a) Aqueous NaOH     (b) Tollens’s reagent
    (c) Molisch reagent  (d) Neutral FeCl₃

17. Trichloroacetaldehyde was subjected to Cannizzaro’s reaction by using NaOH. The mixture of the products contains sodium trichloroacetate and another compound. The other compound is: [2011]

   (a) 2, 2, 2-Trichloroethanol  (b) Trichloromethanol
   (c) 2, 2, 2-Trichloropropanol (d) Chloroform

18. The strongest acid amongst the following compounds is: [2011]
    (a) CH₃COOH       (b) HCOOH
    (c) CH₃CH₂CH(Cl)CO₂H (d) ClCH₂CH₂CH₂COOH

19. Sodium ethoxide has reacted with ethanoyl chloride. The compound that is produced in the above reaction is: [2011]
    (a) Diethyl ether   (b) 2-Butanone
    (c) Ethyl chloride  (d) Ethyl ethanoate

20. Silver Mirror test is given by which one of the following compounds? [2011]
    (a) Acetaldehyde   (b) Acetone
    (c) Formaldehyde   (d) Benzophenone

21. Iodoform can be prepared from all except: [2012]
    (a) Ethyl methyl ketone (b) Isopropyl alcohol
    (c) 3-Methyl 2-butanoic (d) Isobutyl alcohol

22. In the given transformation, which of the following is the most appropriate reagent? [2012]

[R](CHCH₂COCH₃) \rightarrow [HOT]

23. The most suitable reagent for the conversion of R – CH₂ – OH → R – CHO is: [JEE M 2014]
    (a) K₂Cr₂O₇  (b) K₂CrO₂₇
    (c) Na, Liq NH₃  (d) NaBH₄

24. In the reaction,

CH₃COOH LiAH₄ → A → PCl₅ → B → Alc KOH → C,

the product C is: [JEE M 2014]
    (a) Acetaldehyde  (b) Acetylene
    (c) Ethylene      (d) Acetyl chloride

25. In the following sequence of reactions: [JEE M 2015]

Toluene → K₂Cr₂O₇ → A → SOCl₂ → B → H₂/Pd → C

the product C is:

   (a) C₆H₅OH     (b) C₆H₅CHO
   (c) C₆H₅COOH   (d) C₆H₅CH₃
CHAPTER 21

Compounds Containing Nitrogen

Section-A

JEE Advanced/ IIT-JEE

A Fill in the Blanks

1. In an acidic medium, ............... behaves as the strongest base. (nitrobenzene, aniline, phenol) (1981 - 1 Mark)
2. Amongst the three isomers of nitrophenol, the one that is least soluble in water is .............. (1992 - 1 Mark)
3. The high melting point and insolubility in organic solvents of sulphanilic acid are due to its...........structure. (1994 - 1 Mark)

C MCQs with One Correct Answer

1. The compound which on reaction with aqueous nitrous acid at low temperature produces an oily nitrosamine is (1981 - 1 Mark)
   (a) methylamine  (b) ethylamine  (c) diethylamine  (d) triethylamine
2. Acetamide is treated separately with the following reagents. Which one of these would give methylamine? (1983 - 1 Mark)
   (a) PCl₅  (b) NaOH + Br₂  (c) soda lime  (d) hot conc. H₂SO₄
3. Carbylamine test is performed in alcoholic KOH by heating a mixture of: (1984 - 1 Mark)
   (a) chloroform and silver powder  (b) trihalogenatedmethane and a primary amine  
     (c) an alkyl halide and a primary amine  (d) an alkyl cyanide and a primary amine
4. The compound that is most reactive towards electrophilic nitration is: (1985 - 1 Mark)
   (a) toluene  (b) benzene  (c) benzoic acid  (d) nitrobenzene
5. If two compounds have the same empirical formula but different molecular formulae they must have (1987 - 1 Mark)
   (a) different percentage composition  (b) different molecular weight  
     (c) same viscosity  (d) same vapour density
6. Amongst the following, the most basic compound is: (1990 - 1 Mark)
   (a) Benzylamine  (b) Aniline  (c) Acetanilide  (d) p-Nitroaniline

7. The formation of cyanohydrin from a ketone is an example of: (1990 - 1 Mark)
   (a) Electrophilic addition  (b) Nucleophilic addition  
     (c) Nucleophilic substitution  (d) Electrophilic substitution
8. Butanenitrile may be prepared by heating: (1992 - 1 Mark)
   (a) Propyl alcohol with KCN  (b) Butyl alcohol with KCN  
     (c) Butyl chloride with KCN  (d) Propyl chloride with KCN
9. In the reaction p-chlorotoluene with KNH₂ in liq. NH₃, the major product is: (1997 - 1 Mark)
   (a) o-toluidine  (b) m-toluidine  (c) p-toluidine  (d) p-chloroaniline.
10. The most unlikely representation of resonance structures of p-nitrophenoxide ion is (1999 - 2 Marks)

   ![Resonance Structure](image)

11. Among the following, the strongest base is (2000S)
    (a) C₆H₅NH₂  (b) p-NO₂C₆H₄NH₂  
      (c) m-NO₂C₆H₄NH₂  (d) C₆H₅CH₂NH₂
12. The correct order of basicities of the following compounds is
   \( \text{CH}_3 - \overset{\text{NH}}{\text{NH}_2} \) \( \text{CH}_3 - \text{CH}_2 - \overset{\text{NH}}{\text{NH}_2} \)
   (a) \(2 > 1 > 3 > 4\)  
   (b) \(1 > 3 > 2 > 4\)  
   (c) \(3 > 1 > 2 > 4\)  
   (d) \(1 > 2 > 3 > 4\)  

13. Compound 'A' (molecular formula \(C_6H_5O\)) is treated with acidified potassium dichromate to form a product 'B' (molecular formula \(C_6H_4O\)). 'B' forms a shining silver mirror on warming with ammonical silver nitrate. 'B' when treated with an aqueous solution of \(H_2NCONHNH_2\), HCl and sodium acetate gives a product 'C'. Identify the structure of 'C'.
   (a) \(\text{CH}_3\text{CH}_2\text{CH} = \overset{\text{NHNCONH}_2}{\text{CH}}\)  
   (b) \(\text{CH}_3 - \overset{\text{C}}{\text{NHNCONH}_2}\)  
   (c) \(\text{CH}_3 - \overset{\text{C}}{\text{NCONNH}_2}\)  
   (d) \(\text{CH}_3\text{CH}_2\text{CH} = \overset{\text{NCONNNH}_2}{\text{CH}}\)

14. \( \text{F} - \overset{\text{NO}_2}{\text{O}} \) to (A) \( \overset{\text{(CH}_3\text{NH})}{\text{DMF, } \Delta} \rightarrow (\text{B}) \). B is:
   (2003S)

15. \( \overset{\text{O}_2\text{N}}{\text{H}_2\text{O}} \) \( \overset{\text{OH}}{\text{OH}} \) \( \overset{\text{CH}}{\text{CH}} \)

The product A will be
   (2003S)

   (a) \(\overset{\text{O}_2\text{N}}{\text{H}_2\text{O}} \) \( \overset{\text{OH}}{\text{OH}} \) \( \overset{\text{CH}}{\text{CH}} \)
   (b) \(\overset{\text{O}_2\text{N}}{\text{H}_2\text{O}} \) \( \overset{\text{OH}}{\text{OH}} \) \( \overset{\text{CH}}{\text{CH}} \)

16. Benzamide on reaction with \(\text{POCl}_3\) gives
   (a) aniline  
   (b) chlorobenzene  
   (c) benzylamine  
   (d) benzonitrile  

17. The major product obtained when \(\text{Br}_2/\text{Fe}\) is treated with
   (2004S)

   (a) \(\overset{\text{H}_3\text{C}}{\text{H}}\text{N} = \overset{\text{O}}{\text{N}}\text{O} \) \( \overset{\text{CH}_3}{\text{CH}} \)  
   (b) \(\overset{\text{H}_3\text{C}}{\text{H}}\text{N} = \overset{\text{O}}{\text{N}}\text{O} \) \( \overset{\text{Br}}{\text{CH}} \)
18. In the compound given below the correct order of the acidity of the positions X, Y and Z is

(a) \( Z > X > Y \)    (b) \( X > Y > Z \)
(c) \( X > Z > Y \)    (d) \( Y > X > Z \)

19. When benzenesulfonic acid and \( p \)-nitrophenol are treated with \( \text{NaHCO}_3 \), the gases released respectively are

(a) \( \text{SO}_2, \text{NO} \)    (b) \( \text{SO}_2, \text{NO}_2 \)
(c) \( \text{CO}_2, \text{CO}_2 \)    (d) \( \text{SO}_2, \text{CO}_2 \)

20. In the following reaction,

\[
\text{CH}_3\text{NH}_2 + \text{CHCl}_3 + \text{KOH} \rightarrow \text{Nitrogen containing compound} + \text{KCl} + \text{H}_2\text{O}.
\]

The nitrogen containing compound is

(a) \( \text{CH}_3 - \text{NH} - \text{CH}_3 \)    (b) \( \text{CH}_3 - \text{C} = \text{N} \)
(c) \( \text{CH}_3 - \overset{+}{\text{N}} = \text{C} \)    (d) \( \text{CH}_3 - \overset{-}{\text{N}} = \overset{+}{\text{C}} \)

21. The correct stability order of the following resonance structures is

\[
\begin{align*}
\text{H}_2\text{C} & = \overset{+}{\text{N}} = \overset{-}{\text{N}} \\
\text{H}_2\text{C} & = \overset{-}{\text{N}} = \overset{+}{\text{N}} \\
\text{H}_2\text{C} & = \overset{+}{\text{N}} = \overset{-}{\text{N}} \\
\text{H}_2\text{C} & = \overset{-}{\text{N}} = \overset{+}{\text{N}}
\end{align*}
\]

(a) (I) > (II) > (IV) > (III)
(b) (I) > (III) > (II) > (IV)
(c) (II) > (I) > (III) > (IV)
(d) (III) > (I) > (IV) > (II)

22. The major product of the following reaction is

\[
\text{CH}_3\text{NH} = \text{C} = \overset{-}{\text{O}} \xrightarrow{(i) \text{KOH}} \xrightarrow{(ii) \text{Br}} \text{CH}_2\text{Cl}
\]

23. Amongst the compounds given, the one that would form a brilliant colored dye on treatment with \( \text{NaNO}_2 \) in dil. \( \text{HCl} \) followed by addition to an alkaline solution of \( \beta \)-naphthol is

(a) \( \text{CH}_3\text{N} = \text{C} \)    (b) \( \text{CH}_3\text{NH} = \text{C} \)
(c) \( \text{CH}_3\text{N} = \overset{+}{\text{C}} \)    (d) \( \text{CH}_3\text{NH} = \overset{-}{\text{C}} \)

D. MCQs with One or More Than One Correct

1. The products of reaction of alcoholic silver nitrite with ethyl bromide are

(a) ethane    (b) ethene
(c) nitroethane    (d) ethyl alcohol
(e) ethyl nitrite

(1991 - 1 Mark)
2. Reaction of $R - C\equiv NH_2$ with a mixture of $Br_2$ and KOH gives $R-NH_2$ as the main product. The intermediates involved in this reaction are: *(1992 - 1 Mark)*

$\begin{align*}
&O \\
&| \\
&(a) \quad R - C\equiv NHBr \\
&(b) \quad R-NHBr \\
&(c) \quad R - N=C = O \\
&(d) \quad R-C\equiv N \quad Br
\end{align*}$

3. When nitrobenzene is treated with $Br_2$ in presence of $FeBr_3$, the major product formed is $m$-bromonitrobenzene. Statements which are related to obtain the $m$-isomer are *(1992 - 1 Mark)*

(a) The electron density on meta carbon is more than that on ortho and para positions
(b) The intermediate carboxonium ion formed after initial attack of $Br^+$ at the meta position is least destabilised
(c) Loss of aromaticity when $Br^+$ attacks at the ortho and para positions and not at meta position
(d) Easier loss of $H^+$ to regain aromaticity from the meta position than from ortho and para positions.

4. Examine the following two structures for the anilinium ion and choose the correct statement from the ones given below: *(1993 - 1 Mark)*

$\begin{align*}
&\begin{align*}
&\begin{array}{c}
&\text{NH}_3 \\
&\text{I}
\end{array}\\
&\begin{array}{c}
&\text{NH}_3 \\
&\text{II}
\end{array}
\end{align*}
\end{align*}$

(a) II is not an acceptable canonical structure because carboxonium ions are less stable than ammonium ions.
(b) II is not an acceptable canonical structure because it is non-aromatic.
(c) II is not an acceptable canonical structure because the nitrogen has 10 valence electrons.
(d) II is an acceptable canonical structure.

5. $p$-Chloroaniline and anilinium hydrochloride can be distinguished by *(1998 - 2 Marks)*

(a) Sandmeyer reaction 
(b) $NaHCO_3$
(c) $AgNO_3$ 
(d) Carbamylamine test

6. Among the following compounds, which will react with acetone to give a product containing $> C = N$ bond? *(1998 - 2 Marks)*

(a) $C_6H_5NH_2$ 
(b) $(CH_3)_2N$
(c) $C_6H_5NHCO_2H$ 
(d) $C_6H_5NNH_2$

7. Benzenediazonium chloride on reaction with phenol in weakly basic medium gives *(1998 - 2 Marks)*

(a) diphenyl ether 
(b) $p$-hydroxyazobenzene
(c) chlorobenzene 
(d) benzene

8. A positive carbylamine test is given by *(1999 - 2 Marks)*

(a) $N,N$—dimethylaniline 
(b) 2,4—dimethylaniline
(c) $N$—methyl-$o$—methylaniline 
(d) $p$—methylbenzylamine

9. In the reaction $2X + B_2H_6 \rightarrow [BH_2(X)_2]^+ [BH_4]^-$, the amine(s) $X$ is (are) *(2009)*

(a) $NH_3$ 
(b) $CH_3NH_2$
(c) $(CH_3)_2NH$ 
(d) $(CH_3)_3N$

10. Hydrogen bonding plays a central role in the following phenomena *(JEE Adv. 2014)*

(a) Ice floats in water
(b) Higher Lewis basicity of primary amines than tertiary amines in aqueous solutions
(c) Formic acid is more acidic than acetic acid
(d) Dimerisation of acetic acid in benzene

11. In the reaction shown below, the major product(s) formed is/are *(JEE Adv. 2014)*

![Reactions](image)

(a) $\text{NH}_2$ 
(b) $\text{NH}_2$
(c) $\text{NH}_3$ 
(d) $\text{NH}_3$

12. The major product of the reaction is *(JEE Adv. 2015)*

![Reactions](image)
Compounds Containing Nitrogen

13. In the following reactions, the major product W is

15. The product(s) of the following reaction sequence is(are)

(JEE Adv. 2016)

subjective problems

1. Show with equations how the following compounds are prepared (equations need not be balanced):

   (i) n-propyl amine from ethyl chloride (in two steps)
   (1982 - 1 Mark)

   (ii) chlorobenzene from aniline (in two steps).
   (1982 - 1 Mark)

   (iii) Aniline from benzene
   (1983 - 1 Mark)

   (iv) Acetoxime from acetaldehyde using the reagents, 
       [K_2Cr_2O_7/II^+, Ca(OH)_2 and NH_2OH.HCl].
       (1984 - 2 Marks)

   (v) aniline to chlorobenzene
       (1985 - 1 Mark)

   (vi) benzaldehyde to cyanobenzene. (in not more than 6
       steps)
       (1986 - 2 Marks)

   (vii) toluene to m-nitrobenzoic acid?
       (1987 - 1 Mark)

   (viii) 4-nitroaniline to 1, 2, 3-tribromobenzene.
       (1990 - 2 Marks)

   (ix) p-bromonitrobenzene from benzene in two steps.
       (1993 - 2 Marks)

   (x) 4-nitrobenzaldehyde from benzene.
       (1994 - 2 Marks)

   (xi) benzamide from nitrobenzene
       (1994 - 2 Marks)

   (xii) Aniline → Benzylamine (in 3 steps)
       (2000 - 3 Marks)

   (xiii) 
       (in not more than 3 steps)
       (2003 - 2 Marks)
2. Give reasons for the following:
   (i) Cyclohexylamine is a stronger base than aniline. \( \text{(1982 - 1 Mark)} \)
   (ii) \( o \)-Nitrophenol is steam volatile whereas \( p \)-nitrophenol is not; \( \text{(1985 - 1 Mark)} \)
   (iii) Dimethylaniline is a stronger base than trimethylaniline. \( \text{(1998 - 2 Marks)} \)
   (iv) Nitrobenzene does not undergo Friedel-Crafts alkylation \( \text{(1998 - 2 Marks)} \)

3. Arrange the following:
   (i) \( p \)-toluidine, \( N, N \)-dimethyl-\( p \)-toluidine, \( p \)-nitroaniline, aniline in increasing basicity \( \text{(1986 - 1 Mark)} \)
   (ii) methylamine, dimethylaniline, aniline, \( N \)-methylaniline in increasing order of base strength. \( \text{(1988 - 1 Mark)} \)

4. Complete the following with appropriate structures:
   (i) \[
   \text{\( \overset{\text{NH}_2}{\text{C}}\text{H}_3 + \overset{\text{Cl}}{\text{O}}\text{C}_2\text{H}_5 \rightleftharpoons ? \)}
   \( \text{(1986 - 1 Mark)} \)
   (ii) \[
   \text{\( \overset{\text{O}}{\text{C}}\text{H}_3 + \overset{\text{HNO}_2}{\text{H}_2\text{O}} \rightarrow \)}
   \( \text{(1992 - 1 Mark)} \)
   (iii) \[
   \text{\( \overset{\text{C}}{\text{H}_2\text{O}}\text{H} + \overset{\text{P}_2\text{O}_5}{\text{H}_2\text{O}} \rightarrow \overset{\Delta}{\overset{\text{H}^+}{\text{H}_2\text{O}}} \rightarrow \)}
   \( \text{(1992 - 1 Mark)} \)
   (iv) 2, 4-Dinitroaniline
   \[
   \text{\( \overset{\text{C}}{\text{\( \overset{\text{Me}}{\text{Me}} \text{N} \text{O}_2\text{F} \)} \rightleftharpoons \overset{\text{H}_2\text{O}}{\text{H}_2\text{O}} \rightarrow \text{C} \rightarrow \)}
   \( \text{(1995 - 1 Mark)} \)
   (v) \[
   \text{\( \overset{\text{Me}}{\text{CH}_2\text{CH}_2\text{NH}_2 + \overset{\text{\( \overset{\text{C}}{\text{H}_2\text{O})}_2\text{O}, \text{heat} \rightarrow 2 \text{products} \)}{\text{COOEt})_2 + \overset{\text{EtONa}}{\text{C}} \rightarrow \text{C} \rightarrow \)}
   \( \text{(1997 - 1 Mark)} \)
   (vi) \[
   \text{\( \overset{\text{C}}{\text{H}_3\text{CONHCH}_3 \rightarrow \overset{\text{B}\text{Fe}}{\text{B}_2, \text{Fe}} \rightarrow 2 \text{products} \)}
   \( \text{(1998 - 2 Marks)} \)

5. Write balanced equations for the following reaction:
   Acetamide is reacted with bromine in the presence of potassium hydroxide. \( \text{(1987 - 1 Mark)} \)

6. Give a chemical test and the reagents used to distinguish between the following pair of compounds:
   Ethylamine and diethylamine. \( \text{(1988 - 1 Mark)} \)

7. An organic compound \( A \), containing \( C, H, N \) and \( O \), on analysis gives 49.32% carbon, 9.59% hydrogen and 19.18% nitrogen. \( A \) on boiling with \( \text{NaOH} \) gives off \( \text{NH}_3 \) and a salt which on acidification gives a monobasic nitrogen free acid \( B \). The silver salt of \( B \) contains 59.67% silver. Deduce the structures of \( A \) and \( B \). \( \text{(1988 - 3 Marks)} \)

8. A mixture of two aromatic compounds \( A \) and \( B \) was separated by dissolving a chloroform followed by extraction with aqueous KOH solution. The organic layer containing compound \( A \), when heated with alcoholic solution of KOH produced a compound \( C(C\text{\( _7\)H\text{\( _2\)N}) \) associated with an unpleasant odour. The alkaline aqueous layer on the other hand, when heated with chloroform and then acidified gave a mixture of two isomeric compounds \( D \) and \( E \) of molecular formula \( C\text{\( _7\)H\text{\( _6\)O}) \). Identify the compounds \( A, B, C, D, E \) and write their structures. \( \text{(1990 - 4 Marks)} \)

9. A basic, volatile nitrogen compound gave a foul smelling gas when treated with chloroform and alcoholic potash. A 0.295 g sample of the substance. dissolved in aq. HCl and
treated with NaNO₂ solution at 0°C, liberated a colorless, odourless gas whose volume corresponded to 112 ml at STP. After the evolution of the gas was complete, the aqueous solution was distilled to give an organic liquid which did not contain nitrogen and which on warming with alkali and iodine gave a yellow precipitate. Identify the original substance. Assume that it contains one N atom per molecule. 

(1993 - 4 Marks)

10. Identify the major product in the following reactions:

(i) ![Chemical structure](image)

(1993 - 1 Mark)

(ii) ![Chemical structure](image)

(2000 - 1 Mark)

11. Identify, A (C₃H₅N) which reacts with benzensulphonyl chloride to give a solid, insoluble in alkali.

(1993 - 1 Mark)

12. Write the structure of the foul-smelling compound obtained when aniline is treated with chloroform in the presence of KOH.

(1996 - 1 Mark)

13. Acetophenone on reaction with hydroxylamine hydrochloride can produce two isomeric oximes. Write structures of the oximes.

(1997 - 2 Marks)

14. Compound A (C₈H₉O) on treatment with NH₃OH. HCl gives B and C. B and C rearrange to give D and E, respectively, on treatment with acid. B, C, D and E are all isomers of molecular formula (C₈H₇NO). When D is boiled with alcoholic KOH an oil F (C₆H₅N) separates out. F reacts rapidly with CH₃COCl to give back D. On the other hand, E on boiling with alkali followed by acidification gives a white solid G (C₆H₅O₂). Identify A-G.

(1999 - 7 Marks)

15. Complete the following reaction with appropriate reagents:

(1999 - 4 Marks)

16. Explain briefly the formation of the products giving the structures of the intermediates.

(1999 - 2 Marks)

17. How would you synthesise 4-methoxyphenol from bromobenzene in NOT more than five steps? State clearly the reagents used in each step and show the structures of the intermediate compounds in your synthetic scheme.

(2001 - 5 Marks)

18. Write structures of the products A, B, C, D and E in the following scheme.

(2002 - 5 Marks)

19. There is a solution of p-hydroxybenzoic acid and p-aminobenzoic acid. Discuss one method by which we can separate them and also write down the confirmatory tests of the functional groups present.

(2003 - 4 Marks)

20. Identify (A) to (D) in the following series of reactions.

(2004 - 4 Marks)
21. \( \text{C}_{5}\text{H}_{13}\text{N} \) (Optical active) \( \xrightarrow{\text{aq NaNO}_2/\text{HCl}} \) \( \xrightarrow{\text{N}_2} \) Y + Some other products

(i) Identify (X) and (Y)
(ii) Is (Y) optically active?
(iii) Give structure(s) of intermediate(s), if any, in the formation of (Y) from (X).

**F** Match the Following

**DIRECTIONS (Q. No.1):** Each question contains statements given in two columns, which have to be matched. The statements in Column-I are labelled A, B, C and D, while the statements in Column-II are labelled p, q, r, s and t. Any given statement in Column-I can have correct matching with ONE OR MORE statement(s) in Column-II. The appropriate bubbles corresponding to the answers to these questions have to be darkened as illustrated in the following example:

If the correct matches are A-p, s and t; B-q and r; C-p and q; and D-s then the correct darkening of bubbles will look like given.

1. Match each of the compounds in Column I with its characteristic reaction(s) in Column II. (2009)

   **Column I**
   
   (A) \( \text{CH}_3\text{CH}_2\text{CH}_2\text{CN} \)
   
   (B) \( \text{CH}_3\text{CH}_2\text{OOCCH}_3 \)
   
   (C) \( \text{CH}_3\text{CH}==\text{CHCH}_2\text{OH} \)
   
   (D) \( \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2 \)

   **Column II**
   
   (p) Reduction with Pd–C/H_2
   
   (q) Reduction with SnCl_2/HCl
   
   (r) Development of foul smell on treatment with chloroform and alcoholic KOH
   
   (s) Reduction with diisobutylaluminium hydride (DIBAL-H)
   
   (t) Alkaline hydrolysis

**DIRECTIONS (Q. No. 2) :** Match the four starting materials (P, Q, R, S) given in List-I with the corresponding reaction schemes (I, II, III, IV) provided in List-II and select the correct answer using the code given below the lists.

2. List - I

   P. \( \text{H} --- \text{H} \)

   Q. \( \text{OH} \)

   R. \( \text{NO}_2 \)

   S. \( \text{OH} \)

   **List - II**

   1. Scheme I

   (i) KMnO_4, HO^\square\, \text{heat}\, (ii) H^\square\, \text{H}_2\text{O}

   (iii) SOCl_2 (iv) NH_3 ?

   \( \rightarrow \text{C}_7\text{H}_6\text{N}_2\text{O}_3 \)

   2. Scheme II

   (ii) Sn/HCl (i) \text{CH}_3\text{COCl} (iii) conc. H_2\text{SO}_4 (iv) HNO_3 (v) dil. H_2\text{SO}_4,

   \text{heat} (vi) H^\square\, \text{?} \rightarrow \text{C}_6\text{H}_6\text{N}_2\text{O}_2

   3. Scheme III

   (i) red hot iron, 873 K (ii) fuming HNO_3, H_2\text{SO}_4, heat

   (iii) H_2\text{S}\text{NH}_3 (iv) NaNO_2, H_2\text{SO}_4 (v) hydrolysis

   \( \rightarrow \text{C}_6\text{H}_3\text{NO}_3 \)
Compounds Containing Nitrogen

4. Scheme IV

(i) conc. H$_2$SO$_4$, 60°C
(ii) conc. HNO$_3$, conc. H$_2$SO$_4$
(iii) dil. H$_2$SO$_4$, heat → C$_6$H$_5$NO$_4$

Code:

<table>
<thead>
<tr>
<th></th>
<th>P</th>
<th>Q</th>
<th>R</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>1</td>
<td>4</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>b</td>
<td>3</td>
<td>1</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>c</td>
<td>3</td>
<td>4</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>d</td>
<td>4</td>
<td>1</td>
<td>3</td>
<td>2</td>
</tr>
</tbody>
</table>

G Comprehension Based Questions

PASSAGE - 1
The conversion of an amide to an amine with one carbon atom less by the action of alkaline hydrohalite is known as Hofmann bromamide degradation.

In this reaction, RCONHBr is formed from which the reaction has derived its name. Hofmann reaction is accelerated if the migrating group is more electron-releasing. Hofmann degradation reaction is an intramolecular reaction.

1. How can the conversion of (i) to (ii) be brought about?
   (2006 - 5M, -2)
   (a) KBr
   (b) KBr + CH$_3$ONa
   (c) KBr + KOH
   (d) Br$_2$ + KOH

2. Which is the rate determining step in Hofmann bromamide degradation?
   (2006 - 5M, -2)
   (a) Formation of (i)
   (b) Formation of (ii)
   (c) Formation of (iii)
   (d) Formation of (iv)

3. What are the constituent amines formed when the mixture of (i) and (ii) undergoes Hofmann bromamide degradation?
   (2006 - 5M, -2)

PASSAGE - 2
Treatment of compound O with KMnO$_4$/H$^+$ gave P, which on heating with ammonia gave Q. The compound Q on treatment with Br$_2$/NaOH produced R. On strong heating, Q gave S, which on further treatment with ethyl 2-bromopropanoate in the presence of KOH followed by acidification, gave a compound T.

(\textit{JEE Adv. 2016})
4. The compound R is

(a) \[ \text{NH}_2 \text{NH}_2 \] (b) \[ \text{Br} \text{Br} \]

(c) \[ \text{NHBr} \text{NHBr} \] (d) \[ \text{O} \text{O} \]

5. The compound T is

(a) glycine (b) alanine
(c) valine (d) serine

Assertion & Reason Type Questions

Read the following Statement-1(Assertion) and Statement -2 (Reason) and answer as per the options given below:

(a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
(b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.
(c) Statement-1 is True, Statement-2 is False
(d) Statement-1 is False, Statement-2 is True

1. Statement - 1: p-Nitrophenol is a stronger acid than o-nitrophenol.
   Statement - 2: Intramolecular hydrogen bonding makes the o-isomer weaker than the p-isomer. \((1989 - 2\text{ Marks})\)

2. Statement - 1: Benzonitrile is prepared by the reaction of chlorobenzene with potassium cyanide.
   Statement - 2: Cyanide \((\text{CN}^-)\) is a strong nucleophile. \((1998 - 2\text{ Marks})\)

3. Statement - 1: In strongly acidic solutions, aniline becomes more reactive towards electrophilic reagents.
   Statement-2: The amino group being completely protonated in strongly acidic solution, the lone pair of electrons on the nitrogen is no longer available for resonance. \((2001S)\)

4. Statement - 1: Aniline on reaction with \(\text{NaNO}_2/\text{HCl}\) at 0°C followed by coupling with β-naphthol gives a dark blue precipitate.
   and
   Statement - 2: The colour of the compound formed in the reaction of aniline with \(\text{NaNO}_2/\text{HCl}\) at 0°C followed by coupling with β-naphthol is due to the extended conjugation. \((2008)\)
1. When primary amine reacts with chloroform in ethanolic KOH then the product is
(a) an isocyanide
(b) an aldehyde
(c) a cyanide
(d) an alcohol.

2. The reaction of chloroform with alcoholic KOH and p-toluidine forms
(a) H₃C<sup>·</sup>C<sub>₆</sub>H₅NHCHCl₂
(b) H₃C<sup>·</sup>C<sub>₆</sub>H₅NH₂<sub>·</sub>N₂Cl
(c) H₃C<sup>·</sup>C<sub>₆</sub>H₅CN
(d) H₃C<sup>·</sup>C<sub>₆</sub>H₅CN

3. The correct order of increasing basic nature for the bases NH₃, CH₃NH₂ and (CH₃)₂NH is
(a) (CH₃)₂NH < NH₃ < CH₃NH₂
(b) NH₃ < CH₃NH₂ < (CH₃)₂NH
(c) CH₃NH₂ < (CH₃)₂NH < NH₃
(d) CH₃NH₂ < NH₃ < (CH₃)₂NH

4. Ethyl isocyanide on hydrolysis in acidic medium generates
(a) propanoic acid and ammonium salt
(b) ethanoic acid and ammonium salt
(c) methylamine salt and ethanoic acid
(d) ethylamine salt and methanoic acid

5. Which one of the following methods is neither meant for the synthesis nor for separation of amines?
(a) Curtius reaction
(b) Wurtz reaction
(c) Hofmann method
(d) Hinsberg method

6. Amongst the following the most basic compound is
(a) p-nitroaniline
(b) acetanilide
(c) aniline
(d) benzylamine

7. An organic compound having molecular mass 60 is found to contain C = 20%, H = 6.67% and N = 46.67% while rest is oxygen. On heating it gives NH₃ alongwith a solid residue. The solid residue give violet colour with alkaline copper sulphate solution. The compound is
(a) CH₃CH₂CONH₂
(b) (NH₃)₂CO
(c) CH₃CONH₂
(d) CH₃NCO

8. Which one of the following is the strongest base in aqueous solution?
(a) Methyamine
(b) Trimethylamine
(c) Aniline
(d) Dimethylamine.

9. In the chemical reaction,
CH₃CH₂NH₂ + CHCl₃ + 3KOH → (A) + (B) + 3H₂O, the compounds (A) and (B) are respectively
(a) C₂H₅NCand 3KCl
(b) C₂H₅CN and 3KCl
(c) CH₃CH₂CONH₂ and 3KCl
(d) C₂H₅NC and K₂CO₃

10. In the chemical reactions,

\[ \text{NH}_2 \xrightarrow{\text{NaNO}_2, \text{HCl}, 278 \text{ K}} \rightarrow \text{A} \xrightarrow{\text{HBF}_4} \rightarrow \text{B} \]

the compounds ‘A’ and ‘B’ respectively are
(a) nitrobenzene and fluorobenzene
(b) phenol and benzene
(c) benzene diazonium chloride and fluorobenzene
(d) nitrobenzene and chlorobenzene

11. A compound with molecular mass 180 is acylated with CH₃COCl to get a compound with molecular mass 390. The number of amino groups present per molecule of the former compound is:
(a) 2
(b) 5
(c) 4
(d) 6

12. An organic compound A upon reacting with NH₃ gives B. On heating B gives C. C in presence of KOH reacts with Br₂ to give CH₃CH₂NH₂. A is:
(a) CH₃COOH
(b) CH₃CH₂CH₂COOH
(c) CH₃ – CH – COOH
(d) CH₃CH₂COOH

13. The gas leaked from a storage tank of the Union Carbide plant in Bhopal gas tragedy was:
(a) Methyl isocyanate
(b) Methyamine
(c) Ammonia
(d) Phosgene

14. On heating an aliphatic primary amine with chloroform and ethanolic potassium hydroxide, the organic compound formed is:
(a) an alkanol
(b) an alkanediol
(c) an alkyl cyanide
(d) an alkyl isocyanide

15. Considering the basic strength of amines in aqueous solution, which one has the smallest pKₐ value?
(a) (CH₃)₂NH
(b) CH₃NH₂
(c) (CH₃)₃N
(d) C₆H₅NH₂
16. In the reaction

\[
\begin{align*}
\text{NH}_2 & \quad \text{NaNO}_3 / \text{HCl} \quad 0-5^\circ \text{C} \quad \text{D} \quad \text{CuCN/KCN} \quad \Delta \quad \text{E} + \text{N}_2 \\
\text{CH}_3 &
\end{align*}
\]

the product E is:

(a) 

(b) 

(c) 

(d) 

17. In the Hofmann bromamide degradation reaction, the number of moles of NaOH and Br\(_2\) used per mole of amine produced are:

(a) Two moles of NaOH and two moles of Br\(_2\).
(b) Four moles of NaOH and one mole of Br\(_2\).
(c) One mole of NaOH and one mole of Br\(_2\).
(d) Four moles of NaOH and two moles of Br\(_2\).
CHAPTER 22

Carbohydrates, Amino Acids, Polymers & Miscellaneous
Match the Following

Section-A

**JEE Advanced/ IIT-JEE**

**C**  MCQs with One Correct Answer

1. The pair of compounds in which both the compounds give positive test with Tollens reagent is (2004S)
   (a) Glucose and Sucrose
   (b) Fructose and Sucrose
   (c) Acetophenone and Hexanal
   (d) Glucose and Fructose

2. The two forms of D-glucopyranose obtained from the solution of D-glucose are called (2005S)
   (a) Isomers
   (b) Anomers
   (c) Epimers
   (d) Enantiomers

3. Cellulose upon acetylation with excess acetic anhydride/H₂SO₄ (catalytic) gives cellulose triacetate whose structure is (2008S)

4. Among cellulose, poly (vinyl chloride), nylon and natural rubber, the polymer in which the intermolecular force of attraction is weakest is (2009S)
   (a) Nylon
   (b) Poly (vinyl chloride)
   (c) Cellulose
   (d) Natural Rubber

5. The correct statement about the following disaccharide is (2010)
   (a) Ring (A) is pyranose with α - glycosidic link
   (b) Ring (A) is furanose with α - glycosidic link
   (c) Ring (B) is furanose with α - glycosidic link
   (d) Ring (B) is pyranose with β - glycosidic link

6. The following carbohydrate is (2011-II)

   (a) a ketohexose
   (b) an aldohexose
   (c) an α-furanose
   (d) an α-pyranose

7. On complete hydrogenation, natural rubber produces
   (a) ethylene–propylene copolymer  (JEE Adv. 2016)
   (b) vulcanised rubber
   (c) polypropylene
   (d) polybutylene

**D**  MCQs with One or More Than One Correct

1. The correct statement(s) about the following sugars X and Y is(are) (2009S)

   ![Chemical structures]
(a) X is a reducing sugar and Y is a non-reducing sugar
(b) X is a non-reducing sugar and Y is a reducing sugar
(c) The glucosidic linkages in X and Y are α and β, respectively
(d) The glucosidic linkages in X and Y are β and α, respectively

2. The correct functional group X and the reagent reaction conditions Y in the following schemes are (2011 - II)

X - (CH₂)₄ - X (i) Y → condensation polymer

(a) X = COOCH₃, Y = H₂/Ni/heat
(b) X = CONH₂, Y = H₂/Ni/heat
(c) X = CONH₂, Y = Br₂/NaOH
(d) X = CN, Y = H₂/Ni/heat

3. The structure of D(+)-glucose is (JEE Adv. 2015)

\[
\begin{align*}
\text{CHO} \\
\text{H} & \quad \text{OH} \\
\text{HO} & \quad \text{H} \\
\text{H} & \quad \text{OH} \\
\text{HO} & \quad \text{OH} \\
\text{CH₂OH}
\end{align*}
\]

The structure of L(-)-glucose is

\[
\begin{align*}
\text{CHO} \\
\text{H} & \quad \text{OH} \\
\text{HO} & \quad \text{H} \\
\text{H} & \quad \text{OH} \\
\text{HO} & \quad \text{OH} \\
\text{CH₂OH}
\end{align*}
\]

4. For ‘invert sugar’, the correct statement(s) is(are)
   (Given: specific rotations of (+)-sucrose, (+)-maltose, L(-)-glucose and L(+)-fructose in aqueous solution are +66°, +140°, -52° and +92° respectively) (JEE Adv. 2016)
   (a) ‘invert sugar’ is prepared by acid catalyzed hydrolysis of maltose
   (b) ‘invert sugar’ is an equimolar mixture of D(-)-glucose and D(-)-fructose
   (c) specific rotation of ‘invert sugar’ is -20°
   (d) on reaction with Br₂ water, ‘invert sugar’ forms saccharic acid as one of the products

E. Subjective Problems

1. Give the structures of the products in each of the following reactions. (2000 - 4 Marks)
   (i) Sucrose $\xrightarrow{\text{H}^+} A + B$

   \[
   \text{NOH} \xrightarrow{\text{H}^+} \text{C} \xrightarrow{\text{Polymerisation}} [-\text{D-}]_n
   \]

2. Write the structures of alanine at pH = 2 and pH = 10. (2000 - 2 Marks)

3. Aspartame, an artificial sweetener, is a peptide and has the following structure: (2001 - 5 Marks)

\[
\text{CH₂-C₆H₅} \quad \text{H₂N} - \text{CH-CONH} - \text{CH} - \text{COOCH₃}
\]

   (i) Identify the four functional groups.
   (ii) Write the zwitterionic structure.
   (iii) Write the structures of the amino acids obtained from the hydrolysis of aspartame.
   (iv) Which of the two amino acids is more hydrophobic?

4. Following two amino acids lysine and glutamine form dipeptide linkage. What are two possible dipeptides? (2003 - 2 Marks)

5. The Fisher projection of D-glucose is drawn below. (2004 - 2 Marks)

6. Which of the following will reduce Tollens’s reagent? Explain. (2005 - 2 Marks)

   (i) Draw the Fisher projection of L-glucose.
   (ii) Give the reaction of L-glucose with Tollens’s reagent
Carbohydrates, Amino Acids, Polymers & Miscellaneous Match the Following

**F** Match the Following

Each question contains statements given in two columns, which have to be matched. The statements in Column-I are labelled A, B, C and D, while the statements in Column-II are labelled p, q, r, s and t. Any given statement in Column-I can have correct matching with ONE OR MORE statement(s) in Column-II. The appropriate bubbles corresponding to the answers to these questions have to be darkened as illustrated in the following example:

If the correct matches are A-p; s and t; B-q and r; C-p and q; and D-s then the correct darkening of bubbles will look like the given.

1. Match the chemical substances in Column I with type of polymers/type of bonds in Column II.  
   (2007)
   **Column I**
   (A) cellulose
   (B) nylon-6, 6
   (C) protein
   (D) sucrose
   **Column II**
   (p) Natural polymer
   (q) Synthetic polymer
   (r) Amide linkage
   (s) Glycoside linkage

2. Match the reaction in Column I with appropriate options in Column II.  
   (2010)
   **Column I**
   (A) \[
   \text{H}_2\text{N} \text{Cl} + \text{H}_2\text{C-C-C\text{H}_3} \rightarrow \text{H}_2\text{N}-\text{C=O} \]
   (p) Racemic mixture
   (q) Addition reaction
   (r) Substitution reaction
   (s) Coupling reaction
   (t) Carbocation intermediate
**Assertion & Reason Type Questions**

1. This question contains Statement-1 (Assertion) and Statement-2 (Reason) and has 4 choices (a), (b), (c) and (d) out of which ONLY ONE is correct.

**Statement-1**: Glucose gives a reddish-brown precipitate with Fehling’s solution.

because

**Statement-2**: Reaction of glucose with Fehling’s solution give CuO and gluconic acid. (2007)

(a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1

(b) Statement-1 is True, Statement-2 is True; Statement-2 is not a correct explanation for Statement-1

(c) Statement-1 is True, Statement-2 is False

(d) Statement-1 is False, Statement-2 is True.

**Integer Value Correct Type**

1. The total number of basic groups in the following form of lysine is (2010)

\[
\text{H}_3\text{N}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}-\text{C}-\text{O}\]

2. A decapeptide (Mol. wt. 796) on complete hydrolysis gives glycine (Mol. wt. 75), alanine and phenylalanine. Glycine contributes 47.0% to the total weight of the hydrolysed products. The number of glycine units present in the decapeptide is (2011)

3. When the following aldohexose exists in its D-configuration, the total number of stereoisomers in its pyranose form is: (2012)

\[
\text{CHO}-\text{CH}_2-\text{CHOH}-\text{CHOH}-\text{CHOH}-\text{CH}_2\text{OH}
\]

**Section-B**

1. Polymer formation from monomers starts by (2002)

   (a) condensation reaction between monomers
   (b) coordinate reaction between monomers
   (c) conversion of monomer to monomer ions by protons
   (d) hydrolysis of monomers.

2. RNA is different from DNA because RNA contains (2002)

   (a) ribose sugar and thymine
   (b) ribose sugar and uracil
   (c) deoxyribose sugar and thymine
   (d) deoxyribose sugar and uracil.

3. The compound \[\text{OCOCH}_3\text{COOH}\] is used as (2002)

   (a) antiseptic
   (b) antibiotic
   (c) analgesic
   (d) pesticide.

4. Which of the following could act as a propellant for rockets? (2003)

   (a) Liquid oxygen + liquid argon
   (b) Liquid hydrogen + liquid oxygen
   (c) Liquid nitrogen + liquid oxygen
   (d) Liquid hydrogen + liquid nitrogen

**Chemistry**

4. The substituents \(R_1\) and \(R_2\) for nine peptides are listed in the table given below. How many of these peptides are positively charged at pH = 7.0? (2012)

\[
\begin{align*}
\text{H}_3\text{N}-&\text{CH-CO-NH-CH-CO-NH-CH-CO-NH-CH-CO-O} \\
&\text{H} \quad \text{R}_1 \quad \text{R}_2 \quad \text{H}
\end{align*}
\]

<table>
<thead>
<tr>
<th>Peptide</th>
<th>(R_1)</th>
<th>(R_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>H</td>
<td>H</td>
</tr>
<tr>
<td>II</td>
<td>H</td>
<td>CH(_3)</td>
</tr>
<tr>
<td>III</td>
<td>CH(_2)COOH</td>
<td>H</td>
</tr>
<tr>
<td>IV</td>
<td>CH(_2)CONH(_2)</td>
<td>(CH(_2)(_4))NH(_2)</td>
</tr>
<tr>
<td>V</td>
<td>CH(_2)CONH(_2)</td>
<td>CH(_2)CONH(_2)</td>
</tr>
<tr>
<td>VI</td>
<td>(CH(_2)(_4))NH(_2)</td>
<td>(CH(_2)(_4))NH(_2)</td>
</tr>
<tr>
<td>VII</td>
<td>CH(_2)COOH</td>
<td>CH(_2)CONH(_2)</td>
</tr>
<tr>
<td>VIII</td>
<td>CH(_2)OH</td>
<td>(CH(_2)(_4))NH(_2)</td>
</tr>
<tr>
<td>IX</td>
<td>(CH(_2)(_4))NH(_2)</td>
<td>CH(_3)</td>
</tr>
</tbody>
</table>

5. A tetrapeptide has —COOH group on alanine. This produces glycine (Gly), valine (Val), phenylalanine (Phe) and alanine (Ala), on complete hydrolysis. For this tetrapeptide, the number of possible sequences (primary structures) with —NH\(_2\) group attached to a chiral center is (JEE Adv. 2013)

6. The total number of distinct naturally occurring amino acids obtained by complete acidic hydrolysis of the peptide shown below is (JEE Adv. 2014)

![Amino Acid Structure](image-url)
5. Nylon threads are made of (a) polyester polymer (b) polyamide polymer (c) polyethylene polymer (d) polyvinyl polymer

6. Complete hydrolysis of cellulose gives (a) D-ribose (b) D-glucose (c) L-glucose (d) D-fructose

7. The reason for double helical structure of DNA is operation of (a) dipole-dipole interaction (b) hydrogen bonding (c) electrostatic attractions (d) van der Waals’ forces

8. Which base is present in RNA but not in DNA? (a) Guanine (b) Cytosine (c) Uracil (d) Thymine

9. Insulin production and its action in human body are responsible for the level of diabetes. This compound belongs to which of the following categories? (a) An enzyme (b) A hormone (c) A co-enzyme (d) An antibiotic

10. The smog is essentially caused by the presence of (a) Oxides of sulphur and nitrogen (b) O₂ and N₂ (c) O₃ and N₂ (d) O₃ and N₂

11. Which of the following is a polyamide? (a) Bakelite (b) Terylene (c) Nylon-66 (d) Teflon

12. Which one of the following types of drugs reduces fever? (a) Tranquiliser (b) Antibiotic (c) Antipyretic (d) Analgesic

13. In both DNA and RNA, heterocyclic base and phosphate ester linkages are at – (a) C₅' and C₃ (b) C₁ and C₃ (c) C₂ and C₃ (d) C₅' and C₁

14. Which of the following is fully fluorinated polymer? (a) PVC (b) Thiokol (c) Teflon (d) Neoprene

15. The term anomers of glucose refers to (a) enantiomers of glucose (b) isomers of glucose that differ in configuration at carbon one (C-1) (c) isomers of glucose that differ in configurations at carbons one and four (C-1 and C-4) (d) a mixture of (D)-glucose and (L)-glucose

16. The pyrimidine bases present in DNA are (a) cytosine and thymine (b) cytosine and uracil (c) cytosine and adenine (d) cytosine and guanine

17. The secondary structure of a protein refers to (a) fixed configuration of the polypeptide backbone (b) α – helical backbone (c) hydrophobic interactions (d) sequence of α – amino acids.

18. Identify the wrong statement in the following: (a) Chlorofluorocarbons are responsible for ozone layer depletion (b) Greenhouse effect is responsible for global warming (c) Ozone layer does not permit infrared radiation from the sun to reach the earth (d) Acid rain is mostly because of oxides of nitrogen and sulphur

19. Bakelite is obtained from phenol by reacting with (a) (CH₂OH)₂ (b) CH₃CHO (c) CH₃COCH₃ (d) HCHO

20. α-D-(+)-glucose and β-D-(+)-glucose are (a) conformers (b) epimers (c) anomers (d) enantiomers

21. Among the following substituted silanes the one which will give rise to cross linked silicone polymer on hydrolysis is (a) R₃Si (b) RSiCl (c) R₂SiCl₂ (d) R₂SiCl₃

22. Buna-N synthetic rubber is a copolymer of: (a) H₂C = CH – CH = CH₂ and H₂C₆ – CH = CH₂ (b) H₂C = CH – CN and H₂C = CH – CH₂ (c) H₂C = CH – CN and H₂C = CH – C = CH₂ (d) H₂C = CH – C = CH₂ and H₂C = CH – CH = CH₂

23. The two functional groups present in a typical carbohydrate are: (a) – CHO and – COOH (b) > C = O and – OH (c) – OH and – CHO (d) – OH and – COOH

24. Biuret test is not given by (a) carbohydrates (b) polypeptides (c) urea (d) proteins

25. The polymer containing strong intermolecular forces e.g. hydrogen bonding, is (a) teflon (b) nylon 6, 6 (c) polystyrene (d) natural rubber
26. The presence or absence of hydroxyl group on which carbon atom of sugar differentiates RNA and DNA? [2011]
   (a) 1st       (b) 2nd       (c) 3rd       (d) 4th

27. Which of the following compounds can be detected by Molisch’s Test? [2012]
   (a) Nitro compounds   (b) Sugars   (c) Amines  (d) Primary alcohols

28. The species which can best serve as an initiator for the cationic polymerization is: [2012]
   (a) LiAlH₄       (b) HNO₃       (c) AlCl₃    (d) BaLi

29. Which one of the following statements is correct? [2012]
   (a) All amino acids except lysine are optically active
   (b) All amino acids are optically active
   (c) All amino acids except glycine are optically active
   (d) All amino acids except glutamic acids are optically active

30. Aspirin is known as: [2012]
   (a) Acetyl salicylic acid   (b) Phenyl salicylate
   (c) Acetyl salicylate       (d) Methyl salicylic acid

31. Synthesis of each molecule of glucose in photosynthesis involves: [JEE M 2013]
   (a) 18 molecules of ATP   (b) 10 molecules of ATP
   (c) 8 molecules of ATP    (d) 6 molecules of ATP

32. Which one is classified as a condensation polymer? [JEE M 2014]
   (a) Dacron       (b) Neoprene
   (c) Teflon       (d) Acrylonitrile

33. Which one of the following bases is **not** present in DNA? [JEE M 2014]
   (a) Quinoline     (b) Adenine
   (c) Cytosine      (d) Thymine

34. Which of the vitamins given below is water soluble? [JEE M 2015]
   (a) Vitamin E     (b) Vitamin K
   (c) Vitamin C     (d) Vitamin D

35. Which of the following compounds is not an antacid? [JEE M 2015]
   (a) Phosphine      (b) Ranitidine
   (c) Aluminium hydroxide (d) Cimetidine

36. Which polymer is used in the manufacture of paints and lacquers? [JEE M 2015]
   (a) Polypropene     (b) Polyvinyl chloride
   (c) Bakelite       (d) Glyptal

37. The concentration of fluoride, lead, nitrate and iron in a water sample from an underground lake was found to be 1000 ppb, 40 ppb, 100 ppm and 0.2 ppm, respectively. This water is unsuitable for drinking due to high concentration of: [JEE M 2016]
   (a) Nitrate       (b) Iron
   (c) Fluoride      (d) Lead

38. Which of the following is an anionic detergent? [JEE M 2016]
   (a) Cetyltrimethyl ammonium bromide.
   (b) Glyceryl oleate.
   (c) Sodium stearate.
   (d) Sodium lauryl sulphate.

39. Which of the following statements about low density polythene is **FALSE**? [JEE M 2016]
   (a) Its synthesis requires dioxygen or a peroxide initiator as a catalyst.
   (b) It is used in the manufacture of buckets, dust-bins etc.
   (c) Its synthesis requires high pressure.
   (d) It is a poor conductor of electricity.
I. Each item from (i) to (x) given below indicates a reaction type, a process or a homologue. Match each of these items with the related phrase by writing the correct phrase in the corresponding vacant space given under each. The correct phrase must be picked only from those given below within brackets:

(Baeyer's process, Nucleophilic addition, Free radical substitution, Ostwald's process, Homologous pair, Cyanamide process, Electrophilic substitution, Homolytic addition, Thermite process, Nucleophilic substitution)

(1981 - 1×10 = 10 Marks)

(i) Cyclopropane, chlorine and light

(ii) Welding

(iii) Propanone and sodium bisulphite

(iv) Production of ammonia

(v) Chloromethane and methanol

(vi) Ore purification

(vii) Ethanolic and methanal

(viii) Benzene, nitric acid and sulphuric acid

(ix) Production of nitric acid

(x) Propene, hydrogen bromide and a peroxide catalyst

(xi) Preparation of alkanes

(xii) Phenol + CHCl₃ (NaOH)

(xiii) C₂H₅Br + alc. KOH

(xiv) Neutrons

(xv) Molecular speed

(xvi) Intermolecular forces

(xvii) Conductance of ions

(xviii) Mass spectrum

(xix) X-ray spectrum

(xx) Paramagnetism

(xxi) Orbital

(xii) Preparation of alkane

(m) Friedel-Crafts reaction

(n) Reimer-Tiemann reaction

(o) Cracking

(1982 - 2 Marks)

D. (1982 - 2 Marks)

(xviii) Mass spectrum

(xix) X-ray spectrum

(xx) Paramagnetism

(xxi) Orbital

(u) Unpaired electrons

(v) Atomic number

(w) Isotopes

II. Match the following, choosing one item from column X and one from column Y. An example is — for item No. (i) – (g)

(1982 - 3 Marks)

<table>
<thead>
<tr>
<th>X</th>
<th>Y</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i) Hg₂Cl₂</td>
<td>(a) cassiterite</td>
</tr>
<tr>
<td>(ii) (NaPO₃)ₙ</td>
<td>(b) lunar caustic</td>
</tr>
<tr>
<td>(iii) NO₃⁻</td>
<td>(c) producer gas</td>
</tr>
<tr>
<td>(iv) SnO₂</td>
<td>(d) water softener</td>
</tr>
<tr>
<td>(v) KCl₂MgCl₂·6H₂O</td>
<td>(e) brown ring test</td>
</tr>
<tr>
<td>(vi) AgNO₃</td>
<td>(f) carnallite</td>
</tr>
<tr>
<td>(vii) CO₁+N₂</td>
<td>(g) calomel</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>X</th>
<th>Y</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i) pyrolysis of alkane + benzene + chloroethane + anhydrous AlCl₃</td>
<td>(j) elimination reaction</td>
</tr>
<tr>
<td>(k) saponification of CH₃COOC₂H₅ + NaOH</td>
<td>(l) Wurtz reaction</td>
</tr>
</tbody>
</table>

A. (1983 - 2 Marks)

(i) Decarboxylation

(ii) Ozonolysis

(iii) Williamson's synthesis

(iv) Dichloroethylene

B. (1983 - 2 Marks)

(i) Luca's test

(ii) Natural FeCl₃ test

(iii) Dye test

(iv) Tollens test

C. (1983 - 2 Marks)

(i) Al

(ii) Cu

(iii) Mg

(iv) Zn

D. (1983 - 2 Marks)

(i) Haber

(ii) Graham

(iii) Arrhenius

(iv) Lewis

E. (1983 - 2 Marks)

(1984 - 1×5 = 5 Marks)

A. (1984 - 1×5 = 5 Marks)

(i) Asbestos

(ii) Fluorocarbons

(iii) Lithium metal

(iv) Nitric oxide

(v) Zeolites

(vi) Zinc oxide

B. (1985 - 2½ × 4 = 10 Marks)

A B C

(i) Asbestos (a) Molecular sieve (1) Air pollutant

(ii) Fluorocarbons (b) Paramagnetic (2) Carcinogen

(iii) Lithium metal (c) Refrigeration (3) Fluorescent paint

(iv) Nitric oxide (d) Reducing agent (4) Electron donor

(v) Zeolites (e) Semi-conductor (5) Ion exchanger

(vi) Zinc oxide (f) Silicates of (Ca + Mg) (6) Propellent

V. Match each item of the right hand column with an appropriate item in the left hand column for each of the following sections:

(1985 - 2½ × 4 = 10 Marks)
(i) Spinel (a) MgAl$_2$O$_4$
(ii) Feldspar (b) PbCO
(iii) Cerussite (c) KAlSi$_4$O$_8$
(iv) Malachite (d) MgSO$_4$$_2$H$_2$O
(v) Kisserite (e) Cu(OH)$_2$CuCO$_3$

B. (vi) Liquid air (f) Deacon process
(vii) Na$_2$CO$_3$ (g) Parke process
(viii) Nitric oxide (h) Claude process
(ix) Silver (i) Ostwald process
(x) Chlorine (j) Solvay process

C. (xi) Phenol (k) Coloured glass
(xii) Na$_2$S$_2$O$_5$ (l) Antichlor
(xiii) Salicylic acid (m) Refractory material
(xiv) Quick lime (n) Antiseptic
(xv) CuO (o) Analgesic

D. (xvi) Aston (p) Radium
(xvii) Priestley (q) Radioactivity
(xviii) Ramsay (r) Oxygen
(xix) Marie Curie (s) Inert gas
(xx) Bocquere (t) Mass spectrum

VI. Match the following choosing one item from column X and the appropriate item from column Y.  
(1986 - $\frac{1}{2} \times 8 = 4$ Marks)

<table>
<thead>
<tr>
<th>X</th>
<th>Y</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i)</td>
<td>Lewis acid</td>
</tr>
<tr>
<td>(ii)</td>
<td>Philosopher’s wool</td>
</tr>
<tr>
<td>(iii)</td>
<td>Electrophile</td>
</tr>
<tr>
<td>(iv)</td>
<td>Preservative</td>
</tr>
<tr>
<td>(v)</td>
<td>Electron emission</td>
</tr>
<tr>
<td>(vi)</td>
<td>Bronsted acid</td>
</tr>
<tr>
<td>(vii)</td>
<td>Black jack</td>
</tr>
<tr>
<td>(viii)</td>
<td>X-ray emission</td>
</tr>
<tr>
<td>(i)</td>
<td>X</td>
</tr>
<tr>
<td>(ii)</td>
<td>Y</td>
</tr>
<tr>
<td>(iii)</td>
<td>Z</td>
</tr>
</tbody>
</table>

VIII. Each entry in column X is in some way related to the entries in column Y and Z. Match the appropriate entries.  
(1989 - 5 \times 1 = 5 Marks)

<table>
<thead>
<tr>
<th>X</th>
<th>Y</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i)</td>
<td>Animal charcol</td>
</tr>
<tr>
<td>(ii)</td>
<td>Invar</td>
</tr>
<tr>
<td>(iii)</td>
<td>Nichrome</td>
</tr>
<tr>
<td>(iv)</td>
<td>Rydberg</td>
</tr>
<tr>
<td>(v)</td>
<td>Stainless steel</td>
</tr>
<tr>
<td>(vi)</td>
<td>Boltzmann</td>
</tr>
<tr>
<td>(i)</td>
<td>X</td>
</tr>
<tr>
<td>(ii)</td>
<td>Y</td>
</tr>
<tr>
<td>(iii)</td>
<td>Z</td>
</tr>
</tbody>
</table>

| A. Mica | (a) Graphite crystallite |
| B. Superphosphate | (b) Cubic |
| C. Carbon fibres | (c) Layer structure |
| D. Rock salt | (d) Diamond structure |
| E. Carborundum | (e) Bone ash |

Example: Yeast Fermentation Ethanol

IX. All the compounds listed in Column I react with water. Match the result of the respective reactions with the appropriate options listed in Column II.  
(2010)

<table>
<thead>
<tr>
<th>Column-I</th>
<th>Column-II</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A)</td>
<td>(CH$_2$)$_2$SiCl$_2$</td>
</tr>
<tr>
<td>(B)</td>
<td>XeF$_4$</td>
</tr>
<tr>
<td>(C)</td>
<td>Cl$_2$</td>
</tr>
<tr>
<td>(D)</td>
<td>VC$_5$</td>
</tr>
<tr>
<td>(A)</td>
<td>Hydrogen halide formation</td>
</tr>
<tr>
<td>(B)</td>
<td>Redox reaction</td>
</tr>
<tr>
<td>(C)</td>
<td>Reacts with glass</td>
</tr>
<tr>
<td>(D)</td>
<td>Polymerization</td>
</tr>
<tr>
<td>(A)</td>
<td>O$_2$ formation</td>
</tr>
</tbody>
</table>
CHAPTER 23

Analytical Chemistry

Section-A

JEE Advanced/ IIT-JEE

A Fill in the Blanks

1. If metal ions of group III are precipitated by NH₄Cl and NH₄OH without prior oxidation by conc. HNO₃.......... is not completely precipitated. (1984 - 1 Mark)

2. The formula of the deep red liquid formed on warming dichromate with KCl in concentrated sulphuric acid is ............. . (1993 - 1 Mark)

B True / False

1. Addition of ammonium chloride to a solution containing ferric and magnesium ions is essential for selective precipitation of ferric hydroxide by aqueous ammonia. (1985 - ½ Mark)

2. From the acidic solution containing copper (+2) and zinc (+2) ions, copper can be selectively precipitated using sodium sulphide. (1987 - 1 Mark)

C MCQs with One Correct Answer

1. The ion that cannot be precipitated by both HCl and H₂S is
   (a) Pb²⁺  (b) Cu⁺ (1982 - 1 Mark)
   (c) Ag⁺  (d) Sn²⁺

2. Which one among the following pairs of ions cannot be separated by H₂S in dilute hydrochloric acid? (1986 - 1 Mark)
   (a) Bi³⁺, Sn⁴⁺  (b) Al³⁺, Hg²⁺
   (c) Zn²⁺, Cu²⁺  (d) Ni²⁺, Cu²⁺

3. An aqueous solution contains Hg²⁺, Hg₂Cl₂, Pb²⁺ and Cd²⁺. The addition of HCl (6N) will precipitate : (1995S)
   (a) HgCl₂ only  (b) PbCl₂ only
   (c) PbCl₂ and Hg₂Cl₂  (d) PbCl₂ and HgCl₂

4. Identify the correct order of solubility of Na₂S, CuS and ZnS in aqueous medium (2002S)
   (a) CuS > ZnS > Na₂S  (b) ZnS > Na₂S > CuS
   (c) Na₂S > CuS > ZnS  (d) Na₂S > ZnS > CuS

5. An aqueous solution of a substance gives a white precipitate on treatment with dilute hydrochloric acid, which dissolves on heating. When hydrogen sulfide is passed through the hot acidic solution, a black precipitate is obtained. The substance is a (2002S)
   (a) Hg₂⁺ salt  (b) Cu²⁺ salt
   (c) Ag⁺ salt  (d) Pb²⁺ salt

6. A gas 'X' is passed through water to form a saturated solution. The aqueous solution on treatment with silver nitrate gives a white precipitate. The saturated aqueous solution also dissolves magnesium ribbon with evolution of a colourless gas 'Y'. Identify 'X' and 'Y'. (2002S)
   (a) X = CO₃, Y = Cl₂  (b) X = Cl₂, Y = CO₃
   (c) X = Cl₂, Y = H₂  (d) X = H₂, Y = Cl₂

   (a) SO₃²⁻, SO₂  (b) Cl⁻, HCl
   (c) S²⁻, H₂S  (d) CO₃²⁻, CO₂

8. A solution which is 10⁻³ M each in Mn²⁺, Fe²⁺, Zn²⁺ and Hg²⁺ is treated with 10⁻¹⁶ M sulphide ion. If Kₛₚ of MnS, FeS, ZnS and HgS are 10⁻¹⁵, 10⁻¹³, 10⁻²⁰ and 10⁻²⁴ respectively, which one will precipitate first? (2003S)
   (a) FeS  (b) MgS  (c) HgS  (d) ZnS

9. A metal nitrate reacts with KI to give a black precipitate which on addition of excess of KI is converted into orange colour solution. The cation of the metal nitrate is (2005S)
   (a) Hg²⁺  (b) Bi³⁺  (c) Pb²⁺  (d) Cu⁺

10. A solution when diluted with H₂O and boiled, gives a white precipitate. On addition of excess NH₄Cl/NH₄OH, the volume of precipitate decreases leaving behind a white gelatinous precipitate. Identify the precipitate which dissolves in NH₄OH/NH₄Cl (2006 - 3M, -I)
    (a) Al(OH)₃  (b) Zn(OH)₂
    (c) Ca(OH)₂  (d) Mg(OH)₂

11. A solution of a metal ion when treated with KI gives a red precipitate which dissolves in excess KI to give a colourless solution. Moreover, the solution of metal ion on treatment with a solution of cobalt (II) thiocyanate gives rise to a deep blue crystalline precipitate. The metal ion is (2007)
    (a) Pb²⁺  (b) Hg²⁺  (c) Cu²⁺  (d) Co²⁺

12. Passing H₂S gas into a mixture of Mn²⁺, Ni²⁺, Cu²⁺ and Hg²⁺ ions in an acidified aqueous solution precipitates (2011)
    (a) CuS and HgS  (b) MnS and CuS
    (c) MnS and NiS  (d) NiS and HgS

13. Upon treatment with ammoniacal H₂S, the metal ion that precipitates as a sulfide is (JEE Adv. 2013)
    (a) Fe(III)  (b) Al(III)  (c) Mg(II)  (d) Zn(II)
D  MCQs with One or More Than One Correct

1. The reagents, NH₄Cl and aqueous NH₃, will precipitate
   (a) Ca²⁺  (b) Al³⁺  (c) Bi³⁺  (d) Mg²⁺  (e) Zn²⁺  (1991 - 1 Mark)

2. Which of the following statement(s) is (are) correct when a mixture of NaCl and K₂Cr₂O₇ is gently warmed with conc. H₂SO₄?
   (a) A deep red vapour is evolved  (b) The vapours when passed into NaOH solution gives a yellow solution of Na₂CrO₄  (c) Chlorine gas is evolved  (d) Chromyl chloride is formed  (1998 - 2 Marks)

3. Which of the following statement(s) is (are) correct with reference to the ferrous and ferric ions?  (1998 - 2 Marks)
   (a) Fe³⁺ gives brown colour with potassium ferricyanide.  (b) Fe²⁺ gives blue precipitate with potassium ferricyanide.  (c) Fe³⁺ gives red colour with potassium thiocyanate.  (d) Fe²⁺ gives brown colour with ammonium thiocyanate.

4. The pair(s) of ions where BOTH the ions are precipitated upon passing H₂S gas in presence of dilute HCl is(are)  (JEE Adv. 2015)
   (a) Ba²⁺, Zn²⁺  (b) Bi³⁺, Fe³⁺  (c) Cu²⁺, Pb²⁺  (d) Hg²⁺, Bi³⁺

5. The reagent(s) that can selectively precipitate S²⁻ from a mixture of S²⁻ and SO₄²⁻ in aqueous solution is(are)  (JEE Adv. 2016)
   (a) CuCl₂  (b) BaCl₂  (c) Pb(OOCCH₃)₂  (d) Na₂[Fe(CN)₆]NO

E  Subjective Problems

1. Account for the following. Limit your answer to two sentences:
   The precipitation of second group sulphides in qualitative analysis is carried out with hydrogen sulphide in presence of hydrochloric acid and not nitric acid.  (1979)

2. Compound A is a light green crystalline solid. It gives the following tests:
   (i) It dissolves in dilute sulphuric acid. No gas is produced.
   (ii) A drop of KMnO₄ is added to the above solution. The pink colour disappears.
   (iii) Compound A is heated strongly. Gases B and C, with pungent smell, come out. A brown residue D is left behind.
   (iv) The gas mixture (B) and (C) is passed into a dichromate solution. The solution turns green.
   (v) The green solution from step (iv) gives a white precipitate E with a solution of barium nitrate.
   (vi) Residue D from step (iii) is heated on charcoal in a reducing flame. It gives a magnetic substance.
   Name the compounds A, B, C, D and E.  (1980)

3. When 16.8 g of white solid X were heated, 4.4 g of acid gas A that turned lime water milky was driven off together with 1.8 g of a gas B which condensed to a colourless liquid. The solid that remained, Y, dissolved in water to give an alkaline solution, which with excess barium chloride solution gave a white precipitate Z. The precipitate effervesced with acid giving off carbon dioxide. Identify A, B and Y and write down the equation for the thermal decomposition of X.  (1984 - 4 Marks)

4. A mixture of two salts was treated as follows:  (1987 - 5 Marks)
   (i) The mixture was heated with manganese dioxide and concentrated sulphuric acid when yellowish green gas was liberated.
   (ii) The mixture on heating with sodium hydroxide solution gave a gas which turned red litmus blue.
   (iii) Its solution in water gave blue precipitate with potassium ferricyanide and red colouration with ammonium thiocyanate.

5. A hydrated metallic salt A, light green in colour, on careful heating gives a white anhydrous residue B. B is soluble in water and its aqueous solution reacts with NO to give a dark brown compound C. B on strong heating gives a brown residue D and a mixture of two gases E and F. The gaseous mixture when passed through acidified permanganate, discharges the pink colour and when passed through acidified BaCl₂ solution gave a white precipitate. Identify A, B, C, D, E and F.  (1988 - 3 Marks)

6. When 20.02 g of a white solid X is heated 4.4 g of an acid gas A and 1.8 g of a neutral gas B are evolved, leaving behind a solid residue Y of weight 13.8 g. A turns lime water milky and B condenses into a liquid which changes anhydrous copper sulphate blue. The aqueous solution of Y is alkaline to litmus and gives 19.7 g of white precipitate Z with barium chloride solution. Z gives carbon dioxide with an acid. Identify A, B, X, Y and Z.  (1989 - 5 Marks)

7. The gas liberated on heating a mixture of two salts with NaOH, gives a reddish brown precipitate with an alkaline solution of K₂[HgI₄]. The aqueous solution of the mixture on treatment with BaCl₂ gives a white precipitate which is sparingly soluble in conc. HCl. On heating the mixture with K₂Cr₂O₇ and conc. H₂SO₄, red vapours of A are produced. The aqueous solution of the mixture gives a deep blue colouration B with potassium ferricyanide solution. Identify the radicals in the given mixture and write the balanced equations for the formation of A and B.  (1991 - 4 Marks)

8. A light bluish green crystalline compound responds to the following tests:
   (i) Its aqueous solution gives a brown precipitate or colour with alkaline K₂[HgI₄] solution.
   (ii) Its aqueous solution gives a blue colour with K₂[Fe(CN)₆] solution.
   (iii) Its solution in hydrochloric acid gives a white precipitate with BaCl₂ solution. Identify the ions present and suggest the formula of the compound.  (1992 - 4 Marks)
9. An orange solid (A) on heating gave a green residue (B), a colourless gas (C) and water vapour. The dry gas (C) on passing over heated Mg gave a white solid (D). (D) on reaction with water gave a gas (E) which formed dense white fumes with HCl. Identify (A) to (E) and give reactions involved. (1993 - 3 Marks)

10. A is a binary compound of a univalent metal, 1.422 g of A reacts completely with 0.321 g of sulphur in an evacuated and sealed tube to give 1.743 g of a white crystalline solid B, that forms a hydrated double salt, C with Al₃(SO₄)₂. Identify A, B and C. (1994 - 5 Marks)

11. A scarlet compound A is treated with conc. HNO₃ to give a chocolate brown precipitate B. The precipitate is filtered and the filtrate is neutralised with NaOH. Addition of KI to the resulting solution gives a yellow precipitate C. The precipitate B on warming with conc. HNO₃ in the presence of Mn(NO₃)₂ produces a pink-coloured solution due to the formation of D. Identify A, B, C and D. Write the reaction sequence. (1995 - 4 Marks)

12. Calcium burns in nitrogen to produce a white powder which dissolves in sufficient water to produce a gas (A) and an alkaline solution. The solution on exposure to air produces a thin solid layer of (B) on the surface. Identify the compounds A and B. (1996 - 2 Marks)

13. A colourless inorganic salt (A) decomposes completely at about 250°C to give only two products, (B) and (C), leaving no residue. The oxide (C) is a liquid at room temperature and neutral to moist litmus paper while the gas (B) is a neutral oxide. White phosphorus burns in excess of (B) to produce a strong white dehydrating agent. Write balanced equations for the reactions involved in the above process. (1996 - 3 Marks)

14. During the qualitative analysis of a mixture containing Cu²⁺ and Zn²⁺ ions, H₂S gas is passed through an acidified solution containing these ions in order to test Cu²⁺ alone. Explain briefly. (1998 - 2 Marks)

15. A white solid is either Na₂O or Na₂O₂. A piece of red litmus paper turns white when it is dipped into a freshly made aqueous solution of the white solid. (1999 - 4 Marks)

(i) Identify the substance and explain with balanced equation.

(ii) Explain what would happen to the red litmus if the white solid were the other compound.

16. An aqueous solution containing one mole of HgI₂ and two moles of NaI is orange in colour. On addition of excess NaI the solution becomes colourless. The orange colour reappears on subsequent addition of NaClO. Explain with equations. (1999 - 3 Marks)

17. An aqueous blue coloured solution of a transition metal sulphate reacts with H₂S in acidic medium to give a black precipitate A, which is insoluble in warm aqueous solution of KOH. The blue solution on treatment with KI in weakly acidic medium, turns yellow and produces a white precipitate B. Identify the transition metal ion. Write the chemical reactions involved in the formation of A and B. (2000 - 4 Marks)

18. Write the chemical reactions associated with the ‘borax bead test’ of cobalt (II) oxide. (2000 - 3 Marks)

19. A white substance (A) reacts with dilute H₂SO₄ to produce a colourless gas (B) and a colourless solution (C). The reaction between (B) and acidiﬁed K₂Cr₂O₇ solution produces a green solution and a slightly coloured precipitate (D). The substance (D) burns in air to produce a gas (E) which reacts with (B) to yield (D) and a colourless liquid. Anhydrous copper sulphate is turned blue on addition of this colourless liquid. Addition of aqueous NH₃ or NaOH to (C) produces a precipitate, which dissolves in the excess of the respective reagent to produce a clear solution in each case. Identify (A), (B), (C), (D) and (E). Write the equations of the reactions involved. (2001 - 10 Marks)

20. When a white crystalline compound X is heated with K₂Cr₂O₇ and concentrated H₂SO₄, a reddish brown gas A is evolved. On passing A into caustic soda solution, a yellow coloured solution of B is obtained. Neutralizing the solution B with acetic acid and on subsequent addition of lead acetate, a yellow precipitate C is obtained. When X is heated with NaOH solution, a colourless gas is evolved and on passing this gas into K₂HgI₄ solution, a reddish brown precipitate D is formed. Identify A, B, C, D and X. Write the equations of reactions involved. (2002 - 5 Marks)

21. A mixture consists of A (yellow solid) and B (colourless solid) which gives lilac colour in flame.

(a) Mixture gives black precipitate C on passing H₂S (g) through its aqueous solution.

(b) C is soluble in aqua-regia and on evaporation of aqua-regia and adding SnCl₂ gives greyish black precipitate D.

The salt solution with NH₄OH gives a brown precipitate.

(i) The sodium carbonate extract of the salt with CCl₄/FeCl₃ gives a violet layer.

(ii) The sodium carbonate extract gives yellow precipitate with AgNO₃ solution which is insoluble in NH₃. Identify A and B, and the precipitates C and D. (2003 - 4 Marks)

G Comprehension Based Questions

PASSAGE-1

p-Amino-N, N-dimethylaniline is added to a strongly acidic solution of X. The resulting solution is treated with a few drops of aqueous solution of Y to yield blue coloration due to the formation of methylene blue. Treatment of the aqueous solution of Y with the reagent potassium hexacyanoferrate (II) leads to the formation of an intense blue precipitate. The precipitate dissolves on excess addition of the reagent. Similarly, treatment of the solution of Y with the solution of potassium hexacyanoferrate (III) leads to a brown coloration due to the formation of Z. (2009)

1. The compound X is

(a) NaNO₃

(b) NaCl

(c) Na₂SO₄

(d) Na₂S

2. The compound Y is

(a) MgCl₂

(b) FeCl₂

(c) FeCl₃

(d) ZnCl₂

3. The compound Z is

(a) Mg₂[Fe(CN)₆]₃

(b) Fe[Fe(CN)₆]₃

(c) Fe₆[Fe(CN)₆]₁₃

(d) K₂Zn₃[Fe(CN)₆]₂
PASSAGE-2
An aqueous solution of a mixture of two inorganic salts, when treated with dilute HCl, gave a precipitate (P) and a filtrate (Q). The precipitate P was found to dissolve in hot water. The filtrate (Q) remained unchanged, when treated with H₂S in a dilute mineral acid medium. However, it gave a precipitate (R) with H₂S in an ammoniacal medium. The precipitate R gave a coloured solution (S), when treated with H₂O₂ in an aqueous NaOH medium.

(JEE Adv. 2013-II)

4. The precipitate P contains
   (a) Pb²⁺  (b) Hg₂²⁺
   (c) Ag⁺  (d) Hg²⁺

5. The solution S contains
   (a) Fe₃(PO₄)₂  (b) CuSO₄
   (c) ZnSO₄  (d) Na₂CrO₄

PASSAGE-3
An aqueous solution of metal ion M₁ reacts separately with reagents Q and R in excess to give tetrahedral and square planar complexes, respectively. An aqueous solution of another metal ion M₂ always forms tetrahedral complexes with these reagents. Aqueous solution of M₂ on reaction with reagent S gives white precipitate which dissolves in excess of S. The reactions are summarized in the scheme given below:

Scheme:

Tetrahedral ↔ Q ↔ M₁ R ↔ Square planar

Tetrahedral Q R ↔ M₂ Excess Square planar

White precipitate R Excess Precipitate dissolves

6. M₁, Q and R, respectively are
   (a) Zn²⁺, KCN and HCl  (b) Ni²⁺, HCl and KCN
   (c) Cd²⁺, KCN and HCl  (d) Co²⁺, HCl and KCN

(JEE Adv. 2014)

7. Reagent S is
   (a) K₄[Fe(CN)₆]  (b) Na₃HPO₄
   (c) K₂CrO₄  (d) KOH

Assertion & Reason Type Questions

1. Read the following statement and explanation and answer as per the options given below: (1989 - 2 Marks)
   **Assertion**: A very dilute acidic solution of Cd²⁺ and Ni²⁺ gives yellow precipitate of CdS on passing hydrogen sulphide.
   **Statement**: Solubility product of CdS is more than that of NiS.
   (a) If both assertion and statement are correct and statement is an explanation of assertion.
   (b) If assertion is correct and statement is wrong, statement is not an explanation of assertion.
   (c) If assertion is wrong and statement is correct, statement is not an explanation of assertion.
   (d) If both assertion and statement are wrong and statement is not explanation of assertion.

2. Read the following statement and explanation and answer as per the options given below: (1998 - 2 Marks)
   **Assertion**: Sulphate is estimated as BaSO₄ and not as MgSO₄.
   **Reason**: Ionic radius of Mg²⁺ is smaller than that of Ba²⁺.
   (a) If both assertion and reason are correct, and reason is the correct explanation of the assertion.
   (b) If both assertion and reason are correct, but reason is not the correct explanation of the assertion.
   (c) If assertion is correct but reason is incorrect.
   (d) If assertion is incorrect but reason is correct.

Integer Value Correct Type

1. Among PbS, Cu₂S, HgS, MnS, Ag₂S, NiS, CoS, Bi₂S₃ and SnS₂, the total number of BLACK coloured sulphides is
   (JEE Adv. 2014)

Section-B

JEE Main / AIEEE

1. When H₂S is passed through Hg₂S we get
   (a) HgS  (b) HgS + H₂S
   (c) HgS + Hg  (d) None of these.

2. How do we differentiate between Fe³⁺ and Cr³⁺ in group III?
   (a) by taking excess of NH₄OH solution
   (b) by increasing NH₄⁺ ion concentration
   (c) by decreasing OH⁻ ion concentration
   (d) both (b) and (c)

3. Which one of the following statements is correct?
   (a) From a mixed precipitate of AgCl and AgI, ammonia solution dissolves only AgCl
   (b) Ferric ions give a deep green precipitate on adding potassium ferrocyanide solution
   (c) On boiling a solution having K⁺, Ca²⁺ and HCO₃⁻ ions we get a precipitate of K₂Ca(CO₃)₂
   (d) Manganese salts give a violet borax bead test in the reducing flame

4. The compound formed in the positive test for nitrogen with the Lassaigne solution of an organic compound is
   (a) Fe₄[Fe(CN)₆]₃  (b) Na₃[Fe(CN)₆]
   (c) Fe(CN)₃  (d) Na₄[Fe(CN)₆]NOS

5. The equation which is balanced and represents the correct product(s) is:
   (JEE M 2014)
   (a) Li₂O + 2KCl → 2LiCl + K₂O
   (b) [CoCl(NH₃)₆]³⁺ + 5H⁺ → Co²⁺ + 5NH₄⁺ + Cl⁻
   (c) [Mg(H₂O)₆]²⁺ + (EDTA)⁴⁻ → excess NaOH → [Mg(EDTA)]²⁺ + 6H₂O
   (d) CuSO₄ + 4KCN → K₂[Cr(CN)₆] + K₂SO₄
Some Basic Concepts of Chemistry

Section-A : JEE Advanced/ IIT-JEE

   2. $6.02 \times 10^{24}$
   3. 0.4 m
   4. 4.14 g
   5. $\frac{7}{3}$
   6. (c)
   7. (a)
   8. (d)
   9. (c)
   10. (c)
   11. (a)
   12. (b)
   13. (b)
   14. (d)
   15. (c)
   16. (b)
   17. (a)
   18. (d)
   19. (a)
   20. (d)
   21. (c)
   22. (a)
   23. (b)
   24. (d)
   25. (a)
   26. (a)
   27. (b)
   28. (d)

F 1. 4.87 g
2. Al 54.87%, Mg 45.13%
3. 59.33%
4. 8.38
5. (a) $9.5 \times 10^{-3}$ gram mole, (b) 0.437 moles
6. CH₄
7. Na₂O = 3.58%, K₂O = 10.62%
8. 24
9. 1.338 gm
10. (a) 1.95 parts; (b) 1 milli equivalents; (c) (i) Mg, (ii) 0.25 g, (iii) 62.5 ml
11. C₂H₈
12. $3.5 \times 10^{-3}$ g
13. 53.53
14. 0.588 N
15. 39.6 g l⁻¹
16. Ca
17. 2
18. (i) 37.92, (ii) 0.065; (iii) 7.74 m, 3.87 m
19. (i) 37.92, (ii) 0.065; (iii) 7.74 m, 3.87 m
20. 2
21. 6.3648 g
22. HI < I₂ < ICl < HIO₄
23. (i) 1.446 g, 0.112 M; (ii) 1.7532 g, 0.1344 M
24. (i) 0.56, (ii) 0.0999
25. 6.5 g
26. +2, +4, +6, 16.66 ml
27. 1.12 g, 0.90 g
28. 3.324 g, 1.676 g
29. 10.43 m
30. 1:2
31. 6
32. Na₂CO₃-26.5%, Na₂SO₄-31.5%
33. 85%
34. 0.0075 M, Pb²⁺ = 0.05357 M, NO₃⁻ = 0.3214 M, Cr³⁺ = 0.0714 M
35. 15.05%
36. 0.25 M, 0.24 m, $4.3 \times 10^{-3}$
37. 49.33%, 34.8%
38. 0.062
39. 8.097 ml
40. $7.09 \times 10^7$
41. 0.1
42. 55.55 M

H 1. (b)

I 1. 3
2. 7
3. 5
4. 4

Section-B : JEE Main/ AIEEE

1. (c)
2. (c)
3. (a)
4. (a)
5. (d)
6. (b)
7. (a)
8. (a)
9. (b)
10. (d)
11. (d)
12. (a)
13. (d)
14. (a)
15. (c)
16. (d)
17. (b)

Section-A : JEE Advanced/ IIT-JEE

A. Fill in the Blanks

1. Carbon (C – 12)
2. $6.02 \times 10^{24}$
   18 ml H₂O = 18 g H₂O (density of water = 1 g/cc) = 1 mole of H₂O
   1 Mole of H₂O = $10 \times 6.02 \times 10^{23}$ electrons
   (\therefore) Number of electrons present in one molecule of water = $2 + 8 = 10$
   = $6.02 \times 10^{24}$ electrons

3. TIPS/Formulæ: Molality = \[ \frac{\text{Moles of solute}}{\text{Mass of solvent in kg}} \]
   = \[ \frac{\text{wt. of solute in gram}}{\text{M. wt. of solute}} \]
4. **TIPS/Formulae**:
   1 Mole = $6.023 \times 10^{23}$ molecules = Molecular weight in gms.
   Weight of $6.023 \times 10^{23}$ (Avogadro’s number) molecules of CuSO$_4$5H$_2$O = Molecular wt. of CuSO$_4$5H$_2$O = 249 g.
   \[
   \therefore \text{Weight of } 1 \times 10^{22} \text{ molecules of CuSO}_45\text{H}_2\text{O} = \frac{249 \times 1 \times 10^{22}}{6.023 \times 10^{23}} = 4.14 \text{ g}
   \]

5. **NOTE**: Sum of oxidation states of all atoms (elements) in a neutral compound is zero.
   **TIPS/Formulae**: As YBa$_2$Cu$_3$O$_y$ is neutral.
   \[(+3) + 2(+2) + 3(x) + 7(-2) = 0\]
   or \[3 + 4 + 3x - 14 = 0\]
   \[\Rightarrow 3x + 7 - 14 = 0 \quad \text{or} \quad x = \frac{7}{3}
   \]

6. **C. MCQs with ONE Correct Answer**
   1. (d) $4 \text{ Al} + 3\text{ O}_2 \rightarrow 2 \text{ Al}_2\text{O}_3$
      At. wt. of Al = 27
      Thus $4 \times 27$ g of Al reacts with oxygen $= 3 \times 32$ g
      \[\therefore 27 \text{ g of Al reacts with oxygen } = \frac{3 \times 32}{4 \times 27} \times 27 \text{ g} = 24 \text{ g}\]
   2. (c) No. of nitrogen atoms = \[
   \frac{\text{Mass in grams}}{\text{Atomic wt.}} = \frac{28}{14} = 2
   \]
      No. of oxygen atoms = \[
   \frac{\text{Mass in grams}}{\text{Atomic wt.}} = \frac{80}{16} = 5
   \]
      \[\therefore \text{Formula of compound is } \text{N}_2\text{O}_5\text{.}\]
   3. (a) (a) $18 \text{ g of H}_2\text{O} = 6.02 \times 10^{23} \text{ molecules of H}_2\text{O}$
      \[\therefore 36 \text{ g of H}_2\text{O} = 2 \times 6.02 \times 10^{23} \text{ molecules of H}_2\text{O} = 12.04 \times 10^{23} \text{ molecules of H}_2\text{O}\]
      (b) $28 \text{ g of CO} = 6.02 \times 10^{23} \text{ molecules of CO}$
      (c) $46 \text{ g of C}_2\text{H}_5\text{OH} = 6.02 \times 10^{23} \text{ molecules of C}_2\text{H}_5\text{OH}$
      (d) $108 \text{ g of N}_2\text{O}_5 = 6.02 \times 10^{23} \text{ molecules of N}_2\text{O}_5$
      \[\therefore 54 \text{ g of N}_2\text{O}_5 = \frac{1}{2} \times 6.02 \times 10^{23} \text{ molecules of N}_2\text{O}_5 = 3.01 \times 10^{23} \text{ molecules of N}_2\text{O}_5\]
      \[\therefore 36 \text{ g of water has highest number of molecules.}\]
   4. (a) No. of e$^-$ in C = 6 and in O = 8
      \[\therefore \text{Total no. of e}^- \text{ in CO}_2 = 6 + 8 \times 2 = 22\]
   5. (c) Let mass of oxygen = 1g. Then mass of nitrogen = 4g
      Mol. wt. of N$_2$ = 28g, Mol. wt. of O$_2$ = 32g
      $28 \text{ g of N}_2 = 6.02 \times 10^{23} \text{ molecules of nitrogen}$
      $4 \text{ g of N}_2 = \frac{6.02 \times 10^{23}}{28} \times 4 \text{ molecules of nitrogen} = \frac{6.02 \times 10^{23}}{7} \text{ molecules of nitrogen}
   \]

7. **Topic-wise Solved Papers - CHEMISTRY**
   32 g of O$_2$ has $= 6.02 \times 10^{23}$ molecules of oxygen
   \[\therefore \text{lg of O}_2 = \frac{6.02 \times 10^{23}}{32} \times 1 = \frac{6.02 \times 10^{23}}{32} \text{ molecules of oxygen}\]
   \[\therefore \text{ratio of molecules of oxygen : nitrogen } = \frac{6.02 \times 10^{23}/32}{6.02 \times 10^{23}/7} = 7:32\]
   \[\therefore \text{Ag}_2\text{CO}_3 \xrightarrow{2.76} \text{Ag}_2\text{O} + \text{CO}_2 \xrightarrow{\Delta} 2\text{Ag} + \frac{1}{2}\text{O}_2 \quad \text{(residue)}\]
   \[\text{NOTE : Ag}_2\text{O is thermally unstable and decompose on heating liberating oxygen}\]
   \[\text{Mol. wt. of Ag}_2\text{CO}_3 = 108 \times 2 + 12 + 16 \times 3 = 276 \text{ g}\]
   \[\therefore 276 \text{ g of Ag}_2\text{CO}_3 \text{ on heating gives}{\text{ residue}} = 2 \times 108 = 216 \text{ g of Ag}\]
   \[\therefore 2.76 \text{ g of Ag}_2\text{CO}_3 \text{ on heating gives} = \frac{216}{276} \times 2.76 = 2.16 \text{g of Ag}\]
   \[\quad \text{(a)} \quad \text{The change involved is } \text{MnO}_4^- + e^- \rightarrow \text{MnO}_4^{2-}\]
   \[\text{i.e. it involves only one electron}\]
   \[\text{Eq wt} = \frac{\text{Mol. wt}}{\text{No.of e}^- \text{ involved}} = \frac{M}{1} = M \quad \text{[Mol. wt.} = M\]

8. (d) **TIPS/Formulae**:
   (i) Write balanced chemical equation for chemical change.
   (ii) Find limiting reagent.
   (iii) Amount of product formed will be determined by amount of limiting reagent.
   The balanced equation is:
   \[3\text{BaCl}_2 + 2\text{Na}_3\text{PO}_4 \rightarrow \text{Ba}_3(\text{PO}_4)_2 + 6\text{NaCl}\]
   \[\text{No. of moles : 3 mole 2 mole 1mole}\]
   \[\text{Limiting reagent is Na}_3\text{PO}_4 (0.2 mol), \text{BaCl}_2 \text{ is in excess.}\]
   \[\text{From the above equation : 2.0 moles of Na}_3\text{PO}_4 \text{ yields Ba}_3(\text{PO}_4)_2 = 1 \text{ mole}\]
   \[\therefore 0.2 \text{ moles of Na}_3\text{PO}_4 \text{ will yield } \text{Ba}_3(\text{PO}_4)_2 = \frac{1}{2} \times 0.2 = 0.1 \text{ mol.}\]

9. (c) **TIPS/Formulae**:
   (i) Find oxidation state of N in N$_2$H$_4$
   (ii) Find change in oxidation number with the help of number of electrons given out during formation of compound Y.
   \[\text{N}_2\text{H}_4 \rightarrow Y + 10 \text{e}^-\text{, Calculation of O.S. of N in N}_2\text{H}_4 : 2x + 4 = 0 \Rightarrow x = -2\]
   \[\text{The two nitrogen atoms will balance the charge of 10 e}^- \text{.}\]
   \[\text{Hence oxidation state of N will increase by +5, i.e. from -2 to +3.}\]
10. (c) **NOTE:**
The sum of oxidation states of all atoms in compound is zero. Calculation of O.S. of C in CH₂O.
\[ x + 2 + (-2) = 0 \Rightarrow x = 0 \]

11. (a) **TIPS/Formulae:**
Molarity = \( \frac{\text{Number of moles of solute}}{\text{Mass of solvent in kg}} \)

A molal solution is one which contains one mole of solute per 1000 g of solvent. \( \therefore 1m = \frac{1\text{mole}}{1\text{kg}} \)

12. (b) **TIPS/Formulae:**
Sum of oxidation state of all atoms in neutral compound is zero. Let the oxidation state of iron in the complex ion \( [\text{Fe}(\text{H₂O})₃\text{(NO)}]^{2+} \) be \( x \); then
\[ x + 5 \times 0 + 1\times(-2) = 0 \Rightarrow x = 2 \]

13. (b) For equivalent weight of \( \text{MnSO₄} \) to be half of its molecular weight, change in oxidation state must be equal to 2. It is possible only when oxidation state of Mn in product is +4. Since oxidation state of Mn in \( \text{MnSO₄} \) is +2. So, \( \text{MnO₂} \) is correct answer.
In \( \text{MnO₂} \), O.S. of Mn = +4
\( \therefore \) Change in O.S. of Mn = +4 - (+2) = +2

14. (d) **TIPS/Formulae:**
(i) Volume of substance changes with temperature and mass is not affected by change in temperature.
(ii) Find expression which does not have volume term in it.

(a) Molarity – Moles of solute/volume of solution in L

(b) Normality – gm equivalents of solute/volume of solution in L

(c) Formality – gm formula wt./volume of solution in L

(d) Molality – Moles of solute/mass of solvent in kg
\( \therefore \) Molality does not involve volume term.
\( \therefore \) It is independent of temperature.

15. (c) 2 + 2 (2 + x – 4) = 0 \( \Rightarrow \) \( \text{BaH₂PO₄} \)₂ is neutral molecule
or 2x – 2 = 0 \( \Rightarrow x = +1 \)

16. (b) **TIPS/Formulae:**
(i) Write balance chemical equation for given change.
(ii) Identify most electronegative element and find its oxidation state.
\( \text{BaO₂} + \text{H₂SO₄} \rightarrow \text{BaSO₄} + \text{H₂O} \)
Oxygen is the most electronegative element in the reaction and has the oxidation states of -1 (in \( \text{H₂O} \)) and -2 (in \( \text{BaSO₄} \)). In \( \text{H₂O} \), peroxo ion is present.

17. (a) **TIPS/Formulae:**
Balance the reaction by ion electron method.
**Oxidation reaction:** \( \text{C₂O₄}^{2-} \rightarrow 2\text{CO₂} + 2e⁻ \times 5 \)
**Reduction reaction:**
\( \text{MnO₄}^{-} + 8\text{H}^{+} + 5e⁻ \rightarrow \text{Mn}^{2+} + 4\text{H₂O} \times 2 \)
**Net reaction:**
\[ 2 \text{MnO₄}^{-} + 16\text{H}^{+} + 5 \text{C₂O₄}^{2-} \rightarrow 2\text{Mn}^{2+} + 10\text{CO₂} + 8\text{H₂O} \]

18. (d) **TIPS/Formulae:**
(i) \( \text{H₂PO₃} \) is dibasic acid as it contains two –OH groups.
\[
\begin{align*}
\text{OH} & \quad \text{P} & \quad \text{OH} \\
\text{HO} & \quad \text{P} & \quad \text{OH}
\end{align*}
\]
(ii) Normality = Molarity \times basicity of acid.
(iii) Basicity of \( \text{H₂PO₃} \) = 2
\( \therefore \) Normality = 0.3 \times 2 = 0.6

19. (a) **TIPS/Formulae:**
(i) Oxidation state of element in its free state is zero.
(ii) Sum of oxidation states of all atoms in compound is zero.
O.N. of S in \( \text{S}_₈ \) = 0; O.N. of S in \( \text{S}_₂\text{F}_₂ \) = +1;
O.N. of S in \( \text{H₂S} \) = -2;

20. (d) **TIPS/Formulae:**
(i) In an ion sum of oxidation states of all atoms is equal to charge on ion and in a compound sum of oxidation states of all atoms is always zero.
Oxidation state of Mn in \( \text{MnO₄} \)⁻ = +7
Oxidation state of \( \text{Cr} \) in \( \text{Cr(CN)}₆^{3⁻} \) = +3
Oxidation state of \( \text{Ni} \) in \( \text{NiF}_₂ \)⁻ = +4
Oxidation state of \( \text{Cr} \) in \( \text{CrOCl}_₂ \) = +6

21. (e) **TIPS/Formulae:**
(i) In a disproportionation reaction same element undergoes oxidation as well as reduction during the reaction.
(ii) In decomposition reaction a molecule breaks down to more than one atoms or molecules
\[ +1 \text{ClO}⁻ \rightarrow +5 \text{ClO}_{aq} + 2\text{Cl}⁻ \text{aq} \]
It is disproportionation reaction because Cl is both oxidised (+1 to +5) and reduced (+1 to -1) during reaction.

22. (a) **TIPS/Formulae:**
Equivalents of \( \text{H₂C₂O₄}.2\text{H₂O} = \) Equivalents of \( \text{NaOH} \)
\( \text{At equivalence point} \)
Strength of \( \text{H₂C₂O₄}.2\text{H₂O} \) (in g/L) = \( \frac{6.3}{250/1000} = 25.2 \text{g/L} \)
Normality of \( \text{H₂C₂O₄}.2\text{H₂O} \) = \( \frac{\text{Strength}}{\text{Eq. wt.}} = \frac{25.2}{63} = 0.4\text{N} \)
\[ \left\{ \text{Eq. wt. of oxalic acid} = \frac{\text{Mol. wt.}}{2} \right\} = \frac{126}{2} = 63 \]
Using normality equation:
\( N₁V₁ = N₂V₂ \)
\( \text{(H₂C₂O₄}.2\text{H₂O)} \text{ (NaOH)} \)
\( 0.4 \times 10 = 0.1 \times V₂ \text{ or } V₂ = \frac{0.4 \times 10}{0.1} = 40 \text{ ml.} \)
23. (b) **TIPS/Formulæ:**

(i) Find change in oxidation number of Cr atom.

(ii) \[ \text{Eq. wt.} = \frac{\text{Molecular wt.}}{\text{charge in O.N.}} \]

In iodometry, \( K_2Cr_2O_7 \) liberates I\(_2\) from iodides (NaI or KI). Thus it is titrated with \( Na_2S_2O_3 \) solution.

\[ 2Na_2S_2O_3 + I_2 \rightarrow 2NaI + Na_2S_4O_6 \]

O.N. of Cr changes from \(+6\) (in \( K_2Cr_2O_7 \)) to \(+3\), i.e. \(+3\) change for each Cr atom

\[ Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O \]

Thus, one mole of \( K_2Cr_2O_7 \) accepts 6 mole of electrons.

\[ \therefore \text{Equivalent weight} = \frac{\text{Molecular weight}}{6} \]

24. (d) **TIPS/Formulæ:**

(i) Mass of one electron = \( 9.108 \times 10^{-31} \) kg

(ii) 1 mole of electron = \( 6.023 \times 10^{23} \) electrons

Weight of 1 mole of electron

= Mass of one electron \times Avogadro Number

= \( 9.108 \times 10^{-31} \times 6.023 \times 10^{23} \) kg

\[ \therefore \text{No. of moles of electrons in 1 kg} = \frac{1}{9.108 \times 10^{-31} \times 6.023 \times 10^{23}} = \frac{1}{9.108 \times 6.023} \times 10^8 \]

25. (a) **TIPS/Formulæ:**

Atomic weight in gms = \( 6.023 \times 10^{23} \) atoms = 1 Mole atoms

(i) Number of atoms in 24 g of C

\[ \frac{24}{12} \times 6.023 \times 10^{23} = 2 \times 6.023 \times 10^{23} \text{ atom} \]

= 2 mole atoms

(ii) Number of atoms in 56 g of Fe

\[ \frac{56}{56} \times 6.023 \times 10^{23} = 6.023 \times 10^{23} \text{ atom} \]

= 1 mole atoms

(iii) Number of atoms in 27 g of Al

\[ \frac{27}{27} \times 6.023 \times 10^{23} = 6.023 \times 10^{23} \text{ atom} \]

= 1 mole atoms

(iv) Number of atoms in 108 g of Ag

\[ \frac{108}{108} \times 6.023 \times 10^{23} = 6.023 \times 10^{23} \text{ atom} \]

= 1 mole atoms

\[ \therefore \text{24 g of C has maximum number of atoms.} \]

26. (a) **TIPS/Formulæ:**

Write the reaction for chemical change during reaction and equate moles of products formed.

\[ [\text{Co(NH}_3)_2\text{SO}_4] \text{Br has ionisable Br}^- \text{ions} \& [\text{Co(NH}_3)_5\text{Br}] \text{SO}_4 \text{has ionisable SO}_4^{2-} \text{ion.} \]

27. (b) **TIPS/Formulæ:**

The highest O.S. of an element is equal to the number of its valence electrons

(i) \([\text{Fe(CN)}_6]^{3-}\), O.N. of Fe = +3, \[\text{[Co(CN)}_6]^{3-}\], O.N. of Co = +3

(ii) \(Cr_2O_7^{2-}\), O.N. of Cr = +6, (Highest O.S. of Cr)

\([\text{MnO}_4]^\text{2-}\), O.N. of Mn = +7 (Highest O.S. of Mn)

(iii) \(\text{TiO}_3\), O.N. of Ti = +6, \(\text{MnO}_3\), O.N. of Mn = +4

(iv) \([\text{Co(CN)}_5]^\text{3-}\), O.N. of Co = +3, \(\text{MnO}_3\), O.N. of Mn = +6

28. (d) The following reaction occurs:

\[ 6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \rightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O \]

From the above equation, we find that Mohr's salt of \((\text{FeSO}_4 \cdot \text{NH}_3)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}\) and dichromate react in 6 : 1 molar ratio.

**E. Subjective Problems**

1. **TIPS/Formulæ:**

Write the balance chemical equation and use mole concept for limiting reagent.

\[ \text{AgNO}_3 + \text{NaCl} \rightarrow \text{NaNO}_3 + \text{AgCl} \]

\[ \text{AgNO}_3 \quad 170 \text{ g} \\ \text{NaCl} \quad 58.5 \text{ g} \\ \text{AgCl} \quad 143.5 \text{ g} \]

From the given data, we find \(\text{AgNO}_3\) is limiting reagent as \(\text{NaCl}\) is in excess.
2. **TIPS/Formulæ:**

(i) Find volume of H₂ at N.T.P.

(ii) Total amount of H₂ liberated = H₂ liberated by Mg & HCl + H₂ liberated by Al & HCl.

**Conversion of volume of H₂ to N.T.P**

Given conditions

- \( P₁ = 0.92 \) atm.
- \( P₂ = 1 \) atm.
- \( V₁ = 1.20 \) litres
- \( V₂ = ? \)
- \( T₁ = 0 + 273 = 273 \) K
- \( T₂ = 273 \) K

Applying ideal gas equation,

\[
\frac{P₁V₁}{T₁} = \frac{P₂V₂}{T₂}
\]

\[
\frac{0.92 \times 1.20}{273} = \frac{1 \times V₂}{273}, \quad V₂ = \frac{0.92 \times 1.20 \times 273}{273 \times 1} \text{ litres}
\]

\( = 1.104 \) litres \( = 1104 \) ml

The relevant chemical equations are

(i) \( 2 \text{Al} + 6\text{HCl} \rightarrow 2\text{AlCl}_3 + 3\text{H}_2 \)

\( 2 \times 27 \) \( 3 \times 22400 \)

\( = 54 \) g \( = 67200 \) ml at NTP

(ii) \( \text{Mg} + 2\text{HCl} \rightarrow \text{MgCl}_2 + \text{H}_2 \)

\( 24 \) g \( 22400 \) ml at NTP

\( \text{Wt. of alloy} = 1 \) g

Let the wt. of aluminium in alloy = \( x \) g

\( \therefore \) Wt. of magnesium in alloy = (1 - \( x \)) g

According to equation (i)

\( 54 \) g of Al = 67200 ml of H₂ at N.T.P

\( \therefore x \) g of Al = \( \frac{67200}{54} \times x = 1244.44 \) x ml of H₂ at N.T.P

Similarly, from equation (ii)

\( 24 \) g of Mg = 22400 ml of H₂ at N.T.P

\( (1 - x) \) g of Mg = \( \frac{22400}{24} \times (1 - x) = 933.3 \) (1 - \( x \)) ml of H₂

Hence total vol. of H₂ collected at N.T.P

\( = 1244.44 \times 933.3 \) (1 - \( x \)) ml

But total vol. of H₂ as calculated above \( = 1104 \) ml

\( \therefore 1244.44 \times 933.3 (1 - x) = 1104 \) ml

\( 1244.44 \times 933.3 x = 1104 - 933.3 \)

\( 311.1 \times x = 170.7, x = 0.5487 \)

Hence 1 g of alloy contains Al = 0.5487 g

\( \therefore \) Percentage of Al in alloy = \( \frac{0.5487 \times 100}{1} = 54.87\% \)

\( \% \) of Mg in alloy = \( 100 - 54.87 = 45.13\% \)

3. \( 3 \text{MnO}_2 \rightarrow \text{Mn}_3\text{O}_4 + \text{O}_2 \)

\( 3 \) (54.9 + 32) \( \) (3 x 54.9 + 64)

\( = 260.7 \) g \( \) = 228.7 g

Let the amount of pyrolusite ignited = \( 100 \) g

\( \therefore \) Wt. of MnO₃ = 80 g \( \) (80% of 100 g = 80 g)

Wt. of SiO₂, and other inert substances = 15 g

Wt. of water = \( 100 - (80 + 15) = 5 \) g

According to equation,

\( 260.7 \) g of MnO₂ gives = 228.7 g of Mn_3O_4

\( \therefore 80 \) g of MnO₂ = \( \frac{228.7}{260.7} \times 80 = 70.2 \) g of Mn_3O_4

**NOTE:**

During ignition, H₂O present in pyrolusite is removed while silica and other inert substances remain as such.

\( \therefore \) Total wt. of the residue = 70.2 + 15 = 85.2 g

Calculation of % of Mn in ignited MnO₄

\( 3 \text{Mn} = \text{Mn}_3\text{O}_4 \)

\( 3 \times 54.9 = 164.7 \) g

\( 3 \times 54.9 + 64 = 228.7 \) g

Since, 228.7 g of MnO₄ contains 164.7 g of Mn

\( 70.2 \) g of MnO₄ contains = \( \frac{164.7}{228.7} \times 70.2 = 50.55 \) g of Mn

Weight of residue = 85.2 g

Hence, percentage of Mn is the ignited sample

\( \frac{50.55}{85.2} \times 100 = 59.33\% \)

4. **TIPS/Formulæ:**

(i) Find the volume of CO₂ at NTP

(ii) Find molecular wt. of metal carbonate

(iii) Find the wt. of metal

(iv) Calculate equivalent weight of metal

Given \( P₁ = 700 \) mm, \( P₂ = 760 \) mm, \( V₁ = 1336 \) ml, \( V₂ = ? \)

\( T₁ = 300 \) K, \( T₂ = 273 \) K

\( \frac{P₁V₁}{T₁} = \frac{P₂V₂}{T₂} \), or \( V₂ = \frac{P₁V₁T₂}{P₂T₁} = \frac{700 \times 1336 \times 273}{760 \times 300} \)

\( = 1119.78 \) ml = 1.12 L at NTP

\( \therefore 1.12 \) L of CO₂ is given by carbonate = 4.215 g

Molecular weight of metal carbonate = \( 4.215 \times \frac{1}{1.12} \)

\( = 3.76 \)

Metal carbonate is \( \text{MnCO}_₃ = \text{M} + 12 + 48 = \text{M} + 60 \)

Atomic weight of M = \( 84.3 \) - 60 = 24.3

Eq. wt. of metal = \( \frac{1}{2} \times \text{M. wt.} = \frac{1}{2} \times 24.3 = 12.15 \)

5. (a) Equivalents of \( \text{KMnO}_₄ = \text{Equivalents of FeSO}_₄ \cdot 7\text{H}_₂\text{O} \)

\( 5.4 \) ml 0.1 N \( \text{KMnO}_₄ = \frac{5.4 \times 10^{-4}}{1000} = 5.4 \times 10^{-4} \) equivalents

Amount of \( \text{FeSO}_₄ = 5.4 \times 10^{-4} \times \text{Mol. wt. of FeSO}_₄ \cdot 7\text{H}_₂\text{O} = 5.4 \times 10^{-4} \times 278 = 0.150 \) g

Total weight of mixture = 5.5 g

Amount of ferric sulphate = 5.5 - 0.150 = 5.35 g

Hence Moles of ferric sulphate = \( \frac{\text{Mass}}{\text{M. wt.}} = \frac{5.35}{562} \)

\( = 9.5 \times 10^{-3} \) gram-mole

(b) Using the relation, Mol. wt. = 2 x vapour density, we get

Mol. wt. = 2 x 38.3 = 76.6
No. of moles of \( \text{NO}_2 \) = \( \frac{\text{Mass}}{\text{Mol. wt.}} = \frac{100}{46} = 2.1 \) g

No. of moles of \( \text{N}_2\text{O}_4 \) = \( \frac{\text{Mass}}{\text{Mol. wt.}} = \frac{100 - x}{92} \) g

According to problem
\[ 1.30 = \frac{x}{46} + \frac{100 - x}{92} \]

On solving the equation we find, \( x = 20.1 \) g

Moles of \( \text{NO}_2 \) = \( \frac{\text{Mass}}{\text{Mol. wt.}} = \frac{20.1}{46} = 0.437 \) moles.

6. Volume of oxygen taken = 30 ml
Volume of unused oxygen = 15 ml
Volume of \( \text{CO}_2 \) used = Volume of \( \text{O}_2 \) added – Volume of \( \text{O}_2 \) left = 30 – 15 = 15 ml
Volume of \( \text{CO}_2 \) produced = Volume of gaseous mixture after explosion – Volume of unused oxygen
or Volume of \( \text{CO}_2 \) produced = 25 – 15 = 10 ml
Volume of hydrocarbon = 5 ml

General equation for combustion of a hydrocarbon is as follows:

\[ \text{C}_x\text{H}_y + \left(x + \frac{y}{4}\right)\text{O}_2 \rightarrow x\text{CO}_2 + \frac{y}{2}\text{H}_2\text{O} \]

\[ \frac{5}{\text{ml}} \times \left(\frac{x + \frac{y}{4}}{\text{ml}}\right) = 5x \]

\[ \therefore \text{Volume of } \text{CO}_2 \text{ produced} = 5x. \text{ Since Volume of } \text{CO}_2 = 10 \text{ ml} \]

\[ 5x = 10 \Rightarrow x = 2, \text{ Volume of } \text{O}_2 \text{ used} = 15 \text{ ml} \]

\[ 5 \left(\frac{x + \frac{y}{4}}{\text{ml}}\right) = 15 \Rightarrow x + \frac{y}{4} = 3 \]

\[ \therefore 2 + \frac{y}{4} = 3 \Rightarrow 8 + y = 12 \Rightarrow y = 4 \]

Hence molecular formula of hydrocarbon is \( \text{C}_2\text{H}_4 \).

TIPS/Formulæ:
(i) Equate given mass of AgCl against mass obtained from NaCl and KCl
(ii) \( 2\text{NaCl} = \text{Na}_2\text{O} \text{ & } 2\text{KCl} = \text{K}_2\text{O} \)
Let amount of NaCl in mixture = \( x \) g
\[ \therefore \text{amount of KCl in mixture} = (0.118 - x) \text{ g} \]
\[ \text{NaCl} + \text{AgNO}_3 \rightarrow \text{AgCl} + \text{NaNO}_3 \]
\[ 58.5 \text{ g} \rightarrow 143.5 \text{ g} \]
\[ \therefore 58.5 \text{ g NaCl gives AgCl} = 143.5 \text{ g} \]
\[ \therefore x \text{ g NaCl gives AgCl} = \frac{143.5}{58.5} \times x \text{ g} \]

Again
\[ \text{KCl} + \text{AgNO}_3 \rightarrow \text{AgCl} + \text{KNO}_3 \]
\[ 74.5 \text{ g} \rightarrow 143.5 \text{ g} \]

\[ 74.5 \text{ g KCl gives AgCl} = 143.5 \text{ g} \]
\[ \therefore (0.118 - x) \text{ g KCl gives AgCl} = \left(\frac{143.5}{74.5} \times 0.118 - x\right) \text{ g} \]

Total weight of AgCl = 0.2451 g
\[ \therefore \left(\frac{143.5}{58.5} \times x\right) + \left[\frac{143.5}{74.5} \times (0.118 - x)\right] = 0.2451 \]
\[ \therefore x = 0.0338 \text{ g} \]
\[ \therefore \text{Amount of NaCl in mixture} = 0.0338 \text{ g} \]
\[ \therefore \text{Amount of KCl in mixture} = 0.118 - 0.0338 = 0.0842 \text{ g} \]
Since \( 2\text{NaCl} = \text{Na}_2\text{O} \)
\[ 2 \times 58.5 = 62 \]
\[ = 117.0 \]
\[ \therefore 117 \text{ g NaCl is equivalent to} = 62 \text{ g} \text{ Na}_2\text{O} \]
\[ \therefore 0.0338 \text{ g NaCl is equivalent to} = \frac{62.0}{117} \times 0.0338 \text{ g} \text{ Na}_2\text{O} \]
\[ = 0.0179 \text{ g} \]

% of Na\(_2\)O in 0.5 g of feldspar = \( \frac{0.0179}{0.5} \times 100 = 3.58\% \)

\[ \text{KCl} = \text{K}_2\text{O} \]
\[ 2 \times 74.5 = 149 \]
\[ = 94 \]
\[ \therefore 149 \text{ g of KCl is equivalent to} = 94 \text{ g} \text{ K}_2\text{O} \]
\[ \therefore 0.0842 \text{ g of KCl is equivalent to} = \frac{94}{149} \times 0.0842 \]
\[ = 0.0531 \text{ g} \text{ K}_2\text{O} \]
\[ \therefore \% \text{ of } \text{K}_2\text{O} \text{ in feldspar} = \frac{0.0531}{0.5} \times 100 = 10.62\% \]

% of Na\(_2\)O in feldspar = 3.58\%
% of K\(_2\)O in feldspar = 10.62\%

8. According to problem, three atoms of M combine with 2 atoms of N
\[ \therefore \text{Formula of compound is } M_3N_2 \text{ (Where M is the metal)} \]
Equivalent wt of N = \( \frac{14}{3} \) (\( \therefore \) valency of N in compound is 3)
\[ 28 \text{ g N combines with} = 72 \text{ g metal} \]
\[ \therefore 14/3 \text{ N combines with} = \frac{72}{28} \times \frac{14}{3} = 12 \]
\[ \therefore \text{Eq. wt. of metal} = 12 \]
At wt of metal = Eq. wt \times valency = 12 \times 2 = 24 \text{ [Valency of metal = 2]}

9. Following reactions take place-
\[ 3\text{MnSO}_4 + 4\text{H}_2\text{O} \rightarrow \text{Mn}_3\text{O}_4 + 4\text{H}_2\text{O} \uparrow + 3\text{SO}_2 \uparrow + \text{O}_2 \uparrow \text{ (residue)} \]
\[ \text{Mn}_3\text{O}_4 + 2\text{FeSO}_4 + 4\text{H}_2\text{SO}_4 \rightarrow \text{Fe}_2\text{(SO}_4)_3 + 3\text{MnSO}_4 + 4\text{H}_2\text{O} \]
Milliequivalents of Fe\(_2\)SO\(_4\) in 30 ml of 0.1N Fe\(_2\)SO\(_4\) = \( 30 \times 0.1 = 3 \text{ m. eq} \)

According to problem step (iv)
25 ml of KMnO\(_4\) reacts with = 3 m eq of FeSO\(_4\)
Thus in step (iii) of the problem,

\[
50 \text{ ml of K}_2\text{MnO}_4 \text{ reacts with } \frac{3}{25} \times 50 \text{ m.eq. of FeSO}_4
\]

\[
= 6 \text{ m.eq of FeSO}_4
\]

Milli eq. of 100 ml of 0.1N FeSO\(_4\) = 100 \times 0.1 = 10 m eq.

FeSO\(_4\) which reacted with Mn\(_2\)O\(_4\) = (10–6) = 4 m eq.

Milli eq of FeSO\(_4\) = Milli eq. of Mn\(_2\)O\(_4\)

\[
(\therefore \text{ Milli eq of oxidising agent and reducing agent are equal})
\]

\[
\therefore \text{ Mn}_2\text{O}_4 = 3\text{MnSO}_4 \cdot 4\text{H}_2\text{O}
\]

\[
\therefore 1 \text{ Meq of Mn}_2\text{O}_4 = 3 \text{ Meq of MnSO}_4 \cdot 4\text{H}_2\text{O}
\]

\[
\therefore 4 \text{ Meq of Mn}_2\text{O}_4 = 12 \text{ Meq of MnSO}_4 \cdot 4\text{H}_2\text{O}
\]

Eq. wt of MnSO\(_4\) \cdot 4H\(_2\)O = \frac{\text{Mol wt}}{2} = \frac{223}{2} = 111.5

Wt of MnSO\(_4\) \cdot 4H\(_2\)O in sample = 12 \times 111.5 = 1338 mg = 1.338g.

<table>
<thead>
<tr>
<th>Element</th>
<th>wt of element</th>
<th>Relative no of atoms</th>
<th>Ratio of atoms</th>
<th>Whole no of atoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>10.5</td>
<td>10.5/12</td>
<td>0.875/0.875</td>
<td>1×7 = 7</td>
</tr>
<tr>
<td>H</td>
<td>1.0</td>
<td>1.0/1</td>
<td>1.0/0.875</td>
<td>1/0.875 = 1.14</td>
</tr>
</tbody>
</table>

\[
= 11.4 \times 7 = 82
\]

\[
\therefore \text{ Empirical formula } = C_8H_8
\]

\[
\text{Empirical formula wt } = 92.10
\]

\[
\text{Molecular formula } = n \times \text{ empirical formula} = 1(C_8H_8) = C_8H_8
\]

11. Given \(P = 1 \text{ atm} \), \(V = 1 \text{ L} \), \(T = 127^\circ C = 127 + 273 = 400 \text{ K} \)

\[
P V = nRT \quad \text{(Ideal gas equation)}
\]

or \(n = \frac{PV}{RT} = \frac{1 \times 1}{0.082 \times 400} = 0.0304\)

\[
\text{Mol. wt of Mass} = \frac{2.8}{0.0304} = 92.10
\]

12. (i) No. of C atoms in 14g of \(^{14}\text{C} = 6.02 \times 10^{23}\) \(\therefore\) No. of C atom in 7 mg (7/1000g) of \(^{14}\text{C}\)

\[
= \frac{6.02 \times 10^{23}}{14 \times 1000} = 3.01 \times 10^{20}
\]

No. of neutrons in 1 carbon atom = 7

\[
\therefore \text{ Total no. of neutrons in 7 mg of } ^{14}\text{C} = 3.01 \times 10^{20} \times 7 = 21.07 \times 10^{20}
\]

Wt of 1 neutron = wt of 1 hydrogen atom

\[
= \frac{1}{6.02 \times 10^{23}} \text{ g}
\]

\[
= \frac{3.0 \times 10^{20}}{6.02 \times 10^{23}} = 3.5 \times 10^{-3} \text{g}
\]

13. Weight of AgCl formed = 2.567 g

Amount of AgCl formed due to MCl = 1.341 g

\(\therefore\) NaCl does not decompose on heating to 300°C

\[
\text{Weight of AgCl formed due to NaCl} = 2.567 - 1.341 = 1.226 g
\]

\[
\text{NaCl} = \text{AgCl} = \text{MCl}
\]

\[
58.5 \quad 143.5
\]

\[
\text{NaCl} + \text{AgNO}_3 \rightarrow \text{AgCl} + \text{NaNO}_3
\]

\[
\text{MCl} + \text{AgNO}_3 \rightarrow \text{AgCl} + \text{MNO}_3
\]
14. The complete oxidation under acidic conditions can be represented as follows:

\[ 5\text{H}_2\text{O}_2 + 2\text{MnO}_4^- + 6\text{H}^+ \rightarrow 5\text{O}_2 + 2\text{Mn}^{2+} + 8\text{H}_2\text{O} \]

Since 34 g of \( \text{H}_2\text{O}_2 \) = 2000 ml of 1N \( \text{H}_2\text{O}_2 \)

\[ \text{Eq. wt or } \text{H}_2\text{O}_2 = \frac{34}{2} \]

\[ \text{or } \frac{X}{100} \text{ g of } \text{H}_2\text{O}_2 = \frac{2000 \times X}{100 \times 34} \text{ ml of 1N } \text{KMnO}_4 \]

Therefore the unknown normality = \[ \frac{2000 \times X}{34 \times 100 \times X} = \frac{10}{17} \text{ or } 0.588 \text{ N} \]

15. Balance the reactions by ion electron method.

(i) \[ \text{Cu}_2\text{O} + 2\text{H}^+ \rightarrow 2\text{Cu}^{2+} + \text{H}_2\text{O} + 2e^- \times 3 \]

(ii) \[ \text{NO}_3^- + 4\text{H}^+ + 3e^- \rightarrow \text{NO} + 2\text{H}_2\text{O} \times 2 \]

(iii) \[ \text{K}_4(\text{Fe(CN})_6\text{)} + 6\text{H}_2\text{SO}_4 + 6\text{H}_2\text{O} \rightarrow 2\text{K}_2\text{SO}_4 + \text{FeSO}_4 + 3(\text{NH}_4)_2\text{SO}_4 + 6\text{CO} + 4\text{I}^- + 8\text{OH}^- \rightarrow \text{CH}_3 + \text{HCO}_3^- + 5\text{I}^- + 6\text{H}_2\text{O} \]

16. Given 2\( \text{NH}_2\text{OH} + 4\text{Fe}^{3+} \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O} + 4\text{Fe}^{2+} + 4\text{H}^+ \]

and \( \text{MnO}_4^- + 5\text{Fe}^{2+} + 8\text{H}^+ \rightarrow \text{Mn}^{2+} + 5\text{Fe}^{3+} + 4\text{H}_2\text{O} \)

\[ \therefore 10\text{NH}_2\text{OH} + 4\text{MnO}_4^- + 12\text{H}^+ \rightarrow 5\text{N}_2\text{O} + 2\text{H}_2\text{O} + 4\text{Mn}^{2+} \]

[On multiplying (i) by 5 and (ii) by 4 and then adding the resulting equations]

Molecular weight of \( \text{NH}_2\text{OH} = 33 \)

Thus 4000 ml of 1M \( \text{MnO}_4^- \) would react with \( \text{NH}_2\text{OH} = 330 \text{g} \)

\[ \therefore 12 \text{ ml of } 0.02 \text{ M } \text{KMnO}_4 \text{ would react with } \text{NH}_2\text{OH} = \frac{330 \times 12 \times 0.02}{400} \text{ g} \]

17. TIPS/Formulae:

(i) Mole fraction = \[ \frac{\text{Moles of substance}}{\text{Total moles}} \]

(ii) 1 mole of \( \text{Na}_2\text{S}_2\text{O}_3 \) gives 2 moles of \( \text{Na}^+ \) and 1 mole of \( \text{S}_2\text{O}_3^{2-} \)

Molecular wt. of sodium thiosulphate solution (\( \text{Na}_2\text{S}_2\text{O}_3 \)) = \[ 23 \times 2 + 32 \times 2 + 16 \times 3 = 158 \]

\[ \text{(i) The percentage by weight of } \text{Na}_2\text{S}_2\text{O}_3 \]

\[ = \frac{\text{wt of } \text{Na}_2\text{S}_2\text{O}_3}{\text{wt of solution}} \times 100 = \frac{3 \times 158 \times 100}{1000 \times 1.25} = 37.92 \text{ %} \]

\[ \text{[Wt. of } \text{Na}_2\text{S}_2\text{O}_3 = \text{Molarity} \times \text{Mol wt]} \]

(ii) Mass of 1 litre solution = 1.25 g = 1250 g

\[ \text{Density = 1.25 g/l} \]

Mole fraction of \( \text{Na}_2\text{S}_2\text{O}_3 \)

\[ = \frac{\text{Number of moles of } \text{Na}_2\text{S}_2\text{O}_3}{\text{Total number of moles}} \]

Moles of water = \[ \frac{1250 - 158 \times 3}{18} = 43.1 \]

Mole fraction of \( \text{Na}_2\text{S}_2\text{O}_3 \) = \[ \frac{3}{3 + 43.1} = 0.065 \]

(iii) 1 mole of sodium thiosulphate (\( \text{Na}_2\text{S}_2\text{O}_3 \)) yields 2 moles of \( \text{Na}^+ \) and 1 mole of \( \text{S}_2\text{O}_3^{2-} \).

Molality of \( \text{Na}_2\text{S}_2\text{O}_3 \) = \[ \frac{3 \times 1000}{776} = 3.87 \]

Molality of \( \text{Na}^+ = 3.87 \times 2 = 7.74 \text{ m} \)

Molality of \( \text{S}_2\text{O}_3^{2-} = 3.87 \text{ m} \)

18. Weight of \( \text{MCO}_3 \) and \( \text{BaO} = 4.08 \text{ g} \) (given)

Weight of residue = 3.64 g (given)

\[ \therefore \text{Weight of } \text{CO}_2 \text{ evolved on heating} = (4.08 - 3.64) \text{ g} \]

\[ = 0.44 \text{ g} \]

\[ \text{Number of moles of } \text{MCO}_3 = \frac{0.44}{44} = 0.01 \text{ mole} \]

\[ \text{Volume of 1N HCl in which residue is dissolved} = 100 \text{ ml} \]

\[ \text{Volume of 1N HCl used for dissolution} = (100 - 2.5 \times 16) \text{ ml} \]

\[ = 60 \text{ ml} \]

\[ = \frac{60}{1000} = 0.06 \text{ equivalents} \]
The chemical equation for dissolution can be written as

\[
\text{BaO} + \text{MO} + 4\text{HCl} \rightarrow \text{BaCl}_2 + \text{MCl}_2 + 2\text{H}_2\text{O} \quad \text{Residue}
\]

[Number of moles of BaO and MO = 1 + 1 = 2]

Number of moles of BaO + Number of moles of MO = \( \frac{0.06}{2} = 0.03 \) moles

Number of moles of BaO = (0.03 – 0.01) = 0.02 moles

Molecular weight of BaO = 138 + 16 = 154

\( \therefore \) Weight of BaO = (0.02 \times 154) g = 3.08 g

Weight of MCO₃ = (4.08 – 3.08) = 1.0 g

Since weight of 0.01 mole of MCO₃ = 1.0 g

\( \therefore \) Mol. wt. of MCO₃ = \( \frac{1}{0.01} = 100 \)

Hence atomic weight of unknown M = (100 – 60) = \( \text{40} \)

The atomic weight of metal is \( \text{40} \) so the metal M is Ca.

19. **TIPS/Formulæ:**

Balance the atoms as well as charges by ion electron/oxidation number method.

While balancing the equations, both the charges and atoms must balance.

(i) \( 4\text{Zn} + \text{NO}_3^- + 10\text{H}^+ \rightarrow 4\text{Zn}^{2+} + \text{NH}_4^+ + 3\text{H}_2\text{O} \)

(ii) \( \text{Cr}_2\text{O}_7^{2-} + 3\text{C}_2\text{H}_4\text{O}_2 + 8\text{H}^+ \rightarrow 3\text{C}_2\text{H}_2\text{O}_4 + 2\text{Cr}^{3+} + 4\text{H}_2\text{O} \)

(iii) \( 2\text{HNO}_3 + 6\text{HCl} \rightarrow 2\text{NO} + 3\text{Cl}_2 + 4\text{H}_2\text{O} \)

(iv) \( 2\text{Ce}^{3+} + \text{S}_2\text{O}_8^{2-} \rightarrow 2\text{SO}_4^{2-} + 2\text{Ce}^{4+} \)

(v) \( \text{Cl}_2 + 2\text{OH}^- \rightarrow \text{Cl}^- + \text{ClO}^- + \text{H}_2\text{O} \)

(vi) \( 2\text{Mn}^{2+} + 5\text{PbO}_2 + 4\text{H}^+ \rightarrow 2\text{MnO}_4^- + 2\text{H}_2\text{O} + 5\text{Pb}^{2+} \)

(vii) \( 4\text{S} + 6\text{OH}^- \rightarrow 2\text{S}^{2-} + \text{S}_2\text{O}_3^{2-} + 3\text{H}_2\text{O} \)

(viii) \( \text{ClO}_4^- + 6\text{I}^- + 6\text{H}_2\text{SO}_4 \rightarrow \text{Cl}^- + 6\text{HSO}_4^- + 3\text{I}_2 + 3\text{H}_2\text{O} \)

(ix) \( 6\text{Ag}^{2+} + \text{AsH}_3 + 3\text{H}_2\text{O} \rightarrow 6\text{Ag} + \text{H}_3\text{AsO}_3 + 6\text{H}^+ \)

\( \therefore \quad \text{N} \text{ of Na}_2\text{CO}_3 = \frac{\text{Meq. of Na}_2\text{CO}_3}{\text{Volume of solution (ml)}} \)

\( \begin{align*}
\text{or, } N_{\text{mixture}} &= \frac{64 + 34V}{2000} \\
\therefore \text{Eq. of wt. of Na}_2\text{CO}_3 \times 10\text{H}_2\text{O} &= \frac{\text{Mol. wt.}}{2} \\
&= \frac{106 + 180}{2} = 143
\end{align*} \)

20. **TIPS/Formulæ:**

Equivalents of \( A \) oxidised = Equivalents of \( A \) reduced.

Since in acidic medium, \( A^{n+} \) is oxidised to \( A\text{O}_3^- \), the change in oxidation state from

\( (+5) \rightarrow (+n) = 5 - n \quad [\therefore \text{O.S. of } A \text{ in } A\text{O}_3^- = +5] \)

\( \therefore \) Total number of electrons that have been given out during oxidation of \( 2.68 \times 10^{-3} \) moles of \( A^{n+} \)

\( = 2.68 \times 10^{-3} \times (5 - n) \)

Thus the number of electrons added to reduce \( 1.61 \times 10^{-3} \)

moles of \( \text{MnO}_4^- \) to \( \text{Mn}^{2+}, \text{i.e.} \)

\( (+7) \rightarrow (+2) = 1.61 \times 10^{-3} \times 5 \)

[Number of electrons involved = + 7 – (+2) = 5]
\[
\text{Eq. wt. of } \text{SO}_4^{2-} = \frac{32 + 64}{2} = 48
\]
\[
= 6.3648 \text{ g of } \text{SO}_4^{2-} \text{ are in } 3.9 \text{ ml of } 17 \text{M H}_2\text{SO}_4
\]

22. HI < I₂ < ICl < HIO₄. O.N. of I in I₂ = 0, HI = -1, ICl = +1, HIO₄ = +7.

23. (i) From the given half-cell reaction,

\[
\text{Eq. wt. of NaBrO}_3 = \frac{\text{Mol. wt.}}{6} = \frac{151}{6} = 25.17
\]
Now we know that
\[
\text{M eq. = Normality \times Vol. in ml} = 85.5 \times 0.672 = 57.456
\]
Also \[\text{M eq.} = \frac{W_{\text{NaBrO}_3}}{\text{Eq. wt.}_{\text{NaBrO}_3}} \times 1000\]
\[
= \frac{W_{\text{NaBrO}_3}}{25.17} \times 1000 = 57.456 \text{ g}
\]
\[
\therefore W_{\text{NaBrO}_3} = 1.446 \text{ g}
\]
Molarity of NaBrO₃ = \[
\frac{\text{Normality}}{\text{Valence factor}} = \frac{0.672}{6} = 0.112 \text{ M}
\]

(ii) From the given half-cell reaction,

\[
\text{Eq. wt of NaBrO}_3 = \frac{\text{Mol. wt.}}{5} = \frac{151}{5} = 30.2
\]
[Numer of electron involved per BrO₃⁻ = \frac{10}{2} = 5]
Thus, the amount of NaBrO₃ required for preparing 1000 ml of 1 N NaBrO₃ = 30.2 g.
\[
\therefore \text{The amount of NaBrO}_3 \text{ required for preparing } 85.5 \text{ ml of } 0.672 \text{N NaBrO}_3.
\]
\[
= \frac{30.2 \times 0.672 \times 85.5}{1000} = 1.7532 \text{ g}
\]
Hence, Molarity = \[
\frac{0.672}{5} = 0.1344 \text{ M}
\]

24. (i) Weight of sugar syrup = 214.2 g
Weight of sugar in the syrup = 34.2 g
\[
\therefore \text{Weight of water in the syrup = 214.2 - 34.2 = 180.0 g}
\]
Mol. wt. of sugar, C₁₂H₂₂O₁₁ = 342
\[
\therefore \text{Molal concentration} = \frac{342 \times 1000}{342 \times 180} = 0.56
\]

(ii) Mol. wt. of water, H₂O = 18
\[
\therefore \text{Mole fraction of sugar} = \frac{34.2/342}{180/18 + 34.2/342} = \frac{0.1}{0.1} = 0.0099
\]

25. TIPS/Formulæ:
No. of equivalents of KMnO₄ = No. of equivalents of hydrazine sulphate.

\[\text{N}_2\text{H}_4 \rightarrow \text{N}_2\]
Change in oxidation state for each N₂H₄ = 2 \times 2 = 4
Equivalent weight of N₂H₄SO₄ = \[
\frac{130}{4} = 32.5
\]
Normality of KMnO₄ = 5 \times 450 \quad (\because \text{valence factor} = 5)
Number of equivalents of KMnO₄ = 20 \times \frac{5}{50 \times 1000} = \frac{1}{500}
and if weight of hydrazin sulphate be x gm then equivalents
of hydrazine sulphate = \[
\frac{x}{32.5}
\]
\[
\therefore \frac{1}{32.5} = \frac{x}{32.5} \quad \text{or} \quad x = \frac{32.5}{500} = 0.065 \text{ g}
\]
Hence wt. of N₂H₄SO₄ in 10 ml solution = 0.065 g
\[
\therefore \text{Wt. of N₂H₄SO₄ in 1000 ml solution = 6.5 g}
\]

26. TIPS/Formulæ:
No. of equivalents of KMnO₄ in neutral medium = No. of equivalents of reducing agent.
Assuming that KMnO₄ shows the following changes during its oxidising nature.

Acidic medium \(\text{Mn}^{7+} + n_1 e^- \rightarrow \text{Mn}^{2+} \quad \therefore n_1 = 7 - a\)
Neutral medium \(\text{Mn}^{7+} + n_2 e^- \rightarrow \text{Mn}^{2+} \quad \therefore n_2 = 7 - b\)
Alkaline medium \(\text{Mn}^{7+} + n_3 e^- \rightarrow \text{Mn}^{2+} \quad \therefore n_3 = 7 - c\)
Let \(V\) ml. of reducing agent be used for KMnO₄ in different medium.
\[
\therefore \text{Meq. of reducing agent} = \text{Meq. of KMnO₄ in acid medium}
\]
Meq. of KMnO₄ in neutral medium
\[
= \text{Meq. of KMnO₄ in alkaline medium}
\]
\[
= 1 \times n_1 \times 20 = 1 \times n_2 \times 33.4 = 1 \times n_3 \times 100
\]
\[
= n_1 \times 1.667 \times n_2 = 5 \times n_3
\]
Since \(n_1, n_2\) and \(n_3\) are integers and \(n_1\) is not greater than 7.
\[
\therefore n_1 = 1
\]
Hence \(n_1 = 5\) and \(n_2 = 3\)
\[
\therefore \text{Different oxidation states of Mn in}
\]
Acidic medium \(\text{Mn}^{7+} + 5e^- \rightarrow \text{Mn}^{2+} \quad \therefore a = +2\)
Neutral medium \(\text{Mn}^{7+} + 3e^- \rightarrow \text{Mn}^{2+} \quad \therefore b = +4\)
Alkaline medium \(\text{Mn}^{7+} + e^- \rightarrow \text{Mn}^{2+} \quad \therefore c = +6\)
Further, same volume of reducing agent is treated with \(K_2\text{Cr}_2\text{O}_7\), and therefore
\[
\text{Meq. of reducing agent} = \text{Meq. of K}_2\text{Cr}_2\text{O}_7
\]
\[
1 \times 5 = 5\times 20 = 1 \times 6 \times V \quad [\therefore \text{Cr}^{3+} + 6e^- \rightarrow 2\text{Cr}^{3+}]
\]
\[
V = 16.66 \text{ mL} \quad \therefore 1 \text{M} = 6 \times 1 \text{N}
\]
27. **TIPS/Formulae**:

No. of equivalents of KMnO₄

= No. of equivalents of reducing agents.

- **Case I.** Reaction of NaOH with H₂C₂O₄ and NaHC₂O₄.
  
  (i) \( \text{H}_2\text{C}_2\text{O}_4 + 2\text{NaOH} \rightarrow \text{Na}_2\text{C}_2\text{O}_4 + 2\text{H}_2\text{O} \)
  
  (ii) \( \text{NaHC}_2\text{O}_4 + \text{NaOH} \rightarrow \text{Na}_2\text{C}_2\text{O}_4 + \text{H}_2\text{O} \)

Number of milliequivalents of NaOH = \( N \times V = 3.0 \times 0.1 = 0.3 \)

\( \therefore \) Combined normality of the mixture titrated with NaOH

\[ = \frac{0.3}{10} = 0.03 \]

- **Case II.** Reaction of \( \text{C}_2\text{O}_4^{2-} \) ion and KMnO₄.
  
  (iii) \( 5\text{C}_2\text{O}_4^{2-} + \text{MnO}_4^- + 16\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 10\text{CO}_2 + 8\text{H}_2\text{O} \)

KMnO₄ will react in the same manner with both NaHC₂O₄ and H₂C₂O₄ as it can be seen from the above reaction.

Number of milliequivalents of KMnO₄ = \( 4.0 \times 0.1 = 0.4 \)

\( \therefore \) Combined normality of the mixture titrated with KMnO₄

\[ = \frac{0.4}{10} = 0.04 \]

The difference (0.04 N - 0.03 N = 0.01 N) is due to NaHC₂O₄.

The total normality of NaHC₂O₄ will be 0.01 + 0.01 = 0.02 N.

From equation (ii) in case I.

Eq. wt. of NaHC₂O₄ = 112

Amount of NaHC₂O₄ in one litre of solution formed

\[ = 0.01 \times 112 = 1.12 \text{ g} \]

Amount of H₂C₂O₄

\[ = 2.02 - \text{Wt. of NaHC}_2\text{O}_4 = 2.02 - 1.12 = 0.90 \text{ g} \]

28. **TIPS/Formulae**:

Let the amount of NaNO₃ in the mixture = \( x \) g

\( \therefore \) The amount of Pb(NO₃)₂ in the mixture = \( (5-x) \) g

Heating effect of sodium nitrate and lead nitrate

\[ \frac{2\text{NaNO}_3}{2(23+14+48)=170 \text{ g}} \xrightarrow{\Delta} \frac{2\text{NaNO}_2 + \text{O}_2}{2 \times 16 = 32 \text{ g}} \]

\[ \frac{2\text{Pb(NO}_3)_2}{2(207+28+96)=662 \text{ g}} \xrightarrow{\Delta} \frac{2\text{PbO}_2 + 4\text{NO}_2 + \text{O}_2}{4(14+32)=184 \text{ g}} \times \frac{2 \times 16 = 32 \text{ g}}{216 \text{ g}} \]

Now since, 170 g of NaNO₃ gives 32 g of O₂

\( \therefore \) \( x \) g of NaNO₃ gives \( \frac{32}{170} \times x \) g of O₂

Similarly, 662 g of Pb(NO₃)₂ gives 216 g of gases

\( (\text{NO}_3^- + \text{O}_2) \)

\( (5-x) \) g of Pb(NO₃)₂ gives \( \frac{216}{662} \times (5-x) \) g of gases

\( (\text{NO}_3^- + \text{O}_2) \)

Actual loss, on heating, is 28% of \( 5 \) g of mixture

\[ = \frac{5 \times 28}{100} = 1.4 \text{ g} \]

\[ \therefore \frac{32x}{170} + \frac{216}{662} \times (5-x) = 1.4 \]

29. **TIPS/Formulae**:

Molality = \( \frac{\text{Mass of solute}}{\text{M. wt. of solute}} \times \frac{\text{Mass of solvent in kg}}{1000} \)

Mass of H₂SO₄ in 100 ml of 93% H₂SO₄ solution = 93 g

\( \therefore \) Mass of H₂SO₄ in 1000 ml of the H₂SO₄ solution = 930 g

Mass of 1000 ml H₂SO₄ solution = 1000 \times 1.84 = 1840 g

Mass of water in 1000 ml of solution = 1840 - 930 g = 910 g = 0.910 kg

Moles of H₂SO₄ = \( \frac{930}{98} \times \frac{1}{0.910} = 10.43 \text{ mol} \)

\( \therefore \) Molality of solution = 10.43 m

30. In the given problem, a solution containing Cu²⁺ and C₂O₄²⁻ is titrated first with KMnO₄ and then with Na₂S₂O₃ in the presence of KI. In titration with KMnO₄, it is the C₂O₄²⁻ ions that react with the MnO₄⁻ ions. The concerned balanced equation may be written as given below.

\( 2\text{MnO}_4^- + 5\text{C}_2\text{O}_4^{2-} + 16\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 10\text{CO}_2 + 8\text{H}_2\text{O} \)

Thus according to the above reaction

2 mmol MnO₄⁻ = 5 mmol C₂O₄²⁻

However,

No. of mmol of MnO₄⁻ used in titration = Vol. in ml \times M

\[ = 22.6 \times 0.2 = 0.452 \text{ mmol MnO}_4^- \]

Since 2 mmol MnO₄⁻ = 5 mmol C₂O₄²⁻

0.452 mmol MnO₄⁻ = \( \frac{5}{2} \times 0.452 = 1.130 \text{ mmol C}_2\text{O}_4^{2-} \)

**Titrination with Na₂S₂O₃ in the presence of KI.**

Here Cu²⁺ react and the reactions involved during titration are

\( 2\text{Cu}^{2+} + 2\text{I}^- \rightarrow 2\text{Cu}^{+} + \text{I}_2, 2\text{S}_2\text{O}_3^{2-} + \text{I}_2 \rightarrow 2\text{I}^- + \text{S}_4\text{O}_6^{2-} \)

Thus 2Cu²⁺ + I₂ = 2 S₂O₃²⁻

No. of m mol of S₂O₃²⁻ used in titration

\[ = 0.05 \times 11.3 = 0.565 \text{ mmol S}_2\text{O}_3^{2-} \]
Now since 2 mmol $\text{S}_2\text{O}_3^{2-} = 2 \text{ mmol} \text{ Cu}^{2+}$ [From above equation]

\[
0.565 \text{ mmol} \text{ S}_2\text{O}_3^{2-} = \frac{2}{2} \times 0.565 \text{ mmol} \text{ Cu}^{2+} = 0.565 \text{ mmol} \text{ Cu}^{2+}
\]

\[\therefore \text{ Molar ratio of Cu}^{2+} \text{ to } \text{C}_2\text{O}_4^{2-} = \frac{0.565 \text{ mmol}}{1.130 \text{ mmol}} = 1 : 2\]

**Balanced equations in two cases**

**Case I.**

$\text{Mn}^{2+} + 5\text{e}^- \rightarrow \text{Mn}^{2+}$

$\text{C}_2\text{O}_4^{2-} \rightarrow 2\text{C}^{4+} + 2\text{e}^-$

**Case II.**

$2\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}^{2+}$

$2\text{I}^- \rightarrow \text{I}_2 + 2\text{e}^-$

and

$\text{I}_2 + 2\text{e}^- \rightarrow 2\text{I}^-$

$2\text{S}_2\text{O}_3^{2-} \rightarrow \text{S}_4\text{O}_6^{32-} + 2\text{e}^-$

31. Mass of $\text{Fe}_2\text{O}_3$ in the sample $= \frac{55.2}{100} \times 1 = 0.552$ g

Number of moles of $\text{Fe}_2\text{O}_3 = \frac{0.552}{159.8} = 3.454 \times 10^{-3}$

Number of moles of $\text{Fe}^{3+}$ ions $= 2 \times 3.454 \times 10^{-3} = 6.9 \times 10^{-3}$ mol $= 6.90$ mmol

Since its only 1 electron is exchanged in the conversion of $\text{Fe}^{3+}$ to $\text{Fe}^{2+}$, the molecular mass is the same as equivalent mass.

\[\therefore \text{ Amount of Fe}^{2+} \text{ ion in 100 ml. of sol.} = 6.90 \text{ meq}\]

Volume of oxidant used for 100 ml of Fe$^{2+}$ sol. $= 17 \times 4 = 68$ ml.

Amount of oxidant used $= 68 \times 0.0167$ mmol $= 1.1356$ mmol

Let the number of electrons taken by the oxidant $= n$

\[\therefore \text{ No. of meq. of oxidant used} = 1.1356 \times n\]

Thus $1.1356 \times n = 6.90 \Rightarrow n = \frac{6.90}{1.1356} = 6$

32. 1.5 g of sample require $= 150 \text{ ml. of } \frac{M}{10} \text{ HCl}$

\[\therefore 2 \text{ g of sample require} = \frac{150 \times 2}{1.5} \text{ ml. of } \frac{M}{10} \text{ HCl} = 200 \text{ ml. of } \frac{M}{10} \text{ HCl}\]

On heating, the sample, only NaHCO$_3$ undergoes decomposition as given below.

$2\text{NaHCO}_3 \rightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} + \text{CO}_2 \uparrow$

2 moles 1 mole 1 mole

2 equ.

Neutralisation of the sample with HCl takes place as given below.

$\text{NaHCO}_3 + \text{HCl} \rightarrow \text{NaCl} + \text{H}_2\text{O} + \text{CO}_2$

1 eq. 1 eq.

Hence, 2 g sample $= 200$ ml. of M/10 HCl

$= 200$ ml. of N/10 HCl = 20 meq = 0.020 eq

Number of moles of CO$_2$ formed, i.e.

\[n = \frac{PV}{RT} = \frac{750 \times 123.9}{760 \times 1000 \times 0.082 \times 298} = 0.005\]

Moles of NaHCO$_3$ in the sample (2 g) $= 2 \times 0.005 = 0.01$

Equivalent of NaHCO$_3$ = 0.01

Wt. of NaHCO$_3 = 0.01 \times 84 = 0.84$ g

\[\frac{0.84 \times 100}{2} = 42\%\]

Equivalent of Na$_2$CO$_3$ = 0.02−0.01 = 0.01

Wt. of Na$_2$CO$_3 = 0.01 \times 42.5 = 0.52$ g

\[\therefore \% \text{ of Na}_2\text{CO}_3 = \frac{0.52 \times 100}{2} = 26.5\%\]

\[\therefore \% \text{ of Na}_2\text{SO}_4 \text{ in the mixture} = 100 - (42 + 26.5) = 31.5\%\]

33. Reaction involved titration is

$\text{KIO}_3 + 2\text{KI} + 6\text{HCl} \rightarrow 3\text{Cl}_2 + 3\text{KCl} + 3\text{H}_2\text{O}$

1 mole 2 moles

20 ml. of stock KI solution $= 30 \text{ ml. of } \frac{M}{10}$ KIO$_3$ solution

Molarity of KI solution $= \frac{30 \times 1 \times 2}{20 \times 10} = \frac{3}{10}$

Millimoles in 50 ml. of KI solution $= 50 \times \frac{3}{10} = 15$

Millimoles of KI left unreacted with AgNO$_3$ solution $= 2 \times 50 \times \frac{1}{10} = 10$

\[\therefore \text{ Millimoles of KI reacted with AgNO}_3 = 15 - 10 = 5\]

Millimoles of AgNO$_3$ present in AgNO$_3$ solution = 5

Molecular weight of AgNO$_3$ = 170

\[\therefore \text{ Wt. of AgNO}_3 \text{ in the solution} = 5 \times 10^{-3} \times 170 = 0.850 \text{ g}\]

\[\% \text{ AgNO}_3 \text{ in the sample} = \frac{0.850}{1} \times 100 = 85\%\]

34. Calculation of number of moles in 45 ml of 0.025 M Pb(NO$_3$)$_2$

Moles of Pb(NO$_3$)$_2 = 0.25 \times \frac{45}{1000} = 0.01125$

\[\therefore \text{ Initial moles of Pb}^{2+} = 0.01125\]

Moles of NO$_3^-$ = 0.01125 $\times 2 = 0.02250$

\[\frac{[1 \text{ mole Pb(NO}_3)_2 = 2 \text{ moles of NO}_3^-]}{\text{ Calculation of number of moles in 25 ml of 0.1 M chromic sulphate}}\]
Some Basic Concepts of Chemistry

Moles of chromic sulphate \((\text{Cr}_2\text{(SO}_4)_3\))
\[
= 0.1 \times \frac{25}{1000} = 0.0025 \text{ moles}
\]

Moles of \(\text{SO}_4^{2-}\) = 0.0025 \times 3 = 0.0075 [1 Mole of chromic sulphate \equiv 3 moles of \text{SO}_4^{2-}\]

Moles of \(\text{Pb}^{2+}\) formed = 0.0075 [\text{SO}_4^{2-}\) is totally consumed]

Moles of \(\text{Pb}^{2+}\) left = 0.01125 – 0.0075 = 0.00375

Moles of NO\(_3^-\) left = 0.02250 [NO\(_3^-\) remain unreacted]

Moles of chromium ions = 0.0025 \times 2 = 0.005

Total volume of the solution = 45 + 25 = 70 ml.

\(\therefore\) Molar concentration of the species left

\[(i)\] \(\text{Pb}^{2+} = \frac{0.00375}{70} \times 1000 = 0.05357 \text{ M}\)

\[(ii)\] \(\text{NO}_3^- = \frac{0.0225}{70} \times 1000 = 0.3214 \text{ M}\)

\[(iii)\] \(\text{Cr}^{3+} = \frac{0.005}{70} \times 1000 = 0.0714 \text{ M}\)

35. In pure iron oxide (FeO), iron and oxygen are present in the ratio 1 : 1.

However, here number of Fe\(^{2+}\) present = 0.93
or No. of Fe\(^{2+}\) ions missing = 0.07

Since each Fe\(^{2+}\) ion has 2 positive charge, the total number of charge due to missing (0.07) Fe\(^{2+}\) ions = 0.07 \times 2 = 0.14

To maintain electrical neutrality, 0.14 positive charge is compensated by the presence of Fe\(^{3+}\) ions. Now since, replacement of one Fe\(^{2+}\) ion by one Fe\(^{3+}\) ion increases one positive charge, 0.14 positive charge must be compensated by the presence of 0.14 Fe\(^{3+}\) ions.

In short, 0.93 Fe\(^{2+}\) ions have 0.14 Fe\(^{3+}\) ions

100 Fe\(^{2+}\) ions have = \(\frac{0.14}{0.93} \times 100 = 15.05\%\)

36. The formula of Glauber’s salt is \(\text{Na}_2\text{SO}_4\cdot10\text{H}_2\text{O}\)

Molecular mass of \(\text{Na}_2\text{SO}_4\cdot10\text{H}_2\text{O}\)
\[
= [2 	imes 23 + 32.1 + 4 \times 16] + 10 \times (1.01 \times 2 + 16) = 322.3 \text{ g mol}^{-1}
\]

Weight of the Glauber’s salt taken = 80.575 gm

Out of 80.575 g of salt, weight of anhydrous \(\text{Na}_2\text{SO}_4\)
\[
= \frac{142.1}{322.3} \times 80.575 = 35.525 \text{ g}
\]

Number of moles of \(\text{Na}_2\text{SO}_4\) per dm\(^3\) of the solution
\[
= \frac{35.525}{142.1} = 0.25
\]

Molarity of the solution = \(0.25 \text{ M}\)

Density of solution = 1077.2 kg m\(^{-3}\)
\[
= \frac{1077.2 \times 10^3}{10^6} \text{ gm cm}^{-3} = 1.0772 \text{ g cm}^{-3}
\]

Total weight of sol = \(V \times d = 1 \text{ dm}^3 \times d\)
\[
= 1000 \text{ cm}^3 \times 1.0772 \text{ g cm}^{-3} = 1077.2 \text{ g}
\]

Weight of water = 1077.2 - 35.525 = 1041.67 \text{ g}

Molality of sol. = \(\frac{0.25}{1041.67 \text{ g}} \times 1000 \text{ g} = 0.2399 = 0.24 \text{ m}\)

Number of moles of water in the solution = \(\frac{1041.67}{18} = 57.87\)

Mole fraction of \(\text{Na}_2\text{SO}_4\)
\[
= \frac{\text{No. of moles of } \text{Na}_2\text{SO}_4}{\text{Total number of moles}} = \frac{0.25}{0.25 + 57.87}
\]
\[
= 0.0043 = 4.3 \times 10^{-3}
\]

37. TIPS/Formulae:

Find the milliequivalents and equate them as per data given in question.

For \(\text{Fe}_2\text{O}_3 \rightarrow 3\text{FeO}\)
\[2e + \text{Fe}_3^{(8/3)+} \rightarrow 3\text{Fe}^{2+}\]

Thus, valence factor for \(\text{Fe}_2\text{O}_3\) is 2 and for \(\text{FeO}\) is 2/3.

For, \(\text{Fe}_2\text{O}_3 \rightarrow 2\text{FeO}; 2e + \text{Fe}_3^{3+} \rightarrow 2\text{Fe}^{2+} \ldots (1)\)

Thus valence factor for \(\text{Fe}_2\text{O}_3\) is 2 and for \(\text{FeO}\) is 1.

Let Meq. of \(\text{Fe}_2\text{O}_3\) and \(\text{FeO}\) be \(a\) and \(b\) respectively.

\(\therefore\) Meq. of \(\text{Fe}_2\text{O}_3\) + Meq. of \(\text{Fe}_2\text{O}_3\) = Meq. of \(\text{I}_2\) liberated

\[a + b = \frac{11 \times 0.5 \times 100}{20} = 27.5\]

Now, the \(\text{Fe}^{2+}\) ions are again oxidised to \(\text{Fe}^{3+}\) by \(\text{KMnO}_4\).

Note that in the change
\[\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + e^{-}\]; valence factor of \(\text{Fe}^{2+}\) is 1.

Thus,

Meq. of \(\text{Fe}^{2+}\) (from \(\text{Fe}_2\text{O}_3\)) + Meq. of \(\text{Fe}^{3+}\) (from \(\text{Fe}_2\text{O}_3\)) = Meq. of \(\text{KMnO}_4\) used \ldots (2)

If valence factor for \(\text{Fe}^{2+}\) is 2/3 from Eq. (1),
then Meq. of \(\text{Fe}^{2+}\) (from \(\text{Fe}_2\text{O}_3\)) = \(a\)
If valence factor for \(\text{Fe}^{2+}\) is 1,
then Meq. of \(\text{Fe}^{2+}\) (from \(\text{Fe}_2\text{O}_3\)) = \(3a/2\) \ldots (3)

Similarly, from Eq. (2), Meq. of \(\text{Fe}^{2+}\) from (\(\text{Fe}_2\text{O}_3\)) = \(b\).

\(\therefore\) \(3a/2 + b = 0.25 \times 5 \times 12.8 \times 100/50 = 32\)

or \(3a + 2b = 64\) \ldots (4)

From Eqs. (3) and (4)
Meq. of \(\text{Fe}_3\text{O}_4 = a = 9\) & Meq. of \(\text{Fe}_2\text{O}_3 = b = 18.5\)

\(\therefore\) \(W_{\text{Fe}_2\text{O}_4} = \frac{9 \times 232}{2 \times 1000} = 1.044 \text{ g}\)

and \(W_{\text{Fe}_2\text{O}_3} = \frac{18.5 \times 160}{2 \times 1000} = 1.48 \text{ g}\)

\(\therefore\) \% of \(\text{Fe}_3\text{O}_4 = \frac{1.044 \times 100}{3} = 34.8\)

and \% of \(\text{Fe}_2\text{O}_3 = \frac{1.48 \times 100}{3} = 49.33\)

38. TIPS/Formulae:

Write the reactions taking place, balance them and equate moles of \(\text{I}_2\) and \(\text{Na}_2\text{SO}_4\).
\[ \text{KIO}_3 + 5\text{KI} \rightarrow 3\text{K}_2\text{O} + 3\text{I}_2 \quad \text{i.e.,} \quad 2\text{I}^{5+} + 10e^- \rightarrow \text{I}_2^0 \]

\[ 2\text{I}^- \rightarrow \text{I}_2^0 + 2e^- \]

Now liberated \( \text{I}_2 \) reacts with \( \text{Na}_2\text{S}_2\text{O}_3 \)

\[ \text{I}_2^+ + 2e^- \rightarrow 2\text{I}^- \]

\[ 2\text{S}_2\text{O}_3^{2-} \rightarrow \text{S}_4\text{O}_6^{2-} + 2e^- \]

\[ \therefore \text{millimole ratio of } \text{I}_2 : \text{S}_2\text{O}_3 = 1 : 2 \]

Thus, \( m \) mole of \( \text{I}_2 \) liberated

\[ = \frac{m \text{ mole of } \text{Na}_2\text{S}_2\text{O}_3 \text{ used}}{2} \times \frac{1}{2} = \frac{45 \times M}{2} \]

\[ [M \text{ is molarity of thiosulphate}] \]

Also \( m \) mole of \( \text{KIO}_3 = \frac{0.1}{214} \times 1000 \]

Now \( m \) mole ratio of \( \text{KIO}_3 : \text{I}_2 = 1 : 3 \)

Thus, \[ \frac{(0.1/214) \times 1000}{(45M/2)} = \frac{1}{3} \]

\[ \therefore \quad M = \frac{0.1 \times 1000 \times 3 \times 2}{214 \times 45} = 0.062 \]

39. TIPS/Formulæ:

Use molarity equation to find volume of \( \text{H}_2\text{SO}_4 \) solution.

\[ \text{CuCO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{CuSO}_4 + \text{H}_2\text{O} + \text{CO}_2 \uparrow \]

\[ 63.5 \times 12 + 48.98 = 123.5 \text{ g} \]

\[ 98 \times 0.5 \]

\[ = \frac{98 \times 0.5}{123.5} \text{ g} = 0.39676 \text{ g H}_2\text{SO}_4 \]

Weight of required \( \text{H}_2\text{SO}_4 = 0.39676 \text{ g} \)

Weight of solute in grams

\[ = \frac{\text{Mol. wt.} \times \text{Molarity} \times \text{Volume in mL}}{1000} \]

\[ 0.39676 = \frac{98 \times 0.5 \times V}{1000} \quad \text{or} \quad V = \frac{0.39676 \times 1000}{90 \times 0.5} \text{ ml} \]

Volume of \( \text{H}_2\text{SO}_4 \) solution = 8.097 ml

40. TIPS/Formulæ:

(i) Volume of virus = \( \pi r^2 \ell \) (Volume of cylinder)

(ii) Mass of single virus = \( \frac{\text{Volume}}{\text{Sp. volume}} \)

(iii) Molecular mass of virus = \( \frac{\text{Mass of single virus}}{6.02 \times 10^{23}} \)

Volume of virus = \( \pi r^2 \ell \)

\[ = \frac{22}{7} \times \frac{150}{2} \times \frac{150}{2} \times 10^{-16} \times 5000 \times 10^{-8} \]

\[ = 0.884 \times 10^{-16} \text{ cm}^3 \]

Weight of one virus

\[ = \frac{0.884 \times 10^{-16}}{0.75} \text{ g} \]

\[ = 1.178 \times 10^{-16} \text{ g} \]

\[ \therefore \text{Mol. wt. of virus} = 1.178 \times 10^{-16} \times 6.02 \times 10^{23} = 7.09 \times 10^7 \]

41. TIPS/Formulæ:

Write the balanced chemical reaction for change and apply mole concept.

The given reactions are

\[ \text{MnO}_2 \downarrow + \text{Na}_2\text{C}_2\text{O}_4 + 2\text{H}_2\text{SO}_4 \]

\[ \rightarrow \text{MnSO}_4 + \text{CO}_2 + \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O} \]

\[ \therefore \text{Meq. of } \text{MnO}_2 = \text{Meq of } \text{Na}_2\text{C}_2\text{O}_4 = 10 \times 0.2 \times 2 = 4 \]

\[ \therefore \text{mM of } \text{MnO}_2 = \frac{4}{2} = 2 \]

\[ = \frac{[\text{Mn}^{4+} + 2e^- \rightarrow \text{Mn}^{2+}]}{\text{Valence factor of } \text{MnO}_2 = 2} \]

Now \( 2\text{KMnO}_4 + 3\text{MnSO}_4 + 2\text{H}_2\text{O} \)

\[ \rightarrow 5\text{MnO}_2 \downarrow + \text{K}_2\text{SO}_4 + 4\text{H}_2\text{O} \]

Since eq. wt. of \( \text{MnO}_2 \) is derived from \( \text{KMnO}_4 \) and \( \text{MnSO}_4 \) both, it is better to proceed by mole concept

\[ \text{mM of } \text{KMnO}_4 = \text{mM of } \text{MnO}_2 \times (2/5) = 4/5 \]

Also \( 5\text{H}_2\text{O}_2 + 2\text{KMnO}_4 + 3\text{H}_2\text{SO}_4 \)

\[ \rightarrow 2\text{MnSO}_4 + \text{K}_2\text{SO}_4 + 8\text{H}_2\text{O} + \text{SO}_2 \]

\[ \therefore \text{mM of } \text{H}_2\text{O}_2 = \text{mM of } \text{KMnO}_4 \times \frac{5}{2} = \frac{4}{2} \times \frac{5}{2} = 2 \]

\[ \therefore \text{M}_{\text{H}_2\text{O}_2} \times 20 = 2 \quad \text{or} \quad \text{M}_{\text{H}_2\text{O}_2} = 0.1 \]

\[ 2\text{KMnO}_4 + 5\text{H}_2\text{O}_2 + 3\text{H}_2\text{SO}_4 \]

\[ \rightarrow \text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 8\text{H}_2\text{O} + \text{SO}_2 \]

\[ 2\text{KMnO}_4 + 3\text{MnSO}_4 + 2\text{H}_2\text{O} \]

\[ \rightarrow 5\text{MnO}_2 + 2\text{H}_2\text{SO}_4 + \text{K}_2\text{SO}_4 \]

\[ \text{MnO}_2 + \text{Na}_2\text{C}_2\text{O}_4 + 2\text{H}_2\text{SO}_4 \]

\[ \rightarrow \text{MnSO}_4 + 2\text{CO}_2 + \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O} \]

42. 1 litre water = 1 kg i.e. 1000 g water (\( \therefore d = 1000 \text{ kg/m}^3 \))

\[ \frac{1000}{18} = 55.55 \text{ moles of water} \]

So, molarity of water = 55.55M

H. Assertion & Reason Type Questions

1. (b) TIPS/Formulæ:

Write reaction for titration between \( \text{Na}_2\text{CO}_3 \) and \( \text{HCl} \).

Method:

\[ \text{Na}_2\text{CO}_3(\text{aq}) + \text{HCl}(\text{aq}) \rightarrow \text{NaHCO}_3 + \text{NaCl}(\text{aq}) \]

(yellow colour with \( \text{HPh} \) i.e. phenolphthalein)

(No colour with \( \text{HPh} \) i.e. phenolphthalein)

\[ \text{(Half neutralisation)} \]

\[ \text{Na}_2\text{CO}_3(\text{aq}) + 2\text{HCl}(\text{aq}) \rightarrow 2\text{NaCl} + \text{H}_2\text{O} + \text{CO}_2 \]

(Complete neutralisation)

\[ \text{NaHCO}_3 + \text{HCl} \rightarrow \text{NaCl} + \text{H}_2\text{O} + \text{CO}_2 \]

(yellow colour with methyl orange)

(red colour with methyl orange)
From these reaction it is clear that
(i) 2 moles of HCl are required for complete neutralization of Na₂CO₃.
(ii) Titre value using phenolphthalein corresponds only to neutralization of Na₂CO₃ to NaHCO₃, i.e. half of value required by Na₂CO₃ solution.
(iii) Titre value using methyl orange corresponds to complete neutralisation of Na₂CO₃.
⇒ Both S and E are correct but S is not correct explanation of E.

1. **Integer Value Correct Type**

1. The least significant figure in titre values is 3.

   Average value = \( \frac{25.2 + 25.25 + 25}{3} = \frac{75.4}{3} = 25.1 \)

   The number of significant figures in average titre value will also be 3.

2. \( d = \frac{\text{mass}}{V} \Rightarrow 10.5 \text{ g/cc means in 1 cc} \)

   \( \Rightarrow 10.5 \text{ g of Ag is present.} \)

   Number of atoms of Ag in 1 cc \( \Rightarrow \frac{10.5}{108} \times N_A \)

   In 1 cm², number of atoms of Ag = \( \sqrt[3]{\frac{10.5}{108}} N_A \)

**Section-B**

**JEE Main/ AIEEE**

1. (c) Percentage R.N.A Simplest ratio

   | C | 9 | \( \frac{9}{12} = \frac{3}{4} \) | 3 |

   | H | 1 | \( \frac{1}{1} = 1 \) | 4 |

   | N | 35 | \( \frac{35}{14} = \frac{1}{4} \) | 1 |

   Empirical formula = \( \text{C}_3\text{H}_4\text{N} \)

   \( (\text{C}_3\text{H}_4\text{N})_n = 108, (12 \times 3 + 4 \times 1 + 14)_n = 108 \)

   \( (54)_n = 108 \Rightarrow n = \frac{108}{54} = 2 \)

   \( \therefore \) molecular formula = \( \text{C}_6\text{H}_8\text{N}_2 \)

2. (c) Among all the given options molarity is correct because the term molarity involve volume which increases on increasing temperature.

3. (a) \( \text{Fe (no. of moles)} = \frac{558.5}{55.85} = 10 \text{ moles} \)

   \( \text{C (no. of moles) in } 60 \text{ g of C} = \frac{60}{12} = 5 \text{ moles.} \)

4. (a) \( 2\text{BCl}_3 + 3\text{H}_2 \rightarrow 2\text{B} + 6\text{HCl} \)

   or \( \text{BCl}_3 + \frac{3}{2}\text{H}_2 \rightarrow \text{B} + 3\text{HCl} \)

   Now, since 10.8 gm boron requires hydrogen

   \( \Rightarrow \frac{3}{2} \times 22.4 \text{L at N.T.P} \)

   hence 21.6 gm boron requires hydrogen

   \( \frac{3}{2} \times 22.4 \times 21.6 = 67.2 \text{L at N.T.P.} \)

5. (d) \( 25 \times N = 0.1 \times 35 ; N = 0.14 \)

   \( \text{Ba(OH)}_2 \) is diacid base

   hence \( N = \frac{M \times 2}{2} \Rightarrow M = \frac{N}{2} = 0.07 \text{ M} \)

6. (b) Moles of urea present in 100 ml of sol. = \( \frac{6.02 \times 10^{20}}{6.02 \times 10^{23}} \)

   \( \therefore M = \frac{6.02 \times 10^{20} \times 1000}{6.02 \times 10^{23} \times 100} = 0.01 \text{M} \)

   \( [ \therefore M = \text{Moles of solute present in 1L of solution} \] \)
7. (a) \( N_1 V_1 = N_2 V_2 \)  
(Note : \( H_3PO_3 \) is dibasic ; : \( M = 2N \)  
\( 20 \times 0.2 = 0.1 \times V \)  
(Thus \( 0.1 \times M = 0.2 \times N \)  
\( \therefore V = 40 \text{ml} \)  
8. (a) \( H_2SO_4 \) is dibasic.  
\( 0.1 \times M \times H_2SO_4 = 0.2N \times H_2SO_4 \)  
\[ \therefore M = 2 \times N \]  
\( M_{eq} \) of \( H_2SO_4 \) taken \( = 100 \times 0.2 = 20 \)  
\( M_{eq} \) of \( H_2SO_4 \) neutralised by \( NaOH \) \( = 20 \times 0.5 = 10 \)  
\( M_{eq} \) of \( H_2SO_4 \) neutralised by \( NH_3 \) \( = 20 - 10 = 10 \)  
\% of \( N_2 = \frac{1.4 \times M_{eq} \text{ of acid neutralised by } NH_3}{\text{wt. of organic compound}} \times 100 \)  
\( = \frac{1.4 \times 10}{0.3} = 46.6 \)  
\% of nitrogen in urea \( = \frac{14 \times 2 \times 100}{60} = 46.6 \)  
[Mol. wt of urea = 60]  
Similarly \% of Nitrogen in Benzamide \( = \frac{14 \times 100}{121} = 11.5\% \)  
[\( C_6H_5CONH_2 = 121 \)]  
Acetamide \( = \frac{14 \times 100}{59} = 23.4\% \)  
[\( CH_3CONH_2 = 59 \)]  
Thiourea \( = \frac{14 \times 2 \times 100}{76} = 36.8\% \)  
[\( NH_2CSNH_2 = 76 \)]  
Hence the compound must be urea.  
9. (b) **TIPS/Formulae:**  
From the molarity equation.  
\( M_1 V_1 + M_2 V_2 = MV \)  
Let \( M \) be the molarity of final mixture,  
\( M = \frac{M_1 V_1 + M_2 V_2}{V} \) \text{ where } V = V_1 + V_2 \)  
\( M = \frac{480 \times 1.5 + 520 \times 1.2}{480 + 520} = 1.344 \text{M} \)  
10. (d) Relative atomic mass  
\( = \frac{\text{Mass of one atom of the element}}{1/12 \text{th part of the mass of one atom of Carbon} - 12} \)  
\( \text{or} \)  
\( \text{Mass of one atom of the element} \times 12 \) \text{mass of one atom of the C} - 12  
Now if we use \( 1/6 \) in place of \( 1/12 \) the formula becomes  
Relative atomic mass \( = \frac{\text{Mass of one atom of element}}{\text{Mass of one atom of carbon}} \times 6 \)  
\( \therefore \) Relative atomic mass decrease twice  
11. (d) 1 Mole of \( Mg_3(PO_4) \) contains 8 mole of oxygen atoms  
\( \therefore 8 \text{ mole of oxygen atoms} = 1 \text{ mole of } Mg_3(PO_4) \) mole of \( Mg_3(PO_4) \)  
12. (a) **TIPS/Formulae:**  
\( d = \frac{M}{M_1 + M_2} \)  
\( \therefore 1.02 = 2.05 \left( \frac{1}{M} + \frac{60}{1000} \right) \)  
\( \therefore 1.02 = 2.05 \left( \frac{1}{M} + \frac{60}{1000} \right) \)  
\( \therefore \text{On solving we get, } m = 2.288 \text{ mol/kg} \)  
13. (d) Since molarity of solution is 3.60 M. It means 3.6 moles of \( H_2SO_4 \) is present in its 1 litre solution.  
Mass of 3.6 moles of \( H_2SO_4 \) \( = \text{Moles} \times \text{Molecular mass} = 3.6 \times 98 \times g = 352.8 \) g  
\( \therefore 1000 \text{ ml solution has 352.8 g of } H_2SO_4 \)  
Given that 29 g of \( H_2SO_4 \) is present in \( 100 \) g of solution  
\( \therefore \) 352.8 g of \( H_2SO_4 \) is present in  
\( \frac{100}{29} \times 352.8 \text{ g of solution} = 1216 \text{ g of solution} \)  
\( \text{Density} = \frac{\text{Mass}}{\text{Volume}} \)  
\( = \frac{1216}{1000} = 1.216 \text{ g/ml} = 1.22 \text{ g/ml} \)  
14. (a) \( 2Al(s) + 6HCl(aq) \rightarrow 2Al^{3+}(aq) + 6Cl^-(aq) + 3H_2(g) \)  
\( \therefore 6 \text{ moles of HCl produces} = 3 \text{ moles of } H_2 \)  
\( = \frac{3 \times 22.4}{6} \text{ L of } H_2 \) at S.T.P  
\( \therefore 1 \text{ mole of } HCl \text{ produces} = \frac{3 \times 22.4}{6} \text{ L of } H_2 \) at S.T.P  
\( = 11.2 \text{ L of } H_2 \) at S.T.P  
15. (e) On balancing the given equations we get  
\( 2MnO_4^- + 5C_2O_4^- + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O \)  
\( \text{So, } x = 2, y = 5 \) & \( z = 16 \)  
16. (d) \( \therefore 18 \text{ g, } H_2O \text{ contains} = 2 \text{ gm } H \)  
\( \therefore 0.72 \text{ gm } H_2O \text{ contains} = \frac{2}{18} \times 0.72 \text{ gm } = 0.08 \text{ gm } H \)  
\( \therefore 44 \text{ gm } CO_2 \text{ contains} = 12 \text{ gm } C \)  
\( \therefore 3.08 \text{ gm } CO_2 \text{ contains} = \frac{12}{44} \times 3.08 = 0.84 \text{ gm } C \)  
\( \therefore C: H = \frac{0.84}{12} : \frac{0.08}{1} = 0.07 : 0.08 \)  
\( \therefore \) Empirical formula = \( C_7H_8 \)  
17. (b) For a one mole of the oxide  
Moles of \( M = 0.98 \), Moles of \( O^2- = 1 \)  
Let moles of \( M^{3+} = x \)  
Moles of \( M^{2+} = 0.98 - x \)  
on balancing charge  
\( (0.98 - x) \times 2 + 3x - 2 = 0 \)  
\( \Rightarrow x = 0.04 \)  
\% of \( M^{3+} = \frac{0.04}{0.98} \times 100 = 4.08\% \)
Section-A : JEE Advanced/ IIT-JEE

A  1. \(1.66 \times 10^{-27}\) Kg  2. neutrons  3. antiparallel or opposite  4. isobars  5. Heisenberg, de-Broglie
6. Photons  7. orbitals  8. orientation in space  9. \(3d^2, 4s^1\)


C  1. (d)  2. (c)  3. (d)  4. (a)  5. (a)  6. (d)  7. (a)
8. (d)  9. (b)  10. (b)  11. (b)  12. (b)  13. (c)  14. (d)
15. (a)  16. (c)  17. (b)  18. (c)  19. (a)  20. (c)  21. (c)
22. (d)  23. (c)  24. (b)  25. (a)  26. (a)  27. (a)  28. (b)
29. (a)  30. (d)  31. (d)  32. (c)  33. (d)  34. (a)  35. (b)
36. (c)  37. (d)

D  1. (b, d)  2. (a, c)  3. (a, c)  4. (b, d)  5. (a)  6. (a, b, c)  7. (a, c, d)
8. (a, d)

E  1. 80\%  2. 6.603 Å  3. 1220 Å  4. \(5.42 \times 10^{-12}\) ergs, \(3.67 \times 10^{-5}\) cm
6. 10  7. 2055 Å  8. 10.22 eV, 2, He\(^+\)  9. \(n = 2\) to \(n = 1\)
10. 3

11. \(2.165 \times 10^{-20}\)  12. \(27419.25\) cm\(^{-1}\)  13. \(-\frac{e^2}{4\pi\varepsilon_0 a_0}\), \(-\frac{e^2}{8\pi\varepsilon_0 a_0}\)
14. 98.17 KJ

15. 22.8 nm  16. \(2a_0\)  17. 6.627 \times 10^{-35} m
18. 3.34 \times 10^{-10} m, \(\sqrt{2}\). \(\frac{h}{2\pi}\)

F  1. (A)-r, (B)-q, (C)-p, (D)-s
2. (A)-q, r; (B)-p, q, r, s; (C)-p, q, r; (D)-p, q
g

G  1. (b)  2. (c)  3. (b)

H  1. (c)  2. (b)  3. (a)

I  1. 4  2. 9  3. 5  4. 6  5. 3

Section-B : JEE Main/ AIEEE

1. (a)  2. (c)  3. (c)  4. (a)  5. (a)  6. (a)  7. (d)
8. (a)  9. (b)  10. (c)  11. (c)  12. (a)  13. (b)  14. (b)
15. (a)  16. (c)  17. (c)  18. (b)  19. (d)  20. (a)  21. (b)
22. (d)  23. (b)  24. (c)  25. (b)  26. (a)  27. (a)  28. (a)  29. (b)

Section-A

JEE Advanced/ IIT-JEE

A. Fill in the Blanks

1. \(1.66 \times 10^{-27}\) kg

\[\text{Mass of hydrogen atom}\]

\[
= \frac{\text{Atomic mass of hydrogen}}{\text{Avogadro number}} = \frac{1.008}{6.02 \times 10^{23}}
\]

\[= 0.166 \times 10^{-23} \text{ g} = 1.66 \times 10^{-27} \text{ kg}\]

2. neutrons;
3. antiparallel; or opposite
4. iso-bars;

5. Heisenberg, de-Broglie;
6. photons
7. orbitals
8. orientation in space
9. \(4s^1, 3d^2\);

\[
\text{The electronic configuration of Cr is: } 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1, 3d^5.
\]

\[\therefore \text{ Outermost electronic configuration is } 3d^5, 4s^1.\]
B. True/False

1. False: The outer electronic configuration of the ground state chromium atom is 3d\(^5\) 4s\(^1\), as half filled orbitals are more stable than nearly half filled orbitals.

2. False: Gamma rays are electromagnetic radiations of wavelengths 10\(^{-9}\) cm to 10\(^{-10}\) cm.

3. True: Although energies of the s and p orbitals for the same principal quantum number are very close to each other; the energy of the corresponding d orbitals is much higher. For example, the energy of 3d orbitals is much more than that of 3s and 3p; orbitals but less than 4s orbitals in case of H atom.

4. False: The orbital 3d\(_{x^2-y^2}\) lie along X and Y axis where electron density is maximum.

5. True: β-particles are deflected more than α-particles because they have very-very large e/m value as compared to α-particles due to the fact that electrons are much lighter than He\(^{2+}\) species.

C. MCQs with One Correct Answer

1. (d) No. of neutrons = Mass number – Atomic number = 70 – 30 = 40.

2. (c) Rutherford's scattering experiment led to the discovery of nucleus.

3. (d) One p-orbital can accommodate up to two electron with opposite spin while p-subshell can accommodate up to six electrons.

4. (a) The principal quantum number (n) is related to the size of the orbital (n = 1, 2, 3, ...)

5. (a) According to Rutherford's experiment. "The central part consisting of whole of the positive charge and most of the mass, called nucleus, is extremely small in size compared to the size of the atom."

6. (d) \(\frac{e}{m}\) for neutron = \(\frac{0}{1}\) = 0; α-particle = \(\frac{2}{4}\) = 0.5;

   proton = \(\frac{1}{1}\) = 1; electron = \(\frac{1}{1/1837}\) = 1837

7. (a) Rb has the configuration: 1s\(^2\) 2s\(^2\) 2p\(^6\) 3s\(^2\) 3p\(^6\) 4s\(^1\) 4p\(^6\) 5s\(^1\);

   so \(n = 5, l = 0, m = 0\) and \(s = +\frac{1}{2}\) is correct set of quantum numbers for valence shell electron of Rb.

8. (d) NOTE: Energy is emitted when electron falls from higher energy level to lower energy level and energy is absorbed when electron moves from lower level to higher level.

   \(1s\) is the lowest energy level of electron in an atom. ∴ An electron in \(1s\) level of hydrogen can absorb energy but cannot emit energy.

9. (b) Bohr model can explain spectrum of atoms/ions containing one electron only.

10. (b) The radius of nucleus is of the order of 1.5 \times 10^{-13} to 6.5 \times 10^{-13} cm or 1.5 to 6.5 Fermi (1 Fermi = 10^{-13} cm)

11. (b) TIPS/Formulae: The following is the increasing order of wavelength or decreasing order of energy of electromagnetic radiations:

   - cosmic rays
   - γ-rays
   - X-rays
   - UV-rays
   - Visible
   - Infra-red radiation
   - Micro waves
   - Radio waves

   Among given choices radio waves have maximum wavelength.

12. (b) Electrons in an atom occupy the extra nuclear region.

13. (c) If \(l = 2, m = -3, m\) will vary from −2 to +2. i.e. possible values of \(m\) are −2, −1, 0, +1 and +2.

14. (d) \(E = \frac{hc}{\lambda}\);

   \(\lambda_1 = 2000\ Å, \lambda_2 = 4000\ Å\);

   so \(\frac{E_1}{E_2} = \frac{\lambda_2}{\lambda_1} = \frac{4000}{2000} = 2\)

15. (a) Isotones have same number of neutrons. All atoms in triad (a) have same number of neutrons (= \(A - Z = 8\)).

16. (c) Difference in the energy of the energy levels involved in the transition.

17. (b) According to Aufbau principle, the orbital of lower energy (2s) should be fully filled before the filling of orbital of higher energy starts.

18. (c) TIPS/Formulae: The element having highest tendency to accept the electron will be most electron negative element.

   Configuration \(ns^2, np^5\) means it requires only one electron to attain nearest noble gas configuration. So, it will be most electron negative element among given choices.

19. (a) NOTE: Exactly half filled orbitals are more stable than nearly half filled orbitals.

   Cr (At. no. 24) has configuration \([Ar\) 3d\(^5\), 4s\(^1\).\]

20. (c) Electronic configuration of chlorine is \([Ne\) 3s\(^2\), 3p\(^5\). ∴ Unpaired electron is found in 3p sub shell.

   \(n = 3, l = 1, m = 1\)

21. (c) X-rays can ionise gases and cannot get deflected by electric and magnetic fields, wavelength of these rays is 150 to 0.1Å. Thus the wavelength of X-rays is shorter than that of u.v. rays.

22. (d) As packet of energy equal to \(hv\), as wave having frequency \(ν\)
23. (c) **TIPS/Formulæ**: Total nodes = $n - l$
   No. of radial nodes = $n - l - 1$
   No. of angular nodes = $l$
   For 3p sub-shell, $n = 3$, $l = 1$
   $\therefore$ No. of radial nodes = $n - l - 1 = 3 - 1 - 1 = 1$
   $\therefore$ No. of angular nodes = $l = 1$

24. (b) **TIPS/Formulæ**: Orbital angular momentum ($mvr = \frac{h}{2\pi} \sqrt{l(l+1)}$)

   For 2s orbital, $l$ (azimuthal quantum number) = 0
   $\therefore$ Orbital angular momentum = 0.

25. (a) The expression for orbital angular momentum is

   \[\text{Angular momentum} = \sqrt{l(l+1)} \left( \frac{h}{2\pi} \right)\]

   For $d$ orbital, $l = 2$.

   Hence, \(L = \sqrt{2(2+1)} \left( \frac{h}{2\pi} \right) = \sqrt{6} \left( \frac{h}{2\pi} \right)\)

26. (a) **TIPS/Formulæ**: The two guiding rules to arrange the various orbitals in the increasing energy are:

   (i) Energy of an orbital increases with increase in the value of $n + l$.
   (ii) Of orbitals having the same value of $n + l$, the orbital with lower value of $n$ has lower energy.

   Thus for the given orbitals, we have

   (i) $n + l = 4 + 1 = 5$
   (ii) $n + l = 4 + 0 = 4$
   (iii) $n + l = 3 + 2 = 5$
   (iv) $n + l = 3 + 1 = 4$

   Hence, the order of increasing energy is

   (iv) < (ii) < (iii) < (i)

27. (a) $p_x$ orbital being dumbbell shaped, have number of nodal planes = 1, in $yz$ plane.

28. (b) $3d^54s^1$ system is more stable than $3d^44s^2$, hence former is the ground state configuration.

29. (a) **TIPS/Formulæ**: According to de-Broglie’s equation

   \[\lambda = \frac{h}{p} = \frac{h}{mv}\]

   Given, $h = 6.6 \times 10^{-34}$ Js, $m = 200 \times 10^{-3}$ kg

   \[v = \frac{5}{60 \times 60} \text{ m/s}\]

   \[\lambda = \frac{6.6 \times 10^{-34}}{200 \times 10^{-3} \times 5/(60 \times 60)} = 2.38 \times 10^{-10} \text{ m}\]

30. (d) The term spin implies that this magnetic moment is produced by the electron charge as the electron rotates about its own axis. Although this conveys a vivid mental picture of the source of the magnetism, the electron is not an extended body and its rotation is meaningless. Electron spin has no classical counterpart, the magnetic moment is a consequence of relativistic shifts in local space and time due to the high effective velocity of the electron in the atom.

31. (d) Rutherford’s experiment was actually $\alpha$-particle scattering experiment. $\alpha$-Particle is doubly positively charged helium ion i.e., He nucleus.

32. (c) As per Pauli Exclusion Principle "no two electrons in the same atom can have all the four quantum numbers equal or an orbital cannot contain more than two electrons and it can accommodate two electrons only when their directions of spins are opposite".

33. (d) **TIPS/Formulæ**: $r_n = 0.529 \frac{n^2}{Z}$ Å

   For hydrogen, $n = 1$ and $Z = 1$; $\therefore r_H = 0.529$

   For Be$^{3+}$, $n = 2$ and $Z = 4$

   $\therefore r_{Be^{3+}} = \frac{0.529 \times 2^2}{4} = 0.529$

34. (a) **TIPS/Formulæ**: Number of radial nodes $= (n - l - 1)$

   For 3s: $n = 3$, $l = 0$ (Number of radial node = 2)

   For 2p: $n = 2$, $l = 1$ (Number of radial node = 0)

35. (b) Average atomic mass of Fe

   \[= \frac{(54 \times 5) + (65 \times 90) + (57 \times 5)}{100} = 55.95\]

36. (c) As per Bohr’s postulate,

   \[mv = \frac{nh}{2\pi}\]

   So, \(v = \frac{nh}{2\pi mr}\)

   \[\text{KE} = \frac{1}{2} mv^2\]

   \(\therefore\) KE = \(\frac{1}{2} \left( \frac{nh}{2\pi mr} \right)^2\)

   Since, \(r = \frac{a_o \times n^2}{z}\)

   So, for 2nd Bohr orbit

   \(r = \frac{a_o \times 2^2}{1} = 4a_o\)

   \[\text{KE} = \frac{1}{2} \left( \frac{4\pi^2 m^2}{4a_o^2} \right) \times \frac{2h^2}{4\pi^2 m \times (4a_o)^2} = \frac{h^2}{32\pi^2 ma_o^2}\]

37. (d) Radial probability function curve for $1s$ is (D). Here P is $4\pi r^2 R^2$. 

\[\begin{array}{c}
\text{P} \\
\end{array}\]
D. MCQs with One or More Than One Correct

1. (b, d) $^{77}_{33}\text{As}$ and $^{78}_{34}\text{Se}$ have same number of neutrons ($= A - Z$) as $^{76}_{32}\text{Ge}$.

2. (a, c) Because they have isotopes with different masses. The average atomic mass is the weighed mean of their presence in nature; eg. Cl$^{35}$ and Cl$^{37}$ are present in ratio 3 : 1 in nature.

So $A = \frac{3 \times 3 + 37 \times 1}{4} = 35.5$

3. (a, c) alpha-particles pass through because most part of the atom is empty.

4. (b, d) In tritium (the isotope of hydrogen) nucleus there is one proton and 2 neutrons. \( n + p = 3 \). In deuterium nucleus there is one proton and one neutron \( n + p = 2 \).

5. (a, d) The energy of an electron on Bohr orbits of hydrogen atoms is given by the expression

\[ E_n = -\frac{\text{Constant}}{n^2} \]

Where \( n \) takes only integral values. For the first Bohr orbit, \( n = 1 \) and it is given that \( E_1 = -13.6 \text{ eV} \)

Hence \( E_n = -\frac{13.6 \text{ eV}}{n^2} \) of the given values of energy, only \( -3.4 \text{ eV} \) and \( -1.5 \text{ eV} \) can be obtained by substituting \( n = 2 \) and \( 3 \) respectively in the above expression.

6. (a, b, c) (a) $^{24}\text{Cr} = 1s^2, 2s^22p^6, 3s^23p^63d^3, 4s^1 = [\text{Ar}] 3d^3, 4s^1$

(b) For magnetic quantum number \( (m) \), negative values are possible.

For \( s - \) subshell, \( l = 0 \), hence \( m = 0 \)

for \( p - \) subshell, \( l = 1 \), hence \( m = -1, 0, +1 \)

(c) $^{47}\text{Ag} = 1s^2, 2s^22p^6, 3s^23p^63d^{10}, 4s^24p^6, 4d^{10}, 5s^1$

Hence 23 electrons have a spin of one type and 24 of the opposite type.

(d) Oxidation state of N in HN$_3$ is -1/3.

7. (a, c, d) (a) $X^A \rightarrow ^{-\alpha} \rightarrow (\alpha - \text{emission})$

(b) $X^A \rightarrow ^{-\beta} \rightarrow Z^A$ (\( \beta - \text{emission})$

(c) $X^A \rightarrow ^{-e^0} \rightarrow D^A$ (positron - emission);

(d) $X^A + _{-1} e^0 \rightarrow _{-1} D^A$ (electron - capture)

Atomic number increases during \( \beta \)-emission

8. (a, d) According to Hund’s rule pairing of electrons starts only when each of the orbital in a sub shell has one electron each of parallel spin.

\( \therefore (a) \) and (d) are correct ground state electronic configurations of nitrogen atom in ground state.

E. Subjective Problems

1. Let the % of isotope with At. wt. 10.01 = \( x \)

\( \therefore \% \) of isotope with At. wt. 11.01 = \( (100-x) \)

At. wt. of boron = \( \frac{x \times 10.01 + (100-x) \times 11.01}{100} \)

\( \Rightarrow 10.81 = \frac{x \times 10.01 + (100-x) \times 11.01}{100} \) \( \therefore x = 20 \)

Hence % of isotope with At. wt. 10.01 = 20%

\( \therefore \% \) of isotope with At. wt. 11.01 = 100 – 20 = 80%.

2. TIPS/Formulae: \( \Delta E = E_2 - E_1 = h v = \frac{hc}{\lambda} \) or

\( \lambda = \frac{hc}{E_2 - E_1} \)

Given \( E_2 = -5.42 \times 10^{-12} \text{ erg}, E_3 = -2.41 \times 10^{-12} \text{ erg} \)

\( \therefore \)

\( \lambda = \frac{6.626 \times 10^{-27} \times 3 \times 10^{10}}{-2.41 \times 10^{-12} - (-5.42 \times 10^{-12})} \)

\( = \frac{19.878 \times 10^{-17}}{3.01 \times 10^{-12}} = 6.604 \times 10^{-5} \text{ cm} = 6.604 \AA \)

3. TIPS/Formulae: (i) Energy of \( n^{th} \) orbit = \( E_n = \frac{E_1}{n^2} \)

(ii) Difference in energy = \( E_1 - E_2 = h v = \frac{hc}{\lambda} \)

or \( \lambda = \frac{hc}{E_1 - E_2} \)

Given \( E_1 = 2.17 \times 10^{-11} \)

\( \therefore \) Energy of second orbit = \( E_2 = \frac{2.17 \times 10^{-11}}{2^2} \)

\( = 0.5425 \times 10^{-11} \text{ erg} \)

\( \Delta E = E_1 - E_2 = 2.17 \times 10^{-11} - 0.5425 \times 10^{-11} \)

\( = 1.6275 \times 10^{-11} \text{ erg} \)

\( \lambda = \frac{6.62 \times 10^{-27} \times 3 \times 10^{10}}{1.6275 \times 10^{-11}} = 12.20 \times 10^{-6} \text{ cm} = 1220 \AA \)

4. TIPS/Formulae: To calculate the energy required to remove electron from atom, \( n = \infty \) is to be taken.

Energy of an electron in the \( n^{th} \) orbit of hydrogen is given by

\( E = -21.7 \times 10^{-12} \times \frac{1}{n^2} \text{ ergs} \)

\( \therefore \Delta E = -21.7 \times 10^{-12} \left( \frac{1}{2^2} - \frac{1}{\infty^2} \right) \)

\( = -21.7 \times 10^{-12} \left( \frac{1}{4} - 0 \right) = -21.7 \times 10^{-12} \times \frac{1}{4} \)

\( = -5.42 \times 10^{-12} \text{ ergs} \)
Structure of Atom

Now we know that \( \Delta E = h\nu \)

\[
\therefore \quad \Delta E = \frac{hc}{\lambda} \quad \text{or} \quad \lambda = \frac{hc}{\Delta E}
\]

Substituting the values, \( \lambda = \frac{6.627 \times 10^{-27} \times 3 \times 10^{10}}{5.42 \times 10^{-12}} \)

\[= 3.67 \times 10^{-5} \text{ cm}\]

5. Ground state electronic configuration of Si

\[\begin{array}{c}
\uparrow \\
\downarrow \\
3s
\end{array} \quad \begin{array}{c}
\uparrow \\
\uparrow \\
3p_x, 3p_y, 3p_z
\end{array}\]

is in accordance with Hund’s rule which states that electron pairing in any orbital (s, p, d or f) cannot take place until each orbital of the same sub-level contains 1 electron each of like spin.

6. For \( n = 3 \) and \( l = 2 \) (i.e., 3d orbital), the values of \( m \) varies from \(-2\) to \(+2\), i.e., \(-2, -1, 0, +1, +2\) and for each ‘\( m \)’ there are 2 values of ‘s’, i.e., \( +\frac{1}{2} \) and \( -\frac{1}{2} \).

\( \therefore \) Maximum no. of electrons in all the five d-orbitals is 10.

7. \( E_n \) of \( H = \frac{-21.76 \times 10^{-19}}{n^2} \) J

\( \therefore \quad E_n \text{ of } He^+ = \frac{-21.76 \times 10^{-19}}{n^2} \times Z^2 \text{ J} \)

\( \therefore \quad E_3 \text{ of } He^+ = \frac{-21.76 \times 10^{-19} \times 4}{9} \text{ J} \)

Hence energy equivalent to \( E_3 \) must be supplied to remove the electron from 3rd orbit of \( He^+ \). Wavelength corresponding to this energy can be determined by applying the relation.

\[
E = \frac{hc}{\lambda} \quad \text{or} \quad \lambda = \frac{hc}{E} = \frac{6.625 \times 10^{-34} \times 3 \times 10^8 \times 9}{21.76 \times 10^{-19} \times 4} \]

\[= 2055 \times 10^{-10} \text{ m} = 2055 \text{ Å} \]

8. TIPS/Formulae : \( \Delta E = RhcZ^2 \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \)

Here, \( R = 1.0967 \times 10^7 \text{ m}^{-1} \)

\( h = 6.626 \times 10^{-34} \text{ J sec, } c = 3 \times 10^8 \text{ m/sec} \)

\( n_1 = 1, n_2 = 2 \) and for H-atom, \( Z = 1 \)

\[
E_2 - E_1 = 1.0967 \times 10^7 \times 6.626 \times 10^{-34} \times 3 \times 10^8 \left( \frac{1}{1} - \frac{1}{4} \right) \]

\[\Delta E = 1.0967 \times 6.626 \times 3 \times \frac{3}{4} \times 10^{-19} \text{ J} \]

\[= 16.3512 \times 10^{-19} \text{ J} \]

\[= 16.3512 \times 10^{-19} \text{ J} \times \frac{1}{1.6 \times 10^{-19}} \text{ ev} = 10.22 \text{ eV} \]

\[
\Delta E = RhcZ^2 \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \]

\[
\frac{1}{\lambda} = RZ^2 \left( \frac{1}{1} - \frac{1}{4} \right) = RZ^2 \times \frac{3}{4} \]

Given, \( \lambda = 3 \times 10^{-8} \text{ m} \)

\( \therefore \quad \frac{1}{3 \times 10^{-8}} = 1.0967 \times 3 \times 4 \times 10^7 \)

\( \therefore \quad Z^2 = \frac{10^8 \times 4}{3 \times 3 \times 1.0967 \times 10^7} = \frac{40}{9 \times 1.0967} \approx 4 \quad \therefore \quad Z = 2 \)

So it corresponds to \( He^+ \) which has 1 electron like hydrogen.

9. For \( He^+ \) ion, we have

\[
\frac{1}{\lambda} = Z^2 R_H \left[ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \]

\[
= (2)^2 R_H \left[ \frac{1}{(2)^2} - \frac{1}{(4)^2} \right] = R_H \frac{3}{4} \quad \ldots(i) \]

Now for hydrogen atom \( \frac{1}{\lambda} = R_H \left[ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \ldots(ii) \)

E rupting equations \((i)\) and \((ii)\), we get

\[
\frac{1}{n_1^2} - \frac{1}{n_2^2} = \frac{3}{4} \]

Obviously, \( n_1 = 1 \) and \( n_2 = 2 \)

Hence, the transition \( n = 2 \) to \( n = 1 \) in hydrogen atom will have the same wavelength as the transition, \( n = 4 \) to \( n = 2 \) in \( He^+ \) species.

10. TIPS/Formulae : Number of waves = \( \frac{n(n-1)}{2} \)

where \( n = \text{Principal quantum number or number of orbit} \)

Number of waves = \( \frac{3(3-1)}{2} = \frac{3 \times 2}{2} = 3 \)

11. Bond energy of \( I_2 = 240 \text{ kJ mol}^{-1} = 240 \times 10^3 \text{ J mol}^{-1} \)

\[= \frac{240 \times 10^3}{6.023 \times 10^{23}} \text{ J molecule}^{-1} \]

\[= 3.984 \times 10^{-19} \text{ J molecule}^{-1} \]

Energy absorbed \( = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \text{ J s} \times 3 \times 10^8 \text{ m s}^{-1}}{4500 \times 10^{-10} \text{ m}} \)

\[= 4.417 \times 10^{-19} \text{ J} \]
Kinetic energy = Absorbed energy – Bond energy
∴ Kinetic energy = \(4.417 \times 10^{-19} - 3.984 \times 10^{-19}\) J
\[= 4.33 \times 10^{-20}\] J
∴ Kinetic energy of each atom of iodine
\[= \frac{4.33 \times 10^{-20}}{2} = 2.165 \times 10^{-20}\]

12. The shortest wavelength transition in the Balmer series corresponds to the transition
\[n = 2 \rightarrow n = \infty\]. Hence, \(n_1 = 2, n_2 = \infty\) Balmer
\[\nu = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = (109677\text{ cm}^{-1}) \left(\frac{1}{2^2} - \frac{1}{\infty^2}\right)\]
\[= 27419.25 \text{ cm}^{-1}\]

13. Work done while bringing an electron infinitely slowly from infinity to proton of radius \(a_0\) is given as follows
\[W = -\frac{e^2}{4\pi \varepsilon_0 a_0}\]

**NOTE:** This work done is equal to the total energy of an electron in its ground state in the hydrogen atom. At this stage, the electron is not moving and do not possess any K.E., so this total energy is equal to the potential energy.

\[\text{T.E.} = \text{P.E.} + \text{K.E.} = \text{P.E.} = -\frac{e^2}{4\pi \varepsilon_0 a_0}\] ...(I)

In order the electron to be captured by proton to form a ground state hydrogen atom it should also attain
\[\text{K.E.} = \frac{e^2}{8\pi \varepsilon_0 a_0}\]

(It is given that magnitude of K.E. is half the magnitude of P.E. Note that P.E. is –ve and K.E. is +ve)
∴ \[\text{T.E.} = \text{P.E.} + \text{K.E.} = -\frac{e^2}{4\pi \varepsilon_0 a_0} + \frac{e^2}{8\pi \varepsilon_0 a_0}\]
or \[\text{T.E.} = -\frac{e^2}{8\pi \varepsilon_0 a_0}\]

\[\text{P.E.} = 2 \times \text{T.E.} = 2 \times -\frac{e^2}{8\pi \varepsilon_0 a_0} \quad \text{or} \quad \text{P.E.} = -\frac{e^2}{4\pi \varepsilon_0 a_0}\]

14. Determination of number of moles of hydrogen gas,
\[n = \frac{PV}{RT} = \frac{1 \times 1}{0.082 \times 298} = 0.0409\]

The concerned reaction is \(H_2 \longrightarrow 2H\); \(\Delta H = 436\) kJ \text{ mol}^{-1}

Energy required to bring 0.0409 moles of hydrogen gas to atomic state = \(436 \times 0.0409 = 17.83\) kJ

Calculation of total number of hydrogen atoms in 0.0409 mole of \(H_2\) gas
1 mole of \(H_2\) gas has \(6.02 \times 10^{23}\) molecules

\[0.0409 \text{ mole of } H_2 \text{ gas} = \frac{6.02 \times 10^{23}}{1}\]

Since 1 molecule of \(H_2\) gas has 2 hydrogen atoms
\[6.02 \times 10^{23} \times 0.0409 \text{ mole of } H_2 \text{ gas}\]
\[= 2 \times 6.02 \times 10^{23} \times 0.0409 = 4.92 \times 10^{22}\] atoms of hydrogen

Since energy required to excite an electron from the ground state to the next excited state is given by
\[E = 13.6 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \text{ eV} = 13.6 \times \frac{1}{1} - \frac{1}{4} = 13.6 \times \frac{3}{4} = 10.2\text{ eV}\]
\[= 1.632 \times 10^{21}\text{ kJ}\]

Therefore energy required to excite 4.92 \times 10^{22} electrons
\[= 1.632 \times 10^{21} \times 4.92 \times 10^{22} \text{ kJ} = 8.03 \times 10 \times 80.3 \text{ kJ}\]

Therefore total energy required = 17.83 + 80.3 = \textbf{98.17 kJ}

15. For maximum energy, \(n_1 = 1\) and \(n_2 = \infty\)
\[\frac{1}{\lambda} = R_H Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)\]

Since \(R_H\) is a constant and transition remains the same
\[\frac{1}{\lambda} \propto Z^2 ; \quad \frac{\lambda_{He}}{\lambda_H} = \frac{Z_{He}^2}{Z_H^2} = \frac{1}{4}\]

Hence, \(\lambda_{He} = \frac{1}{4} \times 91.2 = 22.8\) nm

16. \(\psi_{2s}^2 = \) probability of finding electron within 2s sphere
\(\psi_{2s}^2 = 0\) (at node)

\(\therefore\) probability of finding an electron is zero at node
\[\therefore 0 = \left(\frac{1}{32\pi a_0}\right)^3 \left(2 - \frac{r_0}{a_0}\right)^2 \cdot e^{-\frac{2r_0}{a_0}}\]

(Squaring the given value of \(\psi_{2s}\))

\[2 - \frac{r_0}{a_0} = 0; \quad 2 = \frac{r_0}{a_0}; \quad 2a_0 = r_0\]

17. \(\lambda = \frac{h}{mu} = \frac{6.627 \times 10^{-34}}{0.1 \times 100}\)

or \(\lambda = 6.627 \times 10^{-35}\) m = \textbf{6.627 \times 10^{-25} Å}

18. For hydrogen atom, \(Z = 1, n = 1\)
\[v = 2.18 \times 10^6 \times \frac{Z}{n} \text{ ms}^{-1} = 2.18 \times 10^6 \text{ ms}^{-1}\]

de Broglie wavelength,
\[\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34}}{9.1 \times 10^{-31} \times 2.18 \times 10^6}\]
\[= 3.34 \times 10^{-10}\] m = 3.3 Å

For \(2p, l = 1\)
\[\therefore\) Orbital angular momentum = \(\sqrt{l(l+1)}\) \frac{h}{2\pi} = \sqrt{2} \frac{h}{2\pi}\]
F. Match the Following

1. (A) - (r); (B) - (q); (C) - (p); (D) - (s)
   (i) \[ \frac{V_n}{K_n} = \frac{-Kze^2}{r} = -2, \text{ where } K = \frac{i}{4\pi e_0} \therefore (i) - (c) \]
   (ii) \[ r_n \propto (E_n)^{-1}; \therefore (ii) - (b) \]
   (iii) Angular momentum of electron in lowest (1s) orbital
   \[ \frac{\sqrt{\ell(\ell+1)}}{2\pi} = \sqrt{0(0+1)} \frac{h}{2\pi} = 0; \therefore (iii) - (a) \]
   (iv) \[ \frac{1}{r^n} \propto Z^1; \therefore (iv) - (d) \]

2. A.q,r; B-p,q,r,s; C-p,q,r; D-p,q

G. Comprehension Based Questions

For 1-3
The spherically symmetric state \( S_1 \) of Li\(^{2+} \) with one radial node is 2s. Upon absorbing light, the ion gets excited to state \( S_2 \), which also has one radial node. The energy of electron in \( S_2 \) is same as that of H-atom in its ground state.

\[ E_n = \frac{Z^2}{n^2}E_1 \]
where \( E_1 \) is the energy of H-atom in the ground state
\[ \therefore E_n = \frac{(3)^2}{n^2}E_1 \text{ for } Li^{2+} \]
\[ E_n = E_1 \Rightarrow n = 3 \]
\[ \therefore \text{ State } S_2 \text{ of } Li^{2+} \text{ having one radial node is } 3p. \]

Orbital angular momentum quantum number of 3p is 1. Energy of state \( S_1 = \frac{(3)^2}{(2)^2}E_1 = 2.25E_1 \)

1. (b) 2. (c) 3. (b)

H. Assertion & Reason Type Questions

1. (e) Nuclides having both even number of protons and neutrons have maximum stability. So the reason is incorrect. But the assertion is correct as \(^{40}\text{Ca}_{20}\) has even number of neutrons and protons as compared to \(^{30}\text{Al}_{13}\), which has odd neutrons and protons.

2. (b) Statement-1 is correct because as we go down a group, energy gap between successive orbits decreases which causes decrease in the energy gap between valence band and conduction band. Statement-2 is also correct because each band is a collection of closely spaced large number of atomic energy levels. But this is not true correct explanation of statement-1.

I. Integer Value Correct Type

1. \( n = \frac{h}{\lambda} \)
\[ E = \frac{6.6 \times 10^{-34} \times 3 \times 10^8}{300 \times 10^{-9}} \text{ J} \]
\[ = \frac{6.6 \times 10^{-34} \times 3 \times 10^8}{300 \times 10^{-9} \times 1.6 \times 10^{-19}} \text{ eV} = 4.16 \text{ eV} \]

Photoelectric effect can take place only when \( E_{\text{photon}} > \phi \)
Thus, number of metals showing photoelectric effect will be 4 (i.e. Li, Na, K, and Mg).

2. 9
Maximum number of electrons \( (n^2) \) when \( n = 3 = 3^2 = 9 \)
\[ \therefore \text{ Number of orbitals} = 9 \]
\[ \therefore \text{ Number of electrons with } m_s = -\frac{1}{2} \text{ will be } 9. \]

3. (5) Since,
\[ \lambda = \frac{h}{m \nu} = \frac{h}{\sqrt{2MKE}} \text{ (since K.E. } \propto T) \]
\[ \Rightarrow \lambda \propto \frac{1}{\sqrt{MT}} \]
For two gases,
\[ \frac{\lambda_{\text{He}}}{\lambda_{\text{Ne}}} = \frac{M_{\text{Ne}}}{M_{\text{He}}} \times \frac{v_{\text{Ne}}}{v_{\text{He}}} = \frac{20}{4} \times \frac{1000}{200} = 5 \]

4. (6) \[ |m| = 1 \text{ means } m \text{ can be } +1 \text{ and } -1. \]

So, for \( n = 4 \), six orbitals are possible and each has 1 electron with \( s = -\frac{1}{2} \). So total number of electrons = 6.

5. (3) Ground state configuration:
\[ \text{H}^{-}: 1s \text{ 2s } 2p \]
in second excited state, electron will jump from 1s to 2p, so degeneracy of second excited state of H\(^-\) is 3.
1. (a) 2nd excited state will be the 3rd energy level.
\[ E_n = \frac{13.6}{n^2} \text{ eV} \quad \text{or} \quad E = \frac{13.6}{9} \text{ eV} = 1.51 \text{ eV}. \]

2. (e) **TIPS/Formulae:**
\[ \Delta x \Delta p = \frac{\hbar}{4\pi}; \quad \text{or} \quad \Delta x \Delta m \Delta v = \frac{\hbar}{4\pi} \]
\[ \therefore \Delta v = \frac{6.62 \times 10^{-34}}{4 \times 3.14 \times 0.025 \times 10^{-5}} = 2.1 \times 10^{-28} \text{ m s}^{-1} \]

3. (c) Fe^{2+} (26 – 2 = 24) = 1s^2 2s^2 2p^6 3s^2 3p^6 4s^0 3d^6 hence no. of d electrons retained is 6.
   [Two 4s electron are removed]

4. (a) **TIPS/Formulae:**
For s-electron, \( \ell = 0 \)
\[ \therefore \text{Orbital angular momentum} = \sqrt{\ell(\ell+1)} \frac{\hbar}{2\pi} = 0 \]

5. (a) N^3–, F– and Na^+ contain 10 electrons each.

6. (a) The lines falling in the visible region comprise Balmer series. Hence the third line from red would be \( n_1 = 2, \)
\[ n_2 = 5 \text{ i.e. } 5 \rightarrow 2. \]

7. (d) \[ \lambda = \frac{\hbar}{mv} = \frac{6.6 \times 10^{-34}}{60 \times 10^{-3} \times 10} = 10^{-33} \text{ m} \]

8. (a) The possible quantum numbers for 4f electron are
\[ n = 4, \ell = 3, m = -3, -2, -1, 0, 1, 2, 3 \text{ and } s = \pm \frac{1}{2} \]

9. (b) Electronic configuration of Cr atom (z = 24)
\[ 1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1 \]
when \( \ell = 1, \) p-subshell,
Numbers of electrons = 12
when \( \ell = 2, \) d-subshell,
Numbers of electrons = 5

10. (c) **TIPS/Formulae:**
\[ \frac{1}{\lambda} = R \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \]
\[ \frac{1}{\lambda} = 1.097 \times 10^7 \left( \frac{1}{1} - \frac{1}{1} \right) = 1.097 \times 10^7 \]
\[ \lambda = 91.15 \times 10^{-9} \text{ m} \approx 91 \text{ nm} \]

11. (c) \[ ^{19}\text{K}^+ , \quad ^{20}\text{Ca}^{2+} , \quad ^{22}\text{Sc}^{3+} , \quad ^{17}\text{Cl}^- \]
each contains 18 electrons.

12. (a) The energy of an orbital is given by \((n + \ell)\) in (d) and (c). \((n + \ell)\) value is \((3 + 2) = 5\) hence they will have same energy, since there \( n \) values are also same.

13. (b) Calculating number of electrons
\[ \text{BO}_3^{2–} \rightarrow 5 + 8 \times 3 + 3 = 32 \]
1. \[ \text{CO}_3^{2–} \rightarrow 6 + 8 \times 3 + 2 = 32 \] \text{iso-electronic species}
\[ \text{NO}_3^- \rightarrow 7 + 8 \times 3 + 1 = 32 \]
\[ \text{SO}_3^{2–} \rightarrow 16 + 8 \times 3 + 2 = 42 \]

2. \[ \text{CO}_3^{2–} \rightarrow 32 \] \text{not iso-electronic species}
\[ \text{NO}_3^- \rightarrow 32 \]
\[ \text{CN}^- \rightarrow 6 + 7 + 1 = 14 \] \text{iso-electronic species}
\[ \text{C}_2^2^- \rightarrow 6 \times 2 + 2 = 14 \]
\[ \text{PO}_4^{3–} \rightarrow 15 + 8 \times 4 + 3 = 50 \]
\[ \text{SO}_4^{2–} \rightarrow 16 + 4 + 8 + 2 = 50 \] \text{iso-electronic species}
\[ \text{ClO}_4^- \rightarrow 17 + 8 \times 4 + 1 = 50 \]

Hence the species in option (b) are not isoelectronic.

14. (b) Angular momentum of an electron in \( n \)th orbital is given by,
\[ mvr = \frac{n \hbar}{2\pi} \]
For \( n = 5 \), we have
\[ \text{Angular momentum of electron} = \frac{5\hbar}{2\pi} = \frac{2.5\hbar}{\pi} \]

15. (a) Given \( m = 9.1 \times 10^{-31} \text{kg}, \) \( h = 6.6 \times 10^{-34} \text{Js} \)
\[ \Delta v = \frac{300 \times 0.001}{100} = 0.003 \text{ms}^{-1} \]
From Heisenberg’s uncertainty principle
\[ \Delta x = \frac{6.6 \times 10^{-34}}{4 \times 3.14 \times 0.003 \times 9.1 \times 10^{-31}} = 1.92 \times 10^{-2} \text{ m} \]

16. (c) \[ \text{N}^{3–} = \text{7 + 3} = 10e–, \quad \text{O}^{2–} \rightarrow \text{8 + 2} = 10e– \]
\[ \text{F}^– = \text{9 + 1} = 10e–, \quad \text{S}^{2–} \rightarrow \text{16 + 2} = 18e– \] 
\[ \text{(not iso electronic)} \]
(b) \[ \text{Li}^{+} = \text{3 + 1} = 4e–, \quad \text{Na}^{+} = \text{11 – 1} = 10e–, \]
\[ \text{Mg}^{2+} = \text{12 – 2} = 10e– \]
\[ \text{Ca}^{3+} = \text{20 – 2} = 18e– \] 
\[ \text{(not iso-electronic)} \]
(c) \[ \text{K}^+ = \text{19 – 1} = 18e–, \quad \text{C}^{2+} = \text{17 + 1} = 18e–, \]
\[ \text{Ca}^{3+} = \text{20 – 2} = 18e–, \quad \text{Sc}^{3+} = \text{21 – 3} = 18e– \]
\[ \text{(iso-electronic)} \]
(d) \[ \text{Ba}^{2+} = \text{56 – 2} = 54e–, \quad \text{Sr}^{2+} = \text{38 – 2} = 36e– \]
\[ \text{K}^+ = \text{9 – 1} = 18e–, \quad \text{Ca}^{3+} = \text{20 – 2} = 18e– \]
\[ \text{(not iso-electronic)} \]
17. (c) (a) \( n = 3, \ell = 0 \) means 3s-orbital and \( n + 1 = 3 \)
(b) \( n = 3, \ell = 1 \) means 3p-orbital \( n + 1 = 4 \)
(c) \( n = 3, \ell = 2 \) means 3d-orbital \( n + 1 = 5 \)
(d) \( n = 4, \ell = 0 \) means 4s-orbital \( n + 1 = 4 \)
Increasing order of energy among these orbitals is
\( 3s < 3p < 4s < 3d \)
\[ \therefore 3d \text{ has highest energy.} \]
18. (b) Species having same number of electrons are isoelectronic calculating the number of electrons in each species given here, we get,
\[ \text{CN}^{-}(6 + 7 + 1 = 14); \text{N}_{2}^{+}(7 + 7 + 1 = 14); \]
\[ \text{O}_{2}^{+}(8 + 8 + 2 = 18); \text{C}_{2}^{2-}(6 + 6 + 2 = 14); \]
\[ \text{O}_{2}^{-}(8 + 8 + 1 = 17); \text{N}_{2}^{+}(7 + 8 - 1 = 14) \]
\[ \text{CO}(6 + 8 + 14); \text{NO}(7 + 8 = 15) \]
From the above calculation we find that all the species listed in choice (b) have 14 electrons each so it is the correct answer.
19. (d) \((\Delta E)\), The energy required to excite an electron in an atom of hydrogen from \( n = 1 \) to \( n = 2 \) is \( \Delta E \) (difference in energy \( E_{2} \) and \( E_{1} \))
\[ E_{1} = -1.312 \times 10^{5} \text{ J mol}^{-1} \]
\[ E_{2} = -1.312 \times 10^{6} \times \left( \frac{1}{2} \right)^{2} = -3.28 \times 10^{5} \text{ J mol}^{-1} \]
\( \Delta E \) is given by the relation,
\[ \therefore \Delta E = E_{2} - E_{1} = \left( -3.28 \times 10^{5} \right) - \left( -1.312 \times 10^{6} \right) \text{ J mol}^{-1} \]
\[ = 9.84 \times 10^{5} \text{ J mol}^{-1} \]
Thus the correct answer is (d)
20. (a) \[ \lambda = \frac{hc}{mv} = \frac{6.63 \times 10^{-34}}{1.67 \times 10^{-27} \times 1 \times 10^{3}} \]
\[ = 3.97 \times 10^{-10} \text{ meter} = 0.397 \text{ nanometer} \]
21. (b) According to Heisenberg uncertainty principle.
\[ \Delta x \cdot \Delta \nu = \frac{h}{4\pi}, \Delta x = \frac{h}{4\pi \Delta \nu} \]
Here \( \Delta \nu = \frac{600}{100} = 0.06 \)
So, \( \Delta x = \frac{6.6 \times 10^{-34}}{4 \times 3.14 \times 9.1 \times 10^{-31} \times 0.03} \)
\[ = 1.92 \times 10^{-3} \text{ meter} \]
22. (d) Energy required to break one mole of Cl – Cl bonds in \( \text{Cl}_{2} \)
\[ \text{E} = \frac{242 \times 10^{3}}{6.023 \times 10^{23}} = \frac{6.626 \times 10^{-34} \times 3 \times 10^{8}}{\lambda} \]
\[ \therefore \lambda = \frac{6.626 \times 10^{-34} \times 3 \times 10^{8}}{242 \times 10^{3}} \]
\[ = 0.4947 \times 10^{-6} \text{ m} = 494.7 \text{ nm} \]
23. (b) I.E = \( \frac{Z^{2}}{n^{2}} \times 13.6 \text{ eV} \) (i)
\[ \therefore \frac{I_{1}}{I_{2}} = \frac{Z_{1}^{2}}{n_{1}^{2}} \times \frac{n_{2}^{2}}{Z_{2}^{2}} \]
24. (c) Energy of absorbed photon = Sum of the energies of emitted photon
\[ \frac{1}{\lambda} = \frac{1}{\lambda_{1}} + \frac{1}{\lambda_{2}} \]
\[ \therefore \frac{1}{\lambda} = \frac{1}{355 \times 10^{-9}} = \frac{1}{680 \times 10^{-9}} + \frac{1}{\lambda_{2}} \]
\[ \therefore \frac{1}{\lambda_{2}} = \frac{355 \times 10^{-9} - 680 \times 10^{-9}}{680 \times 10^{-9}} = 1.346 \times 10^{6} \]
or \( \lambda_{2} = 1/1.346 \times 10^{6} = 743 \times 10^{-9} \text{ m} = 743 \text{ nm} \)
25. (b) (a) 4 p (b) 4 s (c) 3 d (d) 3 p
According to Bohr Bury's \((n + \ell)\) rule, increasing order of energy \((n + \ell)\) then the orbital with lower value of \(n\) will be filled first.
26. (a) \[ \Delta E = 2.178 \times 10^{-18} \times \left( \frac{1}{1^{2}} - \frac{1}{2^{2}} \right) = \frac{hc}{\lambda} \]
\[ 2.17 \times 10^{-18} \times \frac{3}{4} = \frac{6.62 \times 10^{-34} \times 3 \times 10^{8}}{\lambda} \]
\[ \therefore \lambda = \frac{6.62 \times 10^{-34} \times 3 \times 10^{8}}{2.17 \times 10^{-18} \times 3} = 1.214 \times 10^{-7} \text{ m} \]
27. (a) The electronic configuration of Rubidium (Rb = 37) is
\[ 1s^{2} 2s^{2} 2p^{6} 3s^{2} 3p^{6} 3d^{10} 4s^{2} 4p^{6} 5s^{1} \]
Since last electron enters in 5s orbital
Hence \( n = 5, l = 0, m = 0, s = \pm \frac{1}{2} \)
28. (a) Total energy = \( \frac{-13.6 Z^{2}}{n^{2}} \) eV
where \( n = 2, 3, 4 \ldots \)
Putting \( n = 2 \)
\[ E_{l} = -13.6 \frac{4}{4} = -3.4 \text{ eV} \]
29. (b) As electron of charge 'e' is passed through 'V' volt, kinetic energy of electron will be eV
Wavelength of electron wave \( (\lambda) = \frac{h}{\sqrt{2mE}} \)
\[ \lambda = \frac{h}{\sqrt{2m(E)}} \Rightarrow \frac{h}{\lambda} = \sqrt{2mE} \]
### Classification of Elements and Periodicity in Properties

#### Section-A : JEE Advanced/ IIT-JEE

<table>
<thead>
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<th>2.</th>
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<tbody>
<tr>
<td>A</td>
<td>Electron affinity</td>
<td>Electronegativity</td>
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#### Section-B : JEE Main/ AIEEE

<table>
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<tr>
<td>B</td>
<td>True / False</td>
<td></td>
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</tbody>
</table>

1. **True**: Ionisation energy decreases on moving down in group IA from Li to Cs, the reducing property should increase in the same order, *i.e.*, from Li to Cs which is found to be so except an anomaly in lithium which is found to be the strongest reducing agent, because of its higher oxidation potential (E°).

2. **False**: Halogens have high electron affinities which decrease as we move down the group. However, fluorine has lower value of E.A. than chlorine which is due to its small size and more repulsion between the electron added and electrons already present. Hence the order Cl > Br > F.

3. **False**: On moving down the group 13 (III)A the basic nature of hydroxides increases. The basic nature increases as the element becomes more electropositive or acquires more metallic character when we move down a group.

#### C. MCQs with One Correct Answer

1. (c) **NOTE**: Ionization potential is amount of energy required to take out most loosely bonded electron from neutral atom. Its value depends on stability of atom (electronic configuration)
   - C – 1s² 2s² 2p¹
   - N – 1s² 2s² 2p³
   - O – 1s² 2s² 2p⁴
   - F – 1s² 2s² 2p⁵
   - (for second ionisation potential, IE₂)
   - As for IE₂ the electron in all the cases is to be removed from 2p orbital so it must follow the order C < N < O < F (i.e. increase across a period)
   - But in case of O⁺, the 2p orbital is half-filled and is more stable as compared to others. So the order becomes : C < N < F < O > O > F > N > C

2. (c) Amongst B, C, N and O, N has the highest first ionization energy, because of its half filled 2p orbital which is more stable.

3. (a) Ionisation potential of nitrogen is more than that of oxygen. This is because nitrogen has more stable half-filled p-orbitals. (N = 1s², 2s², 2p³, O = 1s², 2s², 2p⁴)

4. (a) **TIPS/Formulae** :
   - (i) Noble gases do not have covalent radii. They have only vander waal’s radii.
Classification of Elements and Periodicity in Properties

(ii) Covalent radii is always larger than corresponding van-der Waal’s radii.

Atomic radius of neon being van der Waal’s radius is larger than that of fluorine which is in fact is its covalent radius.

5. (c) NOTE: Electronegativity increases on moving from left to right in a period and decreases on moving from top to bottom in a group.

Si and P are placed in the 3rd period while C and N are placed in the 2nd period. Elements in 2nd period have higher electronegativities than those in the 3rd period. Since N has smaller size and higher nuclear charge than C, its electronegativity is higher than that of C. Similarly, the electronegativity of P is higher than that of Si. Thus, the overall order is: Si, P, C, N.

6. (a) NOTE: First ionisation potential increases from left to right in a period. But Mg is more stable than Al due to fully filled-3s orbitals.

IE1 of Mg is higher than that of Na because of increased nuclear charge and also that of Al because in Mg a 3 s-electron has to be removed while in Al it is the 3 p-electron. The IE1 of Si is, however, higher than those of Mg and Al because of its increased nuclear charge. Thus, the overall order is Na < Mg > Al < Si.

7. (b) Nitrogen, being smallest in size, can give up its lone pair of electrons most easily.

8. (d) TIPS/Formulæ:

For isoelectronic ions, ionic size \( \propto \frac{1}{\text{atomic number}} \)

<table>
<thead>
<tr>
<th>Species</th>
<th>No. of e−</th>
<th>At. No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>N3−</td>
<td>10</td>
<td>7</td>
</tr>
<tr>
<td>O2−</td>
<td>10</td>
<td>8</td>
</tr>
<tr>
<td>F−</td>
<td>10</td>
<td>9</td>
</tr>
<tr>
<td>Na+</td>
<td>10</td>
<td>11</td>
</tr>
</tbody>
</table>

\( \therefore \) \( \text{Na}^+ \) is largest in size.

9. (b) NOTE: Ionisation energy increases with increasing atomic number in a period, while it decreases on moving down a group. IE of element with electronic configuration (d) is lowest because of its biggest size. Among the remaining three elements of the same period (3rd), IE of element with electronic configuration (b) is the highest due to greater stability of the exactly half-filled 3 p-subshell.

10. (d) The electrons are not filled in d-subshell monotonically with increase in atomic number, among transition elements.

11. (b) TIPS/Formulæ:

(i) Ion having half filled or full filled orbital have extra stability.

(ii) Larger the size of cation more will be its stability \( \text{Pb}^{2+} (5d^{10} 6s^2) \), has the most stable +2 oxidation state because here the d-orbital is completely filled and is more stable than \( \text{Fe}^{2+} (3d^6) \). Again \( \text{Ag}^{+} (4d^{10}) \) is more stable as here again the d-orbital is completely filled and \( \text{Ag}^{2+} \) is not easily obtained. \( \text{Pb}^{2+} \) is more stable compared to \( \text{Sn}^{2+} (4d^{10} 5s^2) \) because of its large size.

12. (d) The electronic configuration of the given ions are as follows.

\( 1_{2}\text{Mg}^{2+} = 1s^2, 2s^2 2p^6 \) (No unpaired electron)

\( 25\text{Ti}^{3+} = 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^1 \) (One unpaired electron)

\( 23\text{V}^{3+} = 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^2 \) (Two unpaired electrons)

\( 26\text{Fe}^{2+} = 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^6 \) (Four unpaired electrons)

13. (b) Effective nuclear charge (i.e. \( Z/e \) ratio) decreases from F− to N3− hence the radii follows the order:

\( F^- < O^2- < N^3- \). \( Z/e \) for \( F^- = 9/10 = 0.9 \), for \( O^2- = 8/10 = 0.8 \), for \( N^3- = 7/10 = 0.7 \).

14. (a) Non-metallic oxides are acidic and acidic character decreases with increase in metallic character.

15. (a) TIPS/Formulæ:

(i) Hydrogen bonding increases the boiling point.

(ii) Hydrogen bonds are formed in compounds having F or O or N with hydroxide S, Se, Te cannot undergo hydrogen bond formation because of their larger size and lower electronegativity values.

16. (a) Non-metallic oxides are acidic and metallic oxides are basic. Thus the acidic order is \( \text{CaO} < \text{CuO} < \text{H}_2\text{O} < \text{CO}_2 \).

D. MCQs with One or More than One Correct

1. (a,c,d) Periodic table does not help to predict the stable valency states of the elements.

2. (a, b) TIPS/Formulæ:

For dissolution, Hydration energy > Lattice energy. \( \text{BaSO}_4 \) is sparingly soluble in water because its hydration energy is lesser than the lattice energy and thus ions are not separated from each other. On the contrary in \( \text{Na}_2\text{SO}_4 \), the hydration energy is more than its lattice energy. Thus ions are separated from each other and pass in solution state.

3. (d) Higher the (+) charge, smaller will be radii.

E. Subjective Problems

1. (i) \( \text{O}^{2-} > \text{F}^- > \text{Na}^+ > \text{Mg}^{2+} \)

\( \text{NOTE} \): All the above ions are isoelectronic having 10 electron each.

In such case the greater the nuclear charge, the greater is the attraction for electrons and smaller is the ionic radius. Hence \( \text{O}^{2-} \) has the highest and \( \text{Mg}^{2+} \) has the least ionic size.

(ii) \( \text{Na}_2\text{O}_2 < \text{MgO} < \text{ZnO} < \text{P}_2\text{O}_5 \)

Among oxides the acidic strength increases with oxidation state. So \( \text{Na}_2\text{O}_2 \) is least acidic and \( \text{P}_2\text{O}_5 \) is
most acidic. Further Na₂O₂ and MgO are basic, ZnO is amphoteric and P₂O₅ is acidic.

(iii) The first ionization potential of the 3rd period elements follows the order:

Na < Al < Mg < Si

NOTE: Ionisation energy increases across a period but not regularly. Mg (1s² 2s² 2p⁶, 3s²) is more stable because the electron is to be removed from 3s which is difficult as compared to Al (1s² 2s² 2p⁶, 3s² 3p¹) where electron is to be removed from 3p.

(iv) Ca²⁺ < Ar < Cl⁻ < S²⁻; All of these are isoelectronic. In such cases the greater the nuclear charge, the greater is the attraction for electrons and smaller is ionic size.

\[
\text{ionic radius } \propto \frac{1}{\text{effective nuclear charge}}
\]

(v) Increasing order of ionic size:

Mg²⁺ < Na⁺ < F⁻ < O³⁻ < N³⁻

NOTE: All the above ions are isoelectronic having 10 electrons each.

In such a case the greater the nuclear charge, the greater is the attraction for electrons and smaller is the ionic radius. Hence N³⁻ has the highest and Mg²⁺ has the least ionic size.

(vi) Increasing order of basic character:

NiO < MgO < SrO < K₂O < Cs₂O

The basic character of oxides increases when we move down the group. So, K₂O < Cr₂O and MgO < SrO.

Further higher the group number lesser is the basic character. Hence NiO is the least basic.

(vii) Al³⁺ < Mg²⁺ < Li⁺ < K⁺

In these Al³⁺ & Mg²⁺ are isoelectronic species, so in these size decreases with increase in atomic number because increase in atomic number decreases \(Z_{\text{eff}}\).

\[
\text{Size } \propto \frac{1}{Z_{\text{eff}}}
\]

In Li⁺ & K⁺, K⁺ is bigger in size than Li⁺ because on moving from top to bottom in a group, the group size increases.

2. C (1s² 2s² 2p⁰) has half filled orbitals in its excited state (C → 1s² 2s¹ 2p¹) due to which it becomes more stable and hence IE³ for C is greater than B.

Further for second ionization energy (IE²) in C⁺ (1s² 2s² 2p¹) the electron is to be removed from 2p which is easy as compared to B⁺ (1s² 2s² 2p²), where it has to be removed from 2s.

H. Assertion & Reason Type Questions

1. (c) Assertion is correct but reason is incorrect because the energy of 2s orbital is less than 2p orbital.

I. Integer Value Correct Type

1. Fluorine generally shows 0 and –1 oxidation states while sodium shows 0 and +1 oxidation state.

Section-B

1. (b) According to modern periodic law, the properties of the elements are repeated after certain regular intervals when these elements are arranged in order of their increasing atomic numbers.

2. (d) Na₂O (basic), SO₂ and B₂O₃ (acidic) and ZnO is amphoteric.

3. (a) O⁻ and F⁻ are isoelectronic. Hence have same number of shells, therefore greater the nuclear charge smaller will be the size i.e.

O⁻ > F⁻

further Li⁺ and B³⁺ are isoelectronic. therefore

Li⁺ > B³⁺

Hence the correct order of atomic size is.

O⁻ > F⁻ > Li⁺ > B³⁺

4. (d) As the size increases the basic nature of oxides changes to acidic nature i.e., acidic nature increases.

\[
\text{SO}_2 > \text{P}_2\text{O}_3 > \text{SiO}_2 > \text{Al}_2\text{O}_3
\]

Acidic Weak Acidic Amphoteric

SO₂ and P₂O₃ are acidic as their corresponding acids H₂SO₃ and H₃PO₃ are strong acids.

5. (a) O⁻ ion exerts a force of repulsion on the incoming electron. The energy is required to overcome it.

6. (a) CaO is basic as it form strong base Ca(OH)₂ on reaction with water.

\[
\text{CaO + H}_2\text{O} \rightarrow \text{Ca(OH)}_2
\]

CO₂ is acidic as it dissolve in water forming unstable carbonic acid.

\[
\text{H}_2\text{O} + \text{CO}_2 \rightarrow \text{H}_2\text{CO}_3
\]

Silica (SiO₂) is insoluble in water and acts as a very weak acid.

SnO₂ is amphoteric as it reacts with both acid and base.

\[
\text{SnO}_2 + 2\text{H}_2\text{SO}_4 \rightarrow \text{Sn(SO}_4)_2 + 2\text{H}_2\text{O}
\]

\[
\text{SnO}_2 + 2\text{KOH} \rightarrow \text{K}_2\text{SnO}_3 + \text{H}_2\text{O}
\]

7. (c) In a period the value of ionisation potential increases from left to right with breaks where the atoms have some what stable configuration. In this case N has half filled stable orbitals. Hence has highest ionisation energy. Thus the correct order is

B < C < O < N

and not as given in option (c)
8. (b) The alkali metals are highly reactive because their first ionisation potential is very low and hence they have great tendency to lose electron to form unipositive ion.

**NOTE**: On moving down group-1 from Li to Cs, ionisation enthalpy decreases hence the reactivity increases. The halogens are most reactive elements due to their low bond dissociation energy, high electron affinity and high enthalpy of hydration of halide ion. However, their reactivity decreases with increase in atomic number.

9. (b) In hydrides of 15th group elements, basic character decreases on descending the group i.e.

\[
\text{NH}_3 > \text{PH}_3 > \text{AsH}_3 > \text{SbH}_3.
\]

10. (d) All the given species contains 10 e\(^{-}\) each i.e. isoelectronic.

For isoelectronic species anion having high negative charge is largest in size and the cation having high positive charge is smallest.

11. (a) On moving across a period ionisation energy increases hence the electropositive nature of metals decreases therefore the ease of formation of ion also decreases and hence the basic character decreases. Further basic character of alkali metals oxides increases from Li\(_2\)O to Cs\(_2\)O. Hence the correct order will be

\[
\text{Al}_2\text{O}_3 < \text{MgO} < \text{Na}_2\text{O} < \text{K}_2\text{O}
\]

12. (c) Among isoelectronic species ionic radii increases as the charge increases.

Order of ionic radii: \(\text{Ca}^{2+} < \text{K}^+ < \text{Cl}^- < \text{S}^{2-}\)

The number of electrons remains the same but nuclear charge increases with increase in the atomic number causing decrease in size.

13. (c) On moving along a period from left to right I.E. increases and on moving down a group I.E. decreases. Hence, correct order is:

\[
\text{Ba} < \text{Ca} < \text{Se} < \text{S} < \text{Ar}
\]

14. (b) ∴ For Na \(\rightarrow\) Na\(^+\) + e\(^-\) \ IE_1 = 5.1 \text{ eV}

∴ For Na\(^+\) + e\(^-\) \(\rightarrow\) Na \ EF = 5.1 \text{ eV}

(because the reaction is reverse)

15. (a) For isoelectronic species, size of anion increases as negative charge increases. Thus, the correct order is

\[
\text{N}^{3-} > \text{O}^{2-} > \text{F}^- \\
(1.71) > (1.40) > (1.36)
\]
Section-A : JEE Advanced/ IIT-JEE

A. Fill in the Blanks

1. CO₂; Bond angle in CH₄ is 109°28', in H₂O it is 105° and in CO₂ it is 180°. So it is maximum in case of CO₂

2. H – C – OH and CH₃ – C – OH form strongest hydrogen bonds because of largest difference in electronegativities of bonded atoms.

3. 2; N ≡ N (N₂) has 1σ and 2π bonds. (A triple bond consists of 1σ and 2π bonds)

4. sp³; Hybridisation (H) = \(\frac{1}{2}(5 + 4 - 1 + 0) = 4\)  
   \[
   \therefore \text{sp³ hybridisation.}
   \]

5. Planar; \(^{+}\text{CH}_3\) is a carbocation and such a species has a planar shape.

6. Three centred two electron bonds or banana bond;

**NOTE:** The formation of three centred two electron bond is due to one empty sp³ orbital of one of the B atom, 1s orbital of the bridge hydrogen atom and one of the sp³ (filled) orbital of the other B-atom. This forms a delocalized orbital covering the three nuclei giving the shape of a banana. Thus also known as banana bonds.
7. **Increases, decreases:**

    \[ \therefore \text{Bond order in } \text{N}_2 = 3 \text{ and Bond order in } \text{N}_2^+ = 2.5 \]

Thus conversion of \( \text{N}_2 \) to \( \text{N}_2^+ \) decreases bond order (from 3 to 2.5) and hence increases the N – N bond distance.

    \[ \therefore \text{Bond distance increases with decrease in B.O.} \]

Bond order in \( \text{O}_2 = 2 \) and Bond order in \( \text{O}_2^+ = 2.5 \)

**NOTE:** Thus conversion of \( \text{O}_2 \) to \( \text{O}_2^+ \) increases bond order (from 2 to 2.5) hence decrease O – O bond distance.

---

**B. True / False**

1. **True**: Sigma bond is formed by the overlapping of two s-orbitals or one s and one p or the two p orbitals of the two different atoms. Thus linear overlap of two p-orbitals results in formation of a \( \sigma \)-bond.

   ![Axial p-p overlapping](image)

2. **False**: Symmetrical molecules with polar bonds have zero dipole moment.

3. **True**: SnCl\(_2\) has 2 bond pairs and one lone pair of electrons. It is \( sp^2 \) hybridised and is trigonal planar in shape.

4. **False**: Only two orbitals are used since C in benzene is in \( sp^2 \) hybridised state.

5. **False**: \( sp^2 \) hybrid orbitals do not have equal s and p character. They have 33.3% s-character and 66.7% p-character.

6. **False**: The presence of polar bonds in a polyatomic molecule does not always lead to a definite dipole moment. This is because the dipole moment is a vector quantity and when the bond moment of one bond is cancelled by the equal but opposite bond moment due to other bond(s), the molecule has zero dipole moment, e.g., \( \text{CO}_2, \text{CH}_4, \text{CCl}_4 \), etc.

7. **False**: The \( \text{C – F} \) distance is less than the \( \text{C – Cl} \), although the former involves more charge separation. However, here bond distance has more dominating effect causing dipole moment of \( \text{CH}_3\text{Cl} \) to be more than that of \( \text{CH}_3\text{F} \).

---

**C. MCQ with One Correct Answer**

1. **(e)** In KCN, ionic bond is present between \( \text{K}^+ \) and \( \text{CN}^- \) and covalent bonds are present between carbon and nitrogen \( \text{C} = \text{N} \).

2. **(d)** \( \therefore \) after forming the bonds, C has only 6 \( e^- \) in its valence shell.

---

3. **(a)** \( X^+Y^- \)

    \( \therefore \) Electropositive elements forms cation and electronegative elements forms anion. Except this all compounds are ionic.

4. **(a)** \( \text{H}_2 \)

5. **(c)** \( \text{N} = \text{N} \)

6. **(b)** \( \therefore \) It forms hydrogen bonds with water

7. **(c)** **NOTE**: Dipole moment is vector quantity

   In trigonal planar geometry (for \( sp^2 \) hybridisation), the vector sum of two bond moments is equal and opposite to the dipole moment of third bond.

8. **(a)** **NOTE**: Isoelectronic species have same number of electrons.

    Electrons in \( \text{CO} = 6 + 8 = 14 \)

    Electrons in \( \text{CN}^- = 6 + 7 + 1 = 14 \)

    Electrons in \( \text{O}_2^- = 8 + 8 + 1 = 17 \)

    Electrons in \( \text{O}_2^+ = 8 + 8 - 1 = 15 \)

    \( \therefore \) CO and CN\(^-\) are isoelectronic.

9. **(a)** **TIPS/Formulae**:

    \[ \text{Hybridisation} = \frac{1}{2} (V + \text{M} - \text{C} + \text{A}) \]

    where; \( V = \text{no. of electron in valence shell of central atom} \)

    \( \text{M} = \text{no. of monovalent atoms} \)

    \( \text{C} = \text{charge on cation} \)

    \( \text{A} = \text{charge on anion} \)

    (i) \( \text{CO}_2, \text{H} = \frac{1}{2} (4 + 0 - 0 + 0) = 2 \)

        \( \therefore \) \( sp \) hybridisation

    (ii) \( \text{SO}_2, \text{H} = \frac{1}{2} (6 + 0 - 0 + 0) = 3 \)

        \( \therefore \) \( sp^2 \) hybridisation

    (iii) \( \text{NO}_2 \) has V shaped structure.

    (iv) \( \text{Cl}_2 \) has V shaped structure.

    \( \therefore \) \( \text{CO}_2 \) having \( sp \) hybridisation has linear shape.

10. **(b)** **TIPS/Formulae**:

    (i) Dipole moment is vector quantity. When vector sum of all dipoles in molecule will be zero, then molecule will not have net dipole moment.

    (ii) **NOTE**: For net dipole moment to be equal to zero, all the atoms attached to central atom must be identical and geometry must be regular.

---

![Chemical Bonding and Molecular Structure](image)
11. (b) In regular tetrahedral structure, dipole moment of one bond is cancelled by opposite dipole moment of the other bonds.

12. (d) **TIPS/Formulæ**: Hydrogen bonding is formed in those compounds in which F or O or N atoms are attached to hydrogen atom.
   \[\text{HCl does not have F or N or O} \]
   \[\text{It does not form hydrogen bond.}\]

13. (c) Ionic bond or electrovalent between Cu\(^{2+}\) and SO\(_4^{2-}\),

   covalent and coordinate in SO\(_4^{2-}\):
   
   \[
   \begin{array}{c}
   O \\
   \text{O} \\
   \text{O} \\
   \text{O}
   \end{array}
   \]

14. (b) **TIPS/Formulæ**: \(sp\) type of hybridization involves the intermixing of one \(s\) and one \(p\) (say \(p_x\)) orbitals to give two equivalent hybrid orbitals, known as \(sp\) hybrid orbitals.

   The two \(sp\) hybrid orbitals are directed diagonally, i.e., in a straight line with an angle of 180° (collinear orbitals). The other two \(p\) orbitals (say \(p_y\) and \(p_z\)) remain pure.

15. (a) **NOTE THIS STEP**: Write the electronic configuration of each species according to molecular orbital theory.

   NO (15\(e^{-}\)) – \(\sigma_1s^2, \sigma^*1s^2, \sigma_2s^2, \sigma^*2s^2, \sigma_2p_x^2, \sigma_2p_y^2, \sigma_2p_z^2\),

   \[\{\pi_2p_y^2 = \pi_2p_z^2, \pi_1*2p_y^2 = \pi_1*2p_z^2\}

   1 unpaired electron.

   CO (14\(e^{-}\)) – \(\sigma_1s^2, \sigma^*1s^2, \sigma_2s^2, \sigma^*2s^2, \sigma_2p_x^2, \sigma_2p_y^2\),

   \[\{\pi_2p_y^2 = \pi_2p_z^2, \sigma_2p_x^2\}

   no unpaired electron

   CN\(^-\) (14\(e^{-}\)) – \(\sigma_1s^2, \sigma^*1s^2, \sigma_2s^2, \sigma^*2s^2\),

   \[\{\pi_2p_y^2 = \pi_2p_z^2, \sigma_2p_x^2\}

   1 unpaired electron

   \(O_2\) (16\(e^{-}\)) – \(\sigma_1s^2, \sigma^*1s^2, \sigma_1s^2, \sigma_2s^2, \sigma^*2s^2, \sigma_2p_x^2, \sigma_2p_y^2\),

   \[\{\pi_2p_y^2 = \pi_2p_z^2, \pi_2p_y^2 = \pi_2p_z^2\}

   Two unpaired electrons.

16. (d) In covalent bonds between two identical non-metal atoms share the pair of electrons equally between them, e.g.: F\(_2\), O\(_2\), N\(_2\).

17. (c) **NOTE**: Greater the difference between electronegativities of two covalently bonded atoms more will be strength of hydrogen bond.

   \[\text{F –H ..................F bond is strongest due to largest difference in electronegativity of atoms and smallest size of F atom.}\]

18. (c) **TIPS/Formulae**: \(H = \frac{1}{2} (V + M - C + A)\)

   For SO\(_2\), \(H = \frac{1}{2} (6 + 0 + 0 - 0) = 3\)

   \(sp^2\) hybridisation.

19. (a) **NOTE**: Compounds having F or O or N attached to H form hydrogen bond.

   \[
   \begin{align*}
   \text{CH}_3\text{CH}_2\text{OH} & \quad \text{C}_2\text{H}_5\text{–O} - \text{C}_2\text{H}_5 \\
   \text{ethanol} & \quad \text{ethyl ether} \\
   \text{CH}_3\text{CH}_2\text{Cl} & \quad \text{ethyl chloride}
   \end{align*}
   \]

   \[
   \begin{align*}
   \text{CH}_3 & \quad \text{N} - \text{CH}_3 \\
   \text{trimethyl amine}
   \end{align*}
   \]

   Ethanol having H attached to O atom will form hydrogen bond. Rest of the compounds do not hydrogen bonds.

20. (c) From amongst given species PH\(_3\), NH\(_3\) and SbH\(_3\) are all \(sp^3\) hybridised. Their central atom has both bond pair as well as lone pair of electrons. The lone pair occupy the fourth orbital. CH\(_3^+\) has only three pairs of electrons so it is \(sp^3\) hybridised.

21. (a) **TIPS/Formulæ**: Compound having \(sp\) hybridisation will have linear shape.

   \(\text{CO}_2\) or (O=O=C=O) which has C in sp hybrid state has linear shape.

22. (b) **TIPS/Formulæ**: Dipole moment of compound having regular geometry and same type of atoms is zero. It is vector quantity.

   The zero dipole moment of BF\(_3\) is due to its symmetrical (triangular planar) structure. The three fluorine atoms lie at the corners of an equilateral triangle with boron at the centre.

   **NOTE**: The vectorial addition of the dipole moments of the three bonds gives a net sum of zero because the resultant of any two dipole moments is equal and opposite to the third. The dipole moment of NH\(_3\) is 1.46 D indicating its unsymmetrical structure. The dipole moment of CH\(_3\)Cl\(_2\) (the molecule uses \(sp^3\) hybridisation but is not symmetric) is 1.57D.

23. (a) **TIPS/Formulæ**: Molecule having \(sp^3\) hybridisation and one lone pair of electron will have pyramidal structure.

   (i) CO\(_3^{2-}\) and NO\(_3^{-}\) have tetrahedron structure.

   (ii) In PCl\(_3\), P is \(sp^3\) hybridised and has one lone pair of electrons, hence it is pyramidal in shape.

24. (c) **TIPS/Formulæ**: 4\(\sigma\) bonds – \(sp^3\) hybridisation

   2\(\sigma\) and 2\(\pi\) bonds – \(sp^2\) hybridisation
Chemical Bonding and Molecular Structure

1σ and 3π bonds – sp hybridisation
[For hybridization only σ-bonds are considered]

\[
\begin{array}{c}
\text{O} \\
\text{H} = \text{C} - \text{OH} \\
\text{CH}_3 \\
\text{CH}_3 - \text{C}^* - \text{OH} \\
\text{CH}_3 - \text{C}^* - \text{H}
\end{array}
\]

\[
\begin{array}{c}
\text{NH}_2 \\
\text{H}_2\text{N} - \text{C} = \text{O} \\
\text{O} \\
\text{CH}_3 \\
\text{CH}_3 - \text{C}^* - \text{H}
\end{array}
\]

(a) 3σ, 1π (b) 3σ, 1π (c) 4σ (d) 3σ, 1π

\[\therefore (\text{CH}_3)_2\text{COH has 4σ bonds and thus it has sp}^3 \text{ hybridisation.}\]

25. (a) \[\text{O}_2^- (17e^-) - K K \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_x^2, \{\pi 2p_y^2 = \pi^* 2p_x^1 \}
\]

Thus, \[\text{O}_2^-\] has one unpaired electron; hence it is paramagnetic. Other species have no unpaired electron. All of them have 14 electrons.

26. (a) \[H = \frac{1}{2} (V + M - C + A)\]

where \(H = \text{No. of orbitals involved in hybridisation (viz. 2, 3, 4, 5, 6) and hence nature of hybridisation (viz. sp}^2, \text{sp}^3, \text{sp}^4d, \text{sp}^5d^2\) can be ascertained.

\[V = \text{No. of electrons in valence shell of the central atom, M = No. of monovalent atoms, C = Charge on cation, A = Charge on anion,}\]

For \(\text{ClO}_2^-\), we have, \[H = \frac{1}{2} (7 + 0 - 0 + 1)\]

\[\Rightarrow H = \frac{1}{2} (7 + 1) = 4 \text{ or sp}^3 \text{ hybridisation as 4 orbitals are involved}\]

27. (b) \(\text{H}_2\text{O}\) molecule can form four hydrogen bonds per molecule, two via lone pairs and two via hydrogen atoms.

28. (b) In \(\text{N}_2\), similar atoms are linked to each other and thus there is no polarity.

29. (d) 
\[\text{No. of } e^-\text{ in } \text{CH}_3^+ = 6 + 3 - 1 = 8\]
\[\text{No. of } e^-\text{ in } \text{H}_2\text{O}^+ = 3 + 8 - 1 = 10\]
\[\text{No. of } e^-\text{ in } \text{NH}_3 = 7 + 3 = 10\]
\[\text{No. of } e^-\text{ in } \text{CH}_3^- = 6 + 3 + 1 = 10\]

\[\therefore \text{H}_2\text{O}^+, \text{NH}_3 \text{ and CH}_3^- \text{ are isoelectronic.}\]

30. (c) Tips/Formulae:
(i) Non metallic oxides are more covalent (or less ionic) as compared to metallic oxides.
(ii) Higher the polarising power of cation (higher for higher oxidation state of similar size cations) more will be covalent character.

31. (d) \(\text{O}_2 = \text{Oxygen (Z = 8) has following molecular orbital configuration of } \text{O}_2:\)
\[\text{O}_2 (16e^-) = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_x^2, \{\pi 2p_y^2 = \pi^* 2p_x^1 \}
\]

Thus, \(\text{O}_2^-\) has one unpaired electron; hence it is paramagnetic. Other species have no unpaired electron. All of them have 14 electrons.

32. (c) Structure of a molecule can be ascertained by knowing the number of hybrid bonds in the molecule. Thus

\[\text{In } \text{NF}_3: H = \frac{1}{2} (5 + 3 - 0 + 0) = 4\]

Thus N in \(\text{NF}_3\) is \(\text{sp}^3\) hybridized as 4 orbitals are involved in bonding.

\[\text{In } \text{NO}_3^-: H = \frac{1}{2} (5 + 0 - 0 + 1) = 3\]

Thus N in \(\text{NO}_3^-\) is \(\text{sp}^2\) hybridized as 3 orbitals are involved in bonding.

\[\text{In } \text{BF}_3: H = \frac{1}{2} (3 + 3 - 0 + 0) = 3\]

Thus B in \(\text{BF}_3\) is \(\text{sp}^2\) hybridized and 3 orbitals are involved in bonding.

\[\text{In } \text{H}_3\text{O}^+: H = \frac{1}{2} (6 + 3 - 1 + 0) = 4\]

Thus O in \(\text{H}_3\text{O}^+\) is \(\text{sp}^3\) hybridized as 4 orbitals are involved in bonding.

Thus, isostructural pairs are \([\text{NF}_3, \text{H}_3\text{O}^+]\) and \([\text{NO}_3^-, \text{BF}_3]\).

33. (b) Calcium carbide is an ionic compound (Ca\(^{2+}\) C\(^2-\)) which produces acetylene on reacting with water. Thus the structure of C\(^2-\) is \([\text{C} = \text{C}]^2-\). It has one σ and two π bonds. \([\therefore \text{ A triple bond consists of one } \sigma \text{ and two } \pi \text{ bonds}\)]

34. (c) (a) \[\begin{array}{c}
\text{H} \\
\text{H} \\
\text{H}
\end{array}\]

\[\text{[Cl]}^1- \text{ It has ionic and non-polar covalent bond}\]

(b) \[\text{H} - \text{C} = \text{N} - \text{H} \text{ - It has ionic and polar covalent bonds.}\]
35. (d) Critical temperature of water is higher than O₃ because H₂O molecule has dipole moment which is due to its V-shape.

36. (b) TIPS/Formulae : \( H = \frac{1}{2} (V + M - C + A) \)

(i) \( \text{CO}_2; H = \frac{1}{2} (4 + 0 - 0 + 0) = 2 \)
   \( \therefore \) sp hybridisation.

(ii) \( \text{SO}_2; H = \frac{1}{2} (6 + 0 - 0 + 0) = 3 \)
   \( \therefore \) sp² hybridisation.

(iii) \( \text{CO}; H = \frac{1}{2} (4 + 0 - 0 + 0) = 2 \)
   \( \therefore \) sp hybridisation.

37. (b) \( H = \frac{1}{2} (3 + 3 + 0 - 0) = 3 \)
   \( \therefore \) Boron, in BF₃, is sp² hybridised leading to trigonal planar shape.

38. (d) KEY CONCEPT

(i) Bond length \( \propto \frac{1}{\text{Bond order}} \)

(ii) Bond order is calculated by either the help of molecular orbital theory or by resonance.

(i) Bond order of CO as calculated by molecular orbital theory = \( 3 \left( \text{b.o.} = \frac{1}{2} [N_6 - N_3] \right) \)

(ii) Bond order of \( \text{CO}_2 \) (by resonance method) \( = \frac{\text{No. of bonds in all possible sides}}{\text{No. of resonating structure}} = \frac{4}{2} = 2 \)

(iii) Bond order in \( \text{CO}_3^{2-} \) (by resonance method) \( = \frac{4}{3} = 1.33 \)
   \( \therefore \) Order of bond length of C – O is \( \text{CO} < \text{CO}_2 < \text{CO}_3^{2-} \)

39. (a) Hybridisation of S in \( \text{H}_2\text{S} = \frac{1}{2} (6 + 2 + 0 - 0) = 4 \)
   \( \therefore \) S has sp³ hybridisation and 2 lone pair of electrons in \( \text{H}_2\text{S} \)
   \( \therefore \) It has angular geometry and so it has non-zero value of dipole moment.

40. (d) The structure of species can be predicted on the basis of hybridisation which in turn can be known by knowing the number of hybrid orbitals (H) in that species

41. (b) For \( \text{NO}_2^- \): \( H = \frac{1}{2} (5 + 0 + 0 - 1) = 2 \);
   \( \therefore \) sp hybridisation

For \( \text{NO}_3^- \): \( H = \frac{1}{2} [5 + 0 + 1 - 0] = 3 \);
   \( \therefore \) sp² hybridisation

For \( \text{NH}_4^+ \): \( H = \frac{1}{2} [5 + 4 + 0 - 1] = 4 \);
   \( \therefore \) sp³ hybridisation

42. (a) Number of electrons in each species are

\( \text{CN}^- = 6 + 7 + 1 = 14 \), \( \text{CO} = 6 + 8 = 14 \)
\( \text{NO}^+ = 7 + 8 - 1 = 14 \)

Each of the species has 14 electrons which are distributed in MOs as below

\( \sigma_{1s}^2, \sigma^*_{1s}^2, \sigma_{2s}^2, \sigma^*_{2s}^2, \pi_{2p_y}^2 = \pi_{2p_z}^2, \sigma_{2p_x}^2 \)

Bond order = \( \frac{10 - 4}{2} = 3 \)

43. (b) TIPS/Formulae : \( H = \frac{1}{2} (V + M - C + A) \)

Hybridisation of N in \( \text{NH}_3 \)
\( \frac{1}{2} [5 + 3 - 0 + 0] = 4 \) \( \therefore \) sp³

Hybridisation of Pt in \( [	ext{PtCl}_2]^2- \)
\( \frac{1}{2} [2 + 4 - 0 + 2] = 4 \) \( \therefore \) dsp²

Hybridisation of P in \( \text{PCl}_5 \)
\( \frac{1}{2} [5 + 5 - 0 + 0] = 5 \) \( \therefore \) sp³d

Hybridisation of B in \( \text{BCl}_3 \)
\( \frac{1}{2} [3 + 3 - 0 + 0] = 3 \) \( \therefore \) sp²

44. (a) \( \text{H}_3\text{N} \rightarrow \text{BF}_3 \) where both N, B are attaining tetrahedral geometry.

45. (b) NOTE THIS STEP : Write configuration of all species. Half filled and full filled orbitals are more stable as compared to nearly half filled and nearly full filled orbitals.
46. (c) \( \text{N}_2(7+7=14), \sigma 1s^2, \sigma 1s^2, \sigma^1s^2, \sigma^2s^2, \gamma^* 2p_x^2, \gamma^* 2p_y^2 \),
\( \text{Na}_2(9 + 9 = 18), \sigma 1s^2, \sigma 1s^2, \sigma^1s^2, \sigma^2s^2, \sigma^2 2p_x^2, \gamma^* 2p_y^2 \),
\( \text{F}_2(9 + 9 = 18), \sigma 1s^2, \sigma 1s^2, \sigma^1s^2, \sigma^2s^2, \sigma^2 2p_x^2, \gamma^* 2p_y^2 \),
\( \text{O}_2(8 + 8 + 1 = 17), \sigma 1s^2, \sigma^1s^2, \sigma^2s^2, \sigma^* 2s^2, \sigma 2p_x^2, \gamma^* 2p_y^2 \),
\( \text{O}_2^-(8 + 8 + 2 = 18), \sigma 1s^2, \sigma^1s^2, \sigma^2s^2, \sigma^* 2s^2, \sigma 2p_x^2, \gamma^* 2p_y^2 \),
\( \text{O}_2^-(8 + 8 + 2 = 18), \sigma 1s^2, \sigma^1s^2, \sigma^2s^2, \sigma^* 2s^2, \sigma 2p_x^2, \gamma^* 2p_y^2 \)

\( \therefore \text{O}_2^- \) is the only species having unpaired electron.

47. (a) **Note:** Isoelectronic species have the same number of electrons and isostructural species have the same type of hybridisation at central atom.

\( \text{NO}_3^-; \) No. of \( e^- = 7 + 8 \times 3 + 1 = 32 \), hybridisation of N in \( \text{NO}_3^- \) is sp\(^3\).

\( \text{CO}_3^{2-}; \) No. of \( e^- = 6 + 8 \times 3 + 2 = 32 \), hybridisation of C in \( \text{CO}_3^{2-} \) is sp\(^3\).

\( \text{ClO}_3^-; \) No. of \( e^- = 17 + 8 \times 3 + 1 = 42 \), hybridisation of Cl in \( \text{ClO}_3^- \) is sp\(^3\).

\( \text{SO}_3; \) No. of \( e^- = 16 + 8 \times 3 = 40 \), hybridisation of S in \( \text{SO}_3 \) is sp\(^2\).

\( \therefore \text{NO}_3^- \) and \( \text{CO}_3^{2-} \) are isostructural and isoelectronic.

48. (b) \( \text{O}_2: \sigma 1s^2, \sigma^* 1s^2, \sigma^1s^2, \sigma^2s^2, \sigma^* 2s^2, \sigma 2p_x^2, \gamma^* 2p_y^2 \),
\( \text{O}_2^+: \sigma 1s^2, \sigma^1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma^* 2p_x^2, \gamma^* 2p_y^2 \),
\( \text{O}_2^+: \sigma 1s^2, \sigma^1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma^* 2p_x^2, \gamma^* 2p_y^2 \)

Bond order \( = \frac{10 - 6}{2} = 2 \)

(two unpaired electrons in antibonding molecular orbital)

\( \text{O}_2: \sigma 1s^2, \sigma^1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma^* 2p_x^2, \gamma^* 2p_y^2 \),
\( \text{O}_2^+: \sigma 1s^2, \sigma^1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma^* 2p_x^2, \gamma^* 2p_y^2 \),
\( \text{O}_2^+: \sigma 1s^2, \sigma^1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma^* 2p_x^2, \gamma^* 2p_y^2 \)

Bond order \( = \frac{10 - 5}{2} = 2.5 \)

(One unpaired electron in antibonding molecular orbital)

Hence \( \text{O}_2 \) as well as \( \text{O}_2^+ \) is paramagnetic, and bond order of \( \text{O}_2^+ \) is greater than that of \( \text{O}_2 \).

49. (d) \( \text{ClO}_3^- \)

(d) \( \text{XeF}_4 \)

\( \gamma^* 2p_y^2 \)

Pyramidal

\( \gamma^* 2p_y^2 \)

Irregular tetrahedral

50. (d) (i) In \( \text{Na}_2\text{O}_2 \), we have \( \text{O}_2^- \) ion. Number of valence electrons of the two oxygen in \( \text{O}_2^- \) ion \( = 8 \times 2 + 2 = 18 \) which are present as follows

\( \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_x^2, \gamma^* 2p_y^2 \),
\( \sigma 2p_y^2 = \pi 2p_x^2 \),
\( \sigma^* 2p_y^2 = \pi^* 2p_x^2 \)

\( \therefore \) Number of unpaired electrons \( = 0 \), hence, \( \text{O}_2^- \) is diamagnetic.

(ii) No. of valence electrons of all atoms in \( \text{O}_2 = 6 \times 3 = 18 \).

Thus, it also, does not have any unpaired electron, hence it is diamagnetic.

(iii) No. of valence electrons of all atom in \( \text{Na}_2\text{O} = 2 \times 5 + 6 = 16 \). Hence, here also all electrons are paired. So it is diamagnetic.

(iv) In \( \text{K}_2\text{O} \), we have \( \text{O}_2^- \). No. of valence electrons of all atoms in \( \text{O}_2^- = 2 \times 6 + 1 = 13 \),

Thus it has one unpaired electron, hence it is paramagnetic.

51. (a) Molecular electronic configuration of

\( \text{CO}: \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \pi 2p_y^2, \pi^* 2p_x^2 \)

Therefore, bond order \( = \frac{N_b - N_a}{2} = \frac{10 - 4}{2} = 3 \)

\( \text{NO}^+: \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \pi 2p_y^2, \pi^* 2p_x^2 \)

Bond order \( = \frac{10 - 4}{2} = 3 \)

\( \text{CN}^- = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \pi 2p_y^2, \pi^* 2p_x^2 \)
Bond order $= \frac{10-4}{2} = 3$

$N_2 : \sigma_1s^2, \sigma^*1s^2, \sigma_2s^2, \sigma^*2s^2, \pi_2p_y^2 = \pi_2p_x^2, \sigma_2p_z^2$

Bond order $= \frac{10-4}{2} = 3$

$\text{NO}^- : \sigma_1s^2, \sigma^*1s^2, \sigma_2s^2, \sigma^*2s^2, \sigma_2p_x^2, \pi_2p_y^2, \pi^*2p_y^1 = \pi^*2p_x^1$

Bond order $= \frac{10-6}{2} = 2$

:. $\text{NO}^-$ has different bond order from that in CO.

52. (a) Molecular orbital configuration of $B_2(10)$ as per the condition will be

$\sigma_1s^2, \sigma^*1s^2, \sigma_2s^2, \sigma^*2s^2, \pi_2p_y^2$

Bond order of $B_2 = \frac{6-4}{2} = 1$, $B_2$ will be diamagnetic.

53. (d) $\text{OSF}_2 : \frac{N}{2} = \frac{6+2}{2} = 4$. It has 1 lone pair.

(Shape is trigonal pyramidal)

The shapes of $\text{SO}_3, \text{BrF}_3$ and $\text{SiO}_3^2-$ are triangular planar respectively.

54. (b) $\text{Ni}^{2+} + 4\text{Cl}^- \rightarrow [\text{NiCl}_4]^{2-}$

$[\text{NiCl}_4]^{2-} = 3d^8$ configuration with nickel in +2 oxidation state, $\text{Cl}^-$ being weak field ligand does not compel for pairing of electrons.

So,

$[\text{NiCl}_4]^{2-}$

$3d$

$4s$

$4p$

$\text{sp}^3$ hybridisation

Hence, complex has tetrahedral geometry

$\text{Ni}^{2+} + 4\text{CN}^- \rightarrow [\text{Ni(CN)}_4]^{2-}$

$\text{Ni}^{2+} + 6\text{H}_2\text{O} \rightarrow [\text{Ni(H}_2\text{O)}_6]^{2+}$

$[\text{Ni(H}_2\text{O)}_6]^{2+} = 3d^8$ configuration with nickel in +2 oxidation state. As with $3d^8$ configuration two $d$-orbitals are not available for $d^2sp^3$ hybridisation. So, hybridisation of Ni (II) is $sp^3d^2$ and Ni (II) with six co-ordination will have octahedral geometry.

55. (c) $\text{Be}_2 = \sigma_1s^2 \sigma^*1s^2 \sigma_2s^2 \sigma^*2s^2$

$B_2 = \sigma_1s^2 \sigma^*1s^2 \sigma_2s^2 \sigma^*2s^2 \sigma_2^2 \pi_2p_z^2$

$C_2 = \sigma_1s^2 \sigma^*1s^2 \sigma_2s^2 \sigma^*2s^2 \pi_2p_z^2 \pi_2p_y^1$.

Thus only $C_2$ will be paramagnetic.

56. (a) $\text{Ni}^{2+}$ with $\text{NH}_3$ shows $\text{CN} = 6$ forming $[\text{Ni(NH}_3)_6]^{2+}$

(Octahedral)

$\text{Pr}^{2+}$ with $\text{NH}_3$ shows $\text{CN} = 4$ forming $[\text{Pt(NH}_3)_4]^{2+}$

(5d series CMA, square planer)

$\text{Zn}^{2+}$ with $\text{NH}_3$ shows $\text{CN} = 4$ forming $[\text{Zn(NH}_3)_4]^{2+}$

(3d$^{10}$ configuration, tetrahedral)

D. MCQs with One or More than One Correct

1. (a, c) $\text{CO}_2$, $\text{HgCl}_2$ and $\text{C}_2\text{H}_2$ have linear structure ($sp$ hybridization), while $\text{SnCl}_2$ is trigonal planar ($sp^2$ hybridisation). $\text{NO}_2$ has angular structure ($V$-shape).
### Chemical Bonding and Molecular Structure

#### 2. Lewis dot structure

\[
\begin{align*}
\text{O}_2^-: & \quad \begin{array}{c}
\cdot \cdot \\
\cdot \cdot
\end{array} \\
\text{F}_2: & \quad \begin{array}{c}
\cdot \\
\cdot
\end{array}
\end{align*}
\]

#### 3. Neutral molecule

\[
\begin{align*}
\text{SO}_3: & \quad \begin{array}{c}
\cdot \\
\cdot \\
\cdot
\end{array} \\
\text{N}_2: & \quad \begin{array}{c}
\cdot \cdot \\
\cdot \cdot
\end{array}
\end{align*}
\]

#### 4. (b, c)

- Alkanes (a) and (d) don’t have dipole moment because of symmetry in them.
- cis 3-hexene
  - $\text{C}_2H_5$ $\text{C} = \text{C} \text{CH}_3$
  - trans 2-pentene
  - $\text{C}_2H_5$ $\text{C} = \text{C} \text{CH}_3$

These alkenes are not symmetrical and so they have dipole moment.

#### 5. (b, c)

- **Compounds**
  - BrF$_5$
  - ClF$_3$
  - XeF$_4$
  - SF$_4$

- **Number of lone pairs on central atom**
  - $\rightarrow 1$
  - $\rightarrow 2$
  - $\rightarrow 2$
  - $\rightarrow 1$

#### 6. (a, c)

- **Molecular orbital energy configuration of C$_2^2^-$** is
  \[
  \sigma^2_{1s}, \sigma^*_{1s}, \sigma^2_{2s}, \sigma^2_{2p_x}, \pi^2_{2p_y} = \pi^2_{2p_y}, \sigma^2_{2p_z}
  \]
  - In the MO of C$_2^2^-$, there is no unpaired electron hence it is diamagnetic
- **Bond order of O$_2^2^-$ is 3 and O$_2$ is 2 therefore bond length of O$_2$ is greater than O$_2^2^-$**
- **The molecular orbital energy configuration of N$_2$** is
  \[
  \sigma^2_{1s}, \sigma^*_{1s}, \sigma^2_{2s}, \sigma^2_{2p_x}, \pi^2_{2p_y} = \pi^2_{2p_y}, \sigma^1_{2p_z}
  \]
  - Bond order of N$_2$ = $\frac{1}{2}(9 - 4) = 2.5$
  - The molecular orbital energy configuration of N$_2^+$ is
    \[
    \sigma^2_{1s}, \sigma^*_{1s}, \sigma^2_{2s}, \sigma^2_{2p_x}, \pi^2_{2p_y} = \pi^2_{2p_y}, \sigma^2_{2p_z}, \pi^*_1_{2p_y}
    \]
  - Bond order of N$_2^+$ = $\frac{1}{2}(10 - 5) = 2.5$
- **He$_4^+$ has less energy in comparison to two isolated He atoms because some energy is released during the formation of He$_4^+$ from 2 He atoms.**

#### E. Subjective Problems

1. H$_2$O molecules are held together by hydrogen bonding which is stronger force of attraction but H$_2$S molecules are held together by vander waals forces of attraction, which are weaker forces. As a result water molecules come closer and exist in liquid state.

5. (i) Increasing order of bond dissociation energy.
   
\[
\begin{align*}
\text{F}_2 < \text{Cl}_2 < \text{O}_2 < \text{N}_2
\end{align*}
\]

**NOTE:** Fluorine-fluorine bond energy is less than the Cl–Cl because of larger repulsion between the non-bonded electrons of the two smaller fluorine atoms (chlorine atoms are larger in size; hence their lone pair of electrons exert less repulsion than fluorine). Oxygen having two pairs of lone pairs of electrons on each atom exert less repulsion than that of chlorine or fluorine each having three lone pairs of electrons. Nitrogen having only one lone pair of electrons exert minimum repulsion, hence it is the most stable.

(ii) H-bonding is an electrostatic attractive force between covalently bonded hydrogen atom of one molecule and an electronegative atom (F, O, N). Further, higher the electronegativity and smaller the size of the atom, the stronger is the hydrogen bond.

**NOTE:** Although Cl has the same electronegativity as nitrogen, it does not form effective hydrogen bonds. This is because of its larger size than that of N with the result its electrostatic attractions are weak. Similarly, sulphur forms a very weak hydrogen bond due to its low electronegativity, although oxygen present in the same group forms a strong hydrogen bond.

Hence the order is $S < Cl < N < O < F$

(iii) In KCl, O$_2$ is present as O$_2^-$, while in O$_2$(AsF$_4$)$^+\text{O}_2^-$ is present as O$_2^+$. Write down the MO configuration of O$_2$, O$_2^-$ and O$_2^+$. 

O₂ : \( \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_x^2, (\pi^* 2p_y^2, (\pi^* 2p_y^1) = \pi^* 2p_z^1 \).

\[
\text{Thus the bond order } = \frac{10 - 6}{2} = 2
\]

O₂⁻ : Same as above except \( \pi^* 2p_y^2, \pi^* 2p_x^1 \) in place of \( \pi 2p_y^1, \pi 2p_z^1 \).

\[
\text{Thus the bond order in } O_2^- = \frac{10 - 7}{2} = 1.5
\]

O₂⁺ : Same as in O₂ except \( \pi^* 2p_y^1 = \pi^* 2p_x^0 \) in place of \( \pi 2p_y^1, \pi 2p_z^1 \).

\[\therefore \text{Bond order in } O_2^+ = \frac{10 - 5}{2} = 2.5\]

\[\therefore \text{Bond order in the three species is } O_2^+ > O_2 > O_2^- \text{ or } O_2[AsF_4] > O_2 > K_2O_2\]

6. Dipole moment, \( \mu = e \times d \) coulombs metre

For KCl \( d = 2.6 \times 10^{-10} \) m

For complete separation of unit charge (electronic charge)

(;e) = 1.602 \times 10^{-19} \text{ C}

Hence \( \mu = 1.602 \times 10^{-19} \times 2.6 \times 10^{-10} = 4.1652 \times 10^{-29} \text{ cm} \)

\[\mu_{KCl} = 3.336 \times 10^{-29} \text{ coulomb meter (given)}\]

\[\therefore \% \text{ Ionic character of } KCl = \frac{3.336 \times 10^{-29}}{4.1652 \times 10^{-29}} \times 100 = 80.09\%\]

7. The structure of OF₂ is similar to H₂O and involves \( sp^3 \) hybridization on O atom. The bond angle in F-O-F is not exactly 109°28′, but distorted (103°) due to presence of lone pair of electrons on O as well as F leading to V shape or tetrahedral positions with two positions occupied by lone pair of electrons of the molecule.

Oxidation number of F = -1

\[\therefore \text{Oxidation number of O = +2}\]

8. Magnetic moment (\( \mu \)) = \( \sqrt{n(n+2)} \) BM

where \( n \rightarrow \) number of unpaired electrons

\( \mu = 1.73 \text{ BM for vanadium ion} \)

\[1.73 \text{ BM} = \sqrt{n(n+2)} \quad \text{So, } (1.73)^2 = n(n + 2)\]

\[3.0 = n^2 + 2n \quad \text{or} \quad n^2 + 2n - 3 = 0\]

\[n^2 + 3n - n - 3 = 0 \quad \therefore n(n + 3) - 1(n + 3) = 0\]

\[(n - 1)(n + 3) = 0 \quad \text{Correct value of } n = 1\]

Thus no. of unpaired electrons in vanadium ion = 1

\[V = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^3, 4s^2\]

9. In H₂S, no. of hybrid orbitals = \( \frac{1}{2}(6 + 2 - 0 + 0) = 4 \)

Hence here sulphur is \( sp^3 \) hybridised, so

\[\begin{array}{c}
16S \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^4, 3p^1, 3p^1, 3p^1, 3p^1, 3p^1 \end{array}\]

\( \text{or \hspace{1cm} } \begin{array}{c}
S^+ S^- S^+
\end{array}\]

\[\text{NOTE : Due to repulsion between } lp - lp; \text{ the geometry of } H_2S \text{ is distorted from tetrahedral to V-shape.}\]

In PCl₅, no. of hybrid orbitals = \( \frac{1}{2}(5 + 3 - 0 + 0) = 4 \)

Hence, here P shows \( sp^3 \)-hybridisation

\[\begin{array}{c}
15P \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^4, 3p^1, 3p^1, 3p^1, 3p^1 \end{array}\]

\( \text{or \hspace{1cm} } \begin{array}{c}
P
\end{array}\]

\[\text{Thus due to repulsion between } lp - lp, \text{ geometry is distorted from tetrahedral to pyramidal.}\]

10. MO configuration of O₂⁻:

\[\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_x^2, (\pi^* 2p_y^2, (\pi^* 2p_y^1) = \pi^* 2p_z^1 \).

\[\{\pi^* 2p_y^1 = \pi^* 2p_z^1\}\]

Bond order = \( \frac{1}{2}(10 - 6) = 2\)

Since O₂ molecule has two unpaired electrons, it is paramagnetic.

11. PCl₅ : \( sp^3d \) Trigonal bipyramidal

BrF₅ : \( sp^3d^2 \) Square pyramidal
12. First determine the total number of electron pairs around the central atom.

\[
\text{XeF}_4 = \frac{N}{2} = \frac{8+4}{2} = 6
\]

Thus in \text{XeF}_4, \text{Xe} is sp\text{3}d\text{2} hybridised. The structure of the molecule is octahedral and shape is square planar with two lone pair of electrons.

For \text{OSF}_4: \frac{N}{2} = \frac{6+4}{2} = 5

Thus the central atom (S) is sp\text{3}d hybridised leading to trigonal bipyramidal structure with no lone pair of electrons.

F. Match the Following

1. (e) P. \hspace{1cm} \text{d-d (σ bonding)}

Q. \hspace{1cm} \text{p-d (π bonding)}

R. \hspace{1cm} \text{p-d (π antibonding)}

S. \hspace{1cm} \text{d-d (σ antibonding)}

H. Assertion & Reason Type Questions

1. (a) Both assertion and reason are correct. The reason explains the assertion as the central O-atom cannot have more than 8 electrons (octet).

2. (c) LiCl is a covalent compound since due to the large size of the anion (Cl\textsuperscript{-}) its effective nuclear charge lessens and its valence shells are held less tightly towards its nucleus. Here, assertion is correct but reason is incorrect.

I. Integer Value Correct Type

1. (0) According to VSEPR theory, number of electron pairs around central atom (Br) are 6.

\[
\frac{N}{2} = \frac{7+5}{2} = 6
\] (Five are bond pairs and one is lone pair)

Its geometry is octahedral but due to lone pair-bond pair repulsion, the four fluorine atoms at corner are forced towards the upper fluorine atom thus reducing F–Br–F angle from 90° to 84.8°.

2. (6) Structure of melamine is as follows:

Total no. of lone pairs of electron is ‘6’.

3. (4)

- \text{XeF}_4: \hspace{1cm} \text{Square planar (sp}\text{3}d\text{2})
- \text{SF}_4: \hspace{1cm} \text{See-saw (sp}\text{3}d\text{)}
- \text{SiF}_4: \hspace{1cm} \text{Tetrahedral (sp}\text{3})
- \text{BF}_4\text{–}: \hspace{1cm} \text{Tetrahedral (sp}\text{3})
- \text{BrF}_4\text{–}: \hspace{1cm} \text{Square planar (sp}\text{3}d\text{2})
- [\text{Cu(NH}_3\text{)}_4]^{2\text{+}}: \hspace{1cm} \text{Square planar (dsp}\text{2})
- [\text{FeCl}_4]^{2\text{–}}: \hspace{1cm} \text{Tetrahedral (sp}\text{3})
1. (a) In NH₃ and BF₄⁻, the hybridisation is sp³ and the bond angle is almost 109°28'.

2. (b) O₂⁻(15) = KKσ2s², σ*2s², σ2p⁵, \( \{\pi2p_\pi^2 = \pi2p_y^2, \{\pi*2p_y^1 = \pi2p_\pi^1\} \)

Bond order = \( \frac{1}{2}(8-3) = \frac{5}{2} = 2.5 \)

O₂(16) = KKσ2s², σ*2s², σ2p⁴, \( \{\pi2p_\pi^2 = \pi2p_y^2, \{\pi*2p_y^1 = \pi^*2p_\pi^1\} \)

Bond order = \( \frac{1}{2}(8-4) = 2 \)

O₂⁻(17) = KKσ2s², σ*2s², σ2p⁵, \( \{\pi2p_\pi^2 = \pi2p_y^2, \{\pi*2p_y^1 = \pi^*2p_\pi^1\} \)

Bond order = \( \frac{1}{2}(8-5) = 1.5 \)

O₂⁻(18) = KKσ2s², σ*2s², σ2p⁶, \( \{\pi2p_\pi^2 = \pi2p_y^2, \{\pi*2p_y^1 = \pi^*2p_\pi^1\} \)

Bond order = \( \frac{1}{2}(8-6) = 1 \)

**NOTE**: As we know that as the bond order decreases, stability also decreases and hence the bond strength also decreases. Hence the correct order of their increasing bond strength is

\[ O_2^- < O_2 < O_2^+ \]

3. (a) **TIPS/Formulæ:**

\[
\text{Hybridisation} = \frac{1}{2} \left[ \left( \text{No. of electrons} \right) \text{in valence} + \left( \text{No. of monovalent atoms around it} \right) - \left( \text{charge on cation} \right) + \left( \text{charge on anion} \right) \right]
\]

(a) For AlH₃,

Hybridisation of Al atom = \( \frac{1}{2}[3 + 3 - 0 + 0] = 3 = \text{sp}^2 \)

For AlH₄⁻,

Hybridisation of Al atom = \( \frac{1}{2}[3 + 4 - 0 + 1] = 4 = \text{sp}^3 \)

(b) For H₂O,

Hybridisation of O atom = \( \frac{1}{2}[6 + 2 - 0 + 0] = 4 = \text{sp}^3 \)

For H₂O⁺, Hybridisation of O atom = \( \frac{1}{2}[6 + 3 - 1 + 0] = 4 = \text{sp}^3 \)

(c) For NH₃

Hybridisation of N atom = \( \frac{1}{2}[5 + 3 - 0 + 0] = 4 = \text{sp}^3 \)

For NH₄⁺, Hybridisation of N atom = \( \frac{1}{2}[5 + 4 - 1 + 0] = 4 = \text{sp}^3 \)

Thus hybridisation changes only in option (a).

4. (c) In ether, there is no H-bonding while alcohols have intermolecular H-bonding.

5. (b) Both NO₃ and O₃ have angular shape and hence will have net dipole moment.

6. (b) In H₂S, due to low electronegativity of sulphur the L.P. - L. P. repulsion is more than B. P. - B. P. repulsion and hence the bond angle is minimum.

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<td>H₂O</td>
<td>H₂S</td>
<td>NH₃</td>
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<tr>
<td>Bond angle</td>
<td>119.5°</td>
<td>104.5°</td>
<td>92.5°</td>
<td>106.5°</td>
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7. (a) Both XeF₂ and CO₂ have a linear structure.
F — Xe — F
O = C = O
8. (a) The order of bond angles
BF₃ > SiH₄ > NH₃ > H₂S
120° 109°28' 107° 92.5°
9. (b) Now since bond order of NO⁺ given (3) is higher than that of NO (2.5). Thus bond length of NO⁺ will be shorter.

10. (b)

11. (a) XeF₄ (sp³d² square planar),
[Ni(CN)₄]²⁻ (dsp² square planar ),
BF₄⁻ (sp³ tetrahedral), SF₄ (sp³d see saw shaped)

12. (d)

14. (c) The distribution of electrons in MOs is as follows:
\[ \text{N}_2^+ \text{(electrons 13)} \quad \sigma^2 \sigma^*^2 \sigma^2 \sigma^*^2 \frac{\pi^2 \pi^*}{\sigma^1 \sigma^*} \]
\[ \text{O}_2 \text{(electrons 16)} \quad \sigma^2 \sigma^*^2 \sigma^2 \sigma^*^2 \frac{\pi^2 \pi^*}{\sigma^1 \sigma^*} \]
\[ \text{O}_2^- \text{(electrons 18)} \quad \sigma^2 \sigma^*^2 \sigma^2 \sigma^*^2 \frac{\pi^2 \pi^*}{\sigma^1 \sigma^*} \]
\[ \text{B}_2 \text{(electrons 10)} \quad \sigma^2 \sigma^*^2 \sigma^2 \sigma^*^2 \frac{\pi^2 \pi^*}{\sigma^1 \sigma^*} \]
Only O₂⁻ does not contain any unpaired electron.

15. (d) In SF₄ the hybridisation is sp³d and the shape of molecule is

16. (b) The bond angle decreases on moving down the group due to decrease in bond pair-bond pair repulsion.
NH₃  PH₃  ASH₃  SbH₃  BiH₃
107°  94°  92°  90°  90°

**NOTE:** This can also be explained by the fact that as the size of central atom increases sp³ hybrid orbital becomes more distinct with increasing size of central atom i.e. pure p- orbitals are utilized in M–H bonding

17. (b) Diamagnetic species have no unpaired electrons
\[ \text{O}_2^- \Rightarrow \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_x^2, \]
\[ \{ \pi 2p_y^2 = \pi 2p_z^2, \{ \pi^* 2p_y^2 = \pi^* 2p_x^2 \} \}
Whereas paramagnetic species has one or more unpaired electrons as in
\[ \text{O}_2 \Rightarrow \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_x^2, \}
\[ \{ \pi^* 2p_y^2 = \pi^* 2p_z^2 \} \]
\[ \text{O}_2^- \Rightarrow 1s^2, 1s^2, 2s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_x^2, \]
\[ \{ \pi 2p_y^2 = \pi 2p_z^2 \} \]
\[ \text{NO} \Rightarrow 1s^2, 1s^2, 2s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma^* 2p_x^2, \]
\[ \{ \pi^* 2p_y^2 = \pi^* 2p_z^2 \} \]

18. (d) Smaller the size and higher the charge more will be polarising power of cation. Since the order of the size of cation is K⁺ > Ca²⁺ > Mg²⁺ > Be²⁺. So the correct order of polarising power is
K⁺ < Ca²⁺ < Mg²⁺ < Be²⁺
19. (c) (a) $N_2$: bond order 3, paramagnetic 
   $N_2^-$: bond order 2.5, paramagnetic 
   (b) $C_2^-$: bond order 2, diamagnetic 
   $C_2^+ $: bond order 1.5, paramagnetic 
   (c) NO: bond order 2.5, paramagnetic 
   NO$^+$: bond order 3, diamagnetic 
   (d) O$_2$: bond order 2, paramagnetic 
   O$_2^+$: bond order 2.5, paramagnetic 

20. (c) **NOTE**: Greater the difference between electronegativity of bonded atoms, stronger will be bond. Since F is most electronegative hence F – H ...... F is the strongest bond. 

21. (a) For any species to have same bond order we can expect them to have same number of electrons. Calculating the number of electrons in various species. 
   O$_2^- (8+8+1=17)$; CN$^- (6+7+1=14)$ 
   NO$^+ (7+8-1=14);$ CN$^+ (6+7-1=12)$ 
   We find CN$^-$ and NO$^+$ both have 14 electrons so they have same bond order. Correct answer is (a). 

22. (b) **NOTE**: The delocalised $p\pi - p\pi$ bonding between filled p-orbital of F and vacant p-orbital of B leads to shortening of B–F bond length which results in higher bond dissociation energy of the B–F bond. 

23. (d) Bond order 
   $$\text{Bond order} = \frac{\text{No. of bonding electrons} - \text{No. of antibonding electrons}}{2}$$ 
   Bond order in O$_2^-$ = $\frac{10-5}{2} = 2.5$ 
   Bond order in O$_2^-$ = $\frac{10-7}{2} = 1.5$ 
   Bond order in O$_2^-$ = $\frac{10-8}{2} = 1$ 
   Bond order in O$_2^+$ = $\frac{10-4}{2} = 3$ 
   Since Bond order $\propto \frac{1}{\text{Bond length}}$ 
   $\therefore$ Bond length is shortest in O$_2^+$. 

24. (c) The proportion of covalent character in an ionic bond is decided by polarisability of the metal cation as well as the electronegativity of both elements involved in bonding. Polarisability is further decided by the density of positive charge on the metal cation. AlCl$_3$ is considered to show maximum covalent character among the given compounds. This is because Al$^{3+}$ bears 3 unit of positive charge and shows strong tendency to distort the electron cloud, thus the covalent character in Al-Cl bond dramatically increases. 

25. (b) The formula to find the hybridisation of central atom is 
   $$Z = \frac{1}{2} \left[ \text{Number of valence electrons on central atom} + \text{No. of monovalent atom attached to it} + \text{negative charge if any} - \text{positive charge if any} \right]$$ 
   For NO$_3^-$, $Z = \frac{1}{2} [5+0+1-0] = 3$ 
   $\text{O} = \text{N} = \text{O} \rightarrow \text{sp}^2$ 
   For NO$_2^+$, $Z = \frac{1}{2} [5+0+0-1] = 2$ 
   For NH$_4^+$, $Z = \frac{1}{2} [5+4+0-1] = 4$ 

26. (d) Pentagonal bipyramidal shape. 

27. (b) Compounds involved in chelation become non-polar. Consequently such compounds are soluble in non-polar solvents like ether, benzene etc. and are only sparingly soluble in water whereas meta and para isomers are more soluble in water & less soluble in non-polar solvents.
bond order for He$_2$ = $\frac{1}{2}(2-2) = 0$
so both H$_2^+$ and He$_2$ does not exist

32. (b) Li$_2$ = $\sigma 1s^2 \sigma*1s^2 \sigma 2s^2$, \( \therefore \) Bond order = $\frac{1}{2}(4-2) = 1$

\[ \text{Li}_2^+ = \sigma 1s^2 \sigma*1s^2 \sigma 2s^1, \text{B.O.} = \frac{1}{2}(3-2) = 0.5 \]

\[ \text{Li}_2^- = \sigma 1s^2 \sigma*1s^2 \sigma 2s^2 \sigma *2s^1, \text{B.O.} = \frac{1}{2}(4-3) = 0.5 \]

The bond order of Li$_2^+$ and Li$_2^-$ is same but Li$_2^+$ is more stable than Li$_2^-$ because Li$_2^+$ is smaller in size and has 2 electrons in Anti bonding orbital whereas Li$_2^-$ has 3 electrons in Anti bonding orbital. hence Li$_2^+$ is more stable than Li$_2^-$

33. (d) In both the molecules the bond moments are not canceling with each other and hence the molecules has a resultant dipole and hence the molecule is polar.

34. (c) Hybridization (H) = $\frac{1}{2} \times (\text{no. of valence electrons of central atom + no. of Monovalent atoms attached to it} + (-ve charge if any) - (+ve charge if any)}$

\[ \text{NO}_2^- = \frac{1}{2}[5+0+0-1] = 2 \text{ i.e. } sp^2 \text{ hybridisation} \]

\[ \text{NO}_2 = \frac{1}{2}[5+0+1-0] = 3 \text{ i.e. } sp^2 \text{ hybridisation} \]

\[ \text{NO}_3^- = \frac{1}{2}[5+0+1-0] = 3 \text{ i.e. } sp^2 \text{ hybridisation} \]

The lewis structure of NO$_2$ shows a bent molecular geometry with trigonal planar electron pair geometry hence the hybridization will be sp$^2$
States of Matter

Section-A : JEE Advanced/ IIT-JEE

A. Fill in the Blanks

1. 900; Energy of one mole of an ideal monoatomic gas $= \frac{3}{2} \text{ RT}$
   
   \[ R = 8.314 \text{ J K}^{-1} \text{ mole}^{-1} = 1.99 \text{ cal K}^{-1} \text{ mole}^{-1} \]
   
   \[ T = 27^\circ \text{C} = 273 + 27 = 300 \text{ K} \]
   
   \[ \Rightarrow E = \frac{3}{2} \times 1.99 \times 300 = 900 \text{ cal} \]

2. R. \[ \therefore C_p - C_v = R \]

3. Inversely, time; \[ \frac{r_1}{r_2} = \sqrt\frac{d_1}{d_2} = \frac{l_2}{l_1} = \sqrt\frac{M_2}{M_1} \]

4. 0.25; \[ \therefore 5.6l = \frac{1}{4} \text{ mole of an ideal gas} \]

Using ideal gas equation

\[ PV = nRT = \frac{1}{4} \text{ RT = 0.25 RT} \]

5. 1 : 16; \[ \frac{\text{KE}_{\text{O}_2}}{\text{KE}_{\text{H}_2}} = \frac{(3/2) n_{\text{O}_2} \text{RT}}{(3/2) n_{\text{H}_2} \text{RT}} = \frac{n_{\text{O}_2}}{n_{\text{H}_2}} = \frac{8}{32} = \frac{1}{4} \]

Section-B : JEE Main/ AIEEE
B. True / False

1. False : K.E. = $\frac{3}{2}$ KT, and cannot be zero at 0°C or 273 K.
2. False : The pressure exerted by the gas is the result of collisions of the molecules on the walls of the container.
3. False : The constant ‘a’ reflects the intermolecular attraction between gaseous molecules. The constant ‘b’ reflects the actual volume of one mole of gaseous molecules.
4. False : An ideal gas cannot be liquefied as there exists no intermolecular attraction between molecules.

C. MCQs with One Correct Answer

1. (a) TIPS/Formulae:

Mole fraction of $O_2 = \frac{\text{Moles of } O_2}{\text{Total moles}}$

Partial pressure of $O_2 = $ Mole fraction of $O_2 \times \text{Total Pressure}$

Mole fraction of $O_2 = \frac{32}{W} \times \frac{W}{32} = \frac{1}{3}$

2. (b) The temperature at which a real gas behaves like an ideal gas is called Boyle’s temperature or Boyle’s point.

3. (a) $U_{rms} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{8RT}{\pi M}}$ or $\sqrt{8} : \sqrt{\pi} = 1.086 : 1$

4. (b) Average kinetic energy depends only on temperature and does not depend upon the nature of the gas. (:: K.E. = 3/2 KT)

5. (b) Pressure exerted by hydrogen will be proportional to its mole fraction.

Mole fraction of $H_2 = \frac{w}{2} \times \frac{w}{16} = \frac{8}{9}$

6. (d) $r_1 \div r_2 = \sqrt{\frac{d_2^2}{d_1^2}} = \sqrt{\frac{M_2}{M_1}}$

7. (a) $U_{av} = \sqrt{\frac{8RT}{\pi M}}$; $T_1 = 27 + 273 = 300$ K

$U_{av_1} = \sqrt{\frac{T_1}{T_2}} \div \frac{0.3}{0.3} \div \frac{300}{1200} = \sqrt{1} = 1$

or $U_{av_2} = 0.6$ m/sec.

8. (c) $(P + \frac{a}{V^2})(V - b) = RT$; Here $(P + \frac{a}{V^2})$ represents the intermolecular forces.

9. (b) TIPS/Formulae:

Rate of diffusion $\propto \frac{1}{\sqrt{\text{Molecular mass}}}$

.: Molecular mass of HCl > molecular mass of NH₃

.: HCl diffuses at slower rate and white ammonium chloride is first formed near HCl bottle.

10. (c) ‘a’ is directly related to forces of attraction. Hence greater the value of ‘a’, more easily the gas is liquefied.

11. (b) TIPS/Formulae:

$d = \frac{PM}{RT}$

It means density of gas is directly proportional to pressure and inversely proportional to temperature.

Density of neon will be maximum at highest pressure and lowest temperature.

:: (b) is correct answer.

12. (a) $\frac{KCH_4}{r_x} = 2 = \frac{M_x}{M_{CH_4}} = \sqrt{\frac{M_x}{16}}$, or $M_x = 64$

13. (d) Pressure exerted by the gas, $P = \frac{1}{3} \frac{mn_2}{V}$ ...(1)

Here, $n = \text{root mean square velocity}$

$m = \text{mass of a molecule}$, $n = \text{No. of molecules of the gas}$

Hence (a) & (b) are clearly wrong.

Again $u^2 = \frac{3RT}{M}$ [explained from (1)]

Here, $M = \text{Molecular wt. of the gas}$;

Hence (c) is wrong

Further, Average K.E. = $\frac{3}{2}$ KT; Hence (d) is true.

14. (a) Due to increase in the temperature, the kinetic energy of the gas molecules increases resulting in an increase in average molecular speed. The molecules are bombarded to the walls of the container with a greater velocity resulting in an increase in pressure.

15. (a) The mean free path, $\lambda = \frac{1}{\sqrt{2\pi a^2 N}}$

or $\lambda \propto \frac{1}{a^2}$, where $a = \text{molecular diameter}$

.: Smaller the molecular diameter, longer the mean free path. Hence H₂ is the answer.

16. (c) NOTE : The value of ‘a’ indicates the magnitude of attractive forces between gas molecules.

Value of ‘a’ $\propto \text{size of molecule}$.

.: inert gas will have minimum value of ‘a’ followed by H₂O, C₆H₆ and C₆H₅CH₃

17. (c) The expression of root mean square speed is $U_{rms} = \frac{3RT}{M}$
Hence,
\[
\frac{U_{\text{rms}}(H_2)}{U_{\text{rms}}(O_2)} = \left[ \frac{3R(50K)/(2 \text{ g mol}^{-1})}{3R(800K)/(32 \text{ g mol}^{-1})} \right]^{1/2} = 1
\]

18. (b) Under identical conditions, \( \frac{n_2}{n_1} = \frac{M_2}{M_1} \)

As rate of diffusion is also inversely proportional to time, we will have, \( t_2 = \sqrt{\frac{M_2}{M_1}} t_1 \)

(a) Thus, For He, \( t_2 = \frac{4}{\sqrt{2}} (5s) = 5\sqrt{2}s \approx 10s \)
(b) For O\(_2\), \( t_2 = \frac{32}{2} (5s) = 20s \)
(c) For CO, \( t_2 = \frac{28}{2} (5s) \approx 25s \)
(d) For CO\(_2\), \( t_2 = \frac{44}{2} (5s) \approx 55s \)

19. (b) \( \text{N}_2\text{O}_4 (g) \rightleftharpoons 2 \text{NO}_2(g) \)

At start: 100/92 mol = 1.08 mol
At equilibrium: 80/92 mol = 0.86 mol
20/46 mol = 0.43 mol

According to ideal gas equation, at two conditions
At 300 K; \( P_0 V = n_0 RT_0 \)
\( 1 \times V = 1.08 \times R \times 300 \) \( \cdots \) (i)
At 600 K; \( P_1 V = n_1 RT_1 \)
\( P_1 \times V = (0.86 + 0.43) \times R \times 600 \) \( \cdots \) (ii)

Divide (ii) by (i),
\[ \frac{P_1}{P_0} = \frac{1.29 \times 600}{1.08 \times 300} \]
\[ P_1 = \frac{1.29 \times 2}{1.08} = 2.38 \text{ atm.} = 2.4 \text{ atm.} \]

20. (b) The compressibility factor of a gas is defined as
\[ Z = \frac{pV_m}{RT} \]
For an ideal gas, \( pV_m = RT \). Hence \( Z = 1 \)

21. (c) For an ideal-gas behaviour, the molecules of a gas should be far apart. The factors favouring this condition are high temperature and low pressure.

22. (c) \( \text{TIPS/Formulae} : \)
\[ U_{\text{rms}} = \sqrt{\frac{3RT}{M}} \]
\[ \Rightarrow \sqrt{\frac{3RT_{H_2}}{2}} = \sqrt{\frac{3RT_{N_2}}{28}} \]
\[ \therefore T_{N_2} = 2T_{H_2} \] or \( T_{N_2} > T_{H_2} \)

23. (b) \( \frac{(PV)_{\text{observed}}}{(PV)_{\text{ideal}}} < 1 \)
\[ \Rightarrow V_{\text{obs}} < V_{\text{ideal}}, V_{\text{obs}} < 22.4 \text{ litre.} \]
24. (c) Mass of 1 L of vapour = volume \times density
\[ = 1000 \times 0.0006 = 0.6 \text{ g} \]
\[ V_{\text{of liquid water}} = \frac{\text{mass}}{\text{density}} = \frac{0.6}{1} = 0.6 \text{ cm}^3 \]
25. (d) \( U_{\text{rms}} = \sqrt{\frac{3RT}{M}} \)
Using ideal gas equation,
\[ PV = nRT \]
\[ \Rightarrow \frac{pV}{M} = \frac{RT}{w} = \frac{P}{d} \]
where \( d \) is the density of the gas
\[ \therefore U_{\text{rms}} = \frac{3P}{d} \text{ at constant pressure, } U_{\text{rms}} \propto \frac{1}{\sqrt{d}} \]
26. (c) \( \text{TIPS/Formulae} : \)
Find the volume by either
\[ V = \frac{RT}{p} (PV = RT) \text{ or } P_1 V_1 = P_2 V_2 \text{ and and match it with the values given in graph to find correct answer.} \]
Volume of 1 mole of an ideal gas at 273 K and 1 atm is 22.4 L and that at 373 K and 1 atm pressure is calculated as;
\[ V = \frac{RT}{P} = \frac{0.082 \times 373}{1} = 30.58L = 30.6 \text{ L} \]
27. (b) Upon increase of temperature the internal energy of water or any system increases resulting in decrease in intermolecular force and hence decrease in surface tension. Surface tension decreases with increase in mobility due to increase in temperature.
28. (c) For positive deviation: \( PV = nRT + nPb \)
\[ \Rightarrow \frac{PV}{nRT} = 1 + \frac{b}{RT} \]
Thus, the factor \( nPb \) is responsible for increasing the \( PV \) value, above ideal value. \( b \) is actually the effective volume of molecule. So, it is the finite size of molecules that leads to the origin of \( b \) and hence positive deviation at high pressure.
29. (c) Average KE = \( \frac{1}{2} M u_{\text{rms}}^2 \)
\[ \therefore u_{\text{rms}}^2 = \frac{2E}{M} \text{ or } u_{\text{rms}} = \sqrt{\frac{2E}{M}} \]
30. (b) \( \text{TIPS/Formulae} : \)
Use Graham’s law of diffusion
\[ \frac{n_{\text{He}}}{n_{\text{CH}_4}} = \sqrt{\frac{M_{\text{CH}_4}}{M_{\text{He}}}} = \sqrt{\frac{16}{4}} = 2 \]
31. (a) \( TV^{\gamma-1} = \text{Constant} \) \( \therefore \text{change is adiabatic} \)
\[ T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1} \]

For monoatomic gas \( \gamma = \frac{5}{3} \)
\[ \therefore \ T_1 V_1^{2/3} = T_2 V_2^{2/3} \Rightarrow T(1)^{2/3} = T(2)^{2/3} \]
\[ T_2 = \left( \frac{T}{2^{(2/3)}} \right) \]

32. (b) In general, the molar heat capacity for any process is given by
\[ C = C_v + \frac{R}{1 - n} \], when \( PV^n = \text{constant} \)

Here \( \frac{P}{V} = 1 \), i.e. \( PV^{\gamma-1} = \text{constant} \)

For monoatomic gas, \( C_v = \frac{3}{2} R \)
\[ \therefore C = \frac{3}{2} R + \frac{R}{1 - (-1)} = \frac{3}{2} R + \frac{4R}{2} = 2R \]

33. (b) Correction factor for attractive force for \( n \) moles of real gas is given by the term mentioned in (b).

34. (c) \[ PV = \left( P + \frac{a}{V^2} \right) V = RT \]
\[ PV + a/V = RT, PV = RT - a(V) \]
\[ y = RT - a(x) \]
So, slope \( a = \frac{21.6 - 20.1}{3 - 2} = \frac{1.5}{1} = 1.5 \)

35. (d) A solution of \( \text{CH}_3\text{OH} \) and water shows positive deviation from Raoult’s law, it means by adding \( \text{CH}_3\text{OH} \) intermolecular force of attraction decreases and hence surface tension decreases.

• By adding KCl in water, intermolecular force of attraction bit increases, so surface tension increases by small value.

• By adding surfactant like \( \text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3\text{Na}^+ \), surface tension decreases rapidly and after forming micelle it slightly increases.

D. MCQs with One or More Than One Correct

1. (b) No work is required to tear apart the molecules due to the absence of attractive forces in an ideal gas.

2. (a,b) At constant temp., when gas expands the K.E. of the molecules remains the same, but the pressure decreases. \( \therefore P \propto \frac{1}{V} \)

3. (d) Pressure exerted by \( H_2 \) is proportional to its mole fraction.

\[ \text{Mole fraction of } H_2 = \frac{2}{W} \times \frac{W}{2 + \frac{W}{30}} = \frac{30}{32} = \frac{15}{16} \]

4. (c) According to Graham’s law of diffusion for two gases undergoing diffusion at different pressures through same hole

\[ \frac{r_A}{r_B} = \sqrt{\frac{M_B}{M_A}} \times \frac{P_A}{P_B} \]

\[ \left( r \propto P \sqrt{\frac{1}{M}} \right) \text{ At constant temperature} \]

5. (b) For gas A, \( a = 0, Z = 1 + \frac{Pb}{RT} \) implies \( Z \) varies linearly with pressure.

For gas B, \( b = 0, Z = 1 - \frac{a}{VRT} \). Hence, \( Z \) does not vary linearly with pressure.

Given the intersection data for gas C, it is possible to find the values of ‘a’ and ‘b’. All van der Waal gases, like gas C, give positive slope at high pressures.

6. (a,c) van der Waals equation is

\[ P + \frac{n^2a}{V^2} = nRT \] [For \( n \) moles of a gas]

\( a, b \) are van der Waals constants

The ideal gas equation is \( PV = nRT \) [For \( n \) moles of a gas]

where \( P \) is pressure exerted by ideal gas and \( V \) is volume occupied by ideal gas.

In van der Waals equation the term \( \left( P + \frac{n^2a}{V^2} \right) \)

represents the pressure exerted by the gas and \( (V - nb) \)
the volume occupied by the gas. At low pressure, when
the gas occupies large volume the intermolecular distance between gaseous molecules is quite large and in such case there is no significant role played by intermolecular forces and thus the gas behaves like an ideal gas thus (a) is correct

NOTE: Under high pressure the intermolecular distance decreases and the intermolecular forces play a significant role and the gas shows a deviation from ideal behaviour.

Thus (b) is not correct.

a, b i.e. the van der Waals coefficients defined on the nature of gas and are independent of temperature so (c) is correct.

The pressure \( P + \frac{n^2a}{V} \) is not lower than \( P \) so (d) is not correct.

Hence the correct answer is (a, c).

7. (a, b, c, d)

8. (c) \( PVb = RT \)  
\[ \Rightarrow \frac{PV}{RT} = \frac{Pb}{RT} + 1 \]
\[ \Rightarrow Z = 1 + \frac{Pb}{RT} \]
Hence \( Z > 1 \) at all pressures.

This means, repulsive tendencies will be dominant when interatomic distance are small.

This means, interatomic potential is never negative but becomes positive at small interatomic distances.

E. Subjective Problems

1. **TIPS/Formulæ:**

\[ PV = \frac{m}{M}RT \Rightarrow P = \frac{m}{V} \times \frac{RT}{M} = \frac{d}{M} \Rightarrow d = \frac{MP}{RT} \]

Substituting the value, we get
\[ d = \frac{17 \times 5}{0.082 \times 303} = 3.42 \text{ g/litre} \]

2. Given, moles = \( \frac{\text{mass}}{\text{mol wt}} \)

mass of gas = 3.7g, mass of hydrogen = 0.184g

\( T_1 = 298K, T_2 = 17^\circ C = 273 + 17 = 290K \)

Moles of \( H_2 = n_1 = \frac{\text{Mass}}{\text{M. wt}} = \frac{0.184}{2} = 0.092 \)

Moles of gas = \( n_2 = \frac{\text{Mass}}{M. \text{ wt}} = \frac{3.7}{M} \)

For hydrogen \( P_1V_1 = n_1RT_1 \) .......(i)

For gas \( P_1V_1 = n_2RT_2 \) .......(ii)

\( \therefore \) Pressure and volume of gas are same

\[ \text{From equation (i) and equation (ii)} \]
\[ \frac{P_1V_1}{P_1R_1} = \frac{n_1RT_1}{n_2RT_2} \quad \text{or} \quad 1 = \frac{0.92 \times 298}{n_2 \times 290} \]

or \( n_2 = \frac{0.92 \times 298}{290} \) or \( \frac{3.7}{M} = \frac{0.92 \times 298}{290} \)

or \( 3.7 = 0.945 \text{ or } M = \frac{3.7}{0.945} = 39.15 \)

3. Let NH₃ diffuse through = \( x \) cm

HCL diffuses through = \( y \) cm

According to Graham's law of diffusion

\[ \frac{x}{y} = \sqrt{\frac{\text{Mol. wt HCL}}{\text{Mol. wt of NH}_3}} = \sqrt{\frac{36.5}{17}} = \sqrt{2.14} = 1.465 \]

\[ x = 1.465y \quad \ldots (1) \]

\[ x + y = 200 \text{ cm} \quad \ldots (2) \]

From these equations; \( y = 85.2 \text{ cm} \)

Distance between \( P \) and \( X = y = 85.2 \text{ cm} \).

4. Following reaction takes place in tube

\[ \text{C + CO}_2 \rightarrow 2\text{CO} \]

Volume of mixture of CO and \( \text{CO}_2 = 1 \text{L} \)

Let volume of \( \text{CO}_2 \) in mixture = \( x \)

\( \therefore \) Volume of \( \text{CO} \) in mixture = \( 2x \)

\( \therefore \) Original volume of \( \text{CO} \) in mixture = \( 1 - x \)

Total volume of \( \text{CO} \) after reaction = \( (1 - x) + 2x = 1 + x \)

\[ 1 + x = 1.6 \quad (\because \text{ It is given total volume after reaction = 1.6L}) \]

\[ x = 0.6 \text{ L} \quad \therefore \text{ Volume of } \text{CO}_2 = 0.6 \text{ L} \]

Volume of \( \text{CO} = 0.4 \text{ L} \)

\( \text{CO}_2 : \text{CO} = 3:2 \)

5. Since the pressures of gases are different, and the temperature is constant, the rate at which molecules of the two gases diffuse is directly proportional to the pressure. This rate of diffusion is also directly proportional to the distance travelled by the gas. Hence

\[ r_1 (\text{of HCl gas}) \text{ at pressure } P = 60 = \frac{kP}{\sqrt{36.5}} \quad \ldots (i) \]

and \( r_2 (\text{of NH}_3) \) at 1 atm. pressure \( P = 40 = \frac{k \times 1}{\sqrt{17}} \quad \ldots (ii) \)
From (i) and (ii)
\[
\frac{n}{p_2} = \frac{60}{40} \times \frac{kP}{\sqrt{36.5} \times k \times 1} = 2.197 \text{ atm}
\]

6. **TIPS/Formulæ**:

Total kinetic energy = \( n (3/2) RT \)

where \( n \) = Number of moles of the gas
\( R \) = Gas constant
\( T \) = Absolute temperature

Molecular weight of methane,
\( \text{CH}_4 = 12 + 4 \times 1 = 16 \)

\[
\therefore \text{Number of moles of methane in 8.0 gm of methane} = \frac{8.0}{16.0} = 0.5
\]

\( R = 8.314 \text{ joules/K/mole} \), \( T = 27 + 273 = 300 \text{ K} \)

\[
\therefore \text{Total kinetic energy of the molecules in 8.0 gm of methane at } 27^\circ \text{C} = n \times 3/2 \cdot RT = \frac{0.5 \times 3/2 \times 8.314 \times 300}{1870.65} \text{ joules}
\]

\[
\therefore \text{Average kinetic energy} = \frac{1870.65}{6.023 \times 10^{23} \times 0.5} = 6.21 \times 10^{-21} \text{ joules/mole}
\]

7. **NOTE THIS STEP**: First we should calculate the number of moles of the gas under the given conditions by the relation \( PV = nRT \)

Here \( P = 7.6 \times 10^{-10} \text{ mm Hg} \)

\[
= \frac{7.6 \times 10^{-10}}{760} \text{ atm.} = 1 \times 10^{-12} \text{ atm}
\]

\( V = 1 \text{ litre, } T = 273 + 0 = 273K, R = 0.082 \text{ litre atm/K/mol} \)

Putting the values in equation

\[
n = \frac{PV}{RT} = 1 \times 10^{-12} \times 1 = 0.082 \times 273 \text{ moles}
\]

Now since 1 mole = \( 6.023 \times 10^{23} \) molecules

\[
10^{-12} \text{ moles} = \frac{6.023 \times 10^{23} \times 10^{-12}}{0.082 \times 273} \text{ molecules}
\]

\[
= 2.7 \times 10^{10} \text{ molecules}
\]

8. From ideal gas equation,

\[
PV = nRT \Rightarrow PV = \left( \frac{m}{M} \right) RT \text{ or } M = \frac{mRT}{PV}
\]

Let the molecular wt. of A and B be \( M_A \) and \( M_B \) respectively.

Then \( M_A = \frac{2RT}{1 \times V} \); \( M_B = \frac{3 \times RT}{0.5 \times V} \)

\[
\therefore \frac{M_A}{M_B} = \frac{2RT}{V} \times \frac{0.5V}{3RT} = \frac{2 \times 0.5}{3} = \frac{1}{3}
\]

Therefore, the ratio \( M_A : M_B = 1 : 3 \)

9. \( U_{\text{rms}} = \sqrt{\frac{3RT}{M}} \)

Given \( T = 20^\circ \text{C} = 20 + 273 = 293 \text{ K} \)
\( R = 8.314 \times 10^7 \text{ erg per degree per mol} \)
\( M(\text{of } \text{O}_2) = 48 \)

\[
\therefore U_{\text{rms}} = \sqrt{\frac{3 \times 8.314 \times 10^7 \times 293}{48}} = 3.9 \times 10^4 \text{ cm sec}^{-1}
\]

10. Volume of balloon = 4.851 L \quad \text{(as calculated above)}

Let no. of balloons to be filled = \( n \)

\[
\therefore \text{Total volume occupied by } n \text{ balloons} = 4.851 \times n
\]

Volume of \( \text{H}_2 \) present in cylinder = 2.82 L \text{(given)}

\[
\therefore \text{Total volume of } \text{H}_2 \text{ at NTP} = (4.851n + 2.82) \text{L}
\]

\( P_1 = 1 \text{ atm} \quad P_2 = 20 \text{ atm} \)
\( V_1 = 4.85 \times n + 2.82 \text{ L} \quad V_2 = 2.82 \text{ L} \)
\( T_1 = 273 \text{ K} \quad T_2 = 300 \text{ K} \)

\[
\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \quad \text{or} \quad \frac{1 \times (4.85 \times n + 2.82)}{273} = \frac{20 \times 2.82}{300}
\]

\[
\therefore n = \frac{48.504}{4.851} = 10
\]

11. **TIPS/Formulæ**:

Average velocity = \( \frac{8RT}{\pi M} \)

and Most probable velocity = \( \sqrt{\frac{2RT}{M}} \)

Given -For \( \text{CO}_2 \)
Average velocity at \( T_1 \) = Most probable velocity at \( T_2 \)

\[
= 9 \times 10^4 \text{ cm/sec} = \frac{9 \times 10^4}{100} \text{ m/sec.}
\]

\[
= 9 \times 10^2 \text{ m/sec.}
\]

\[
\therefore 9 \times 10^2 = \sqrt{\frac{8 \times 8.314 \times T_1}{3.14 \times 44 \times 10^{-3}}} \quad \ldots \text{(A)}
\]

[Average velocity at \( T_1 \text{K} \)]

and \( 9 \times 10^2 = \sqrt{\frac{2 \times 8.314 \times T_2}{44 \times 10^{-3}}} \quad \ldots \text{(B)} \)

[Most probable velocity at \( T_2 \text{K} \)]

On solving, \( T_1 = 1682.5 \text{ K, } T_2 = 2143.4 \text{ K} \)

12. Applying the general gas equation

\( PV = nRT = \frac{m}{M}RT \)

Here, Mol. wt. of acetylene i.e., \( \text{C}_2\text{H}_2 \text{ (M)} = 26, P = \frac{740}{760} \text{ atm.} \)
\( T = 50^\circ \text{C} = 50 + 273 = 323 \text{ K} \)

\[
\therefore V = \frac{mRT}{MP} \quad \text{or} \quad V = \frac{5 \times 0.082 \times 323 \times 760}{26 \times 740} = 5.23 \text{ L}
\]
13. Using gas equation, \( PV = nRT \)
Total no. of moles of gases in the mixture (n)
\[
\frac{PV}{RT} = \frac{6 \times 3}{0.0821 \times 300} = 0.7308 \text{ mol.}
\]
Thus no. of moles of unknown gas = 0.7308 - 0.7 = 0.0308 mol.
Now we know that
\[
\frac{r_1}{r_2} = \frac{\text{moles of hydrogen gas}}{\text{moles of unknown gas}} = 0.7
\]
Also we know that \( r_1 = \sqrt{\frac{M_2}{M_1}} \)
\[
\therefore \quad M_2 = \left( \frac{r_1}{r_2} \right)^2 M_1 \quad \text{or} \quad M_2 = \left( \frac{0.7}{0.0308} \right)^2 \times 2 = 1033
\]

14. \( 2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2 \rightarrow \text{N}_2\text{O}_4 \)
Calculating the number of moles of NO and O\(_2\) by applying
the formula, \( n = \frac{PV}{RT} \)
Moles of NO in the larger flask = \( 1.053 \times 0.250 \times 0.082 \times 300 = 0.0107 \quad \text{[250 mL = 0.250 L]} \]
Moles of O\(_2\) in the smaller flask = \( 0.789 \times 0.100 \times 0.082 \times 300 = 0.0032 \quad \text{[100 mL = 0.100 L]} \]
The reaction takes place as follows.
\[
\begin{align*}
2\text{NO} & \quad + \quad \text{O}_2 \\
\text{Mols before reaction} & \quad 0.0107 \quad 0.0032 \quad 0 \\
\text{Mole after reaction} & \quad (0.0107 - 0 \quad 0.0032) \\
\end{align*}
\]
Hence moles of NO reacting completely with 0.0032 moles of O\(_2\) = \( 2 \times 0.0032 = 0.0064 \)
Moles of NO left = 0.0107 - 0.0064 = 0.0043
NOTE: Oxygen will be completely changed into NO\(_2\) which in turn is completely converted into N\(_2\)O\(_4\) which solidifies at 262 K. Hence at 220 K, the dimer is in the solid state and only NO present in excess will remain in the gaseous state occupying volume equal to 350 ml.
Hence pressure (P) of NO gas left
\[
\frac{nRT}{V} = \frac{0.0043 \times 0.082 \times 220}{0.350} = 0.221 \text{ atm}
\]

15. Given: \( V = 1 \text{L} = 10^{-3} \text{m}^3, P = 7.57 \times 10^{-3} \text{Nm}^{-2}, R = 8.314 \text{J}, \)
\( n = 2 \times 10^{21} / 6.023 \times 10^{23} \text{ moles} \)

16. TIPS/Formulae:
Partial pressure = Mole fraction \( \times \) Total pressure
\[
\begin{align*}
\text{P}_{\text{He}} &= \chi_{\text{He}} \times P = \frac{4}{5} \times 20 = 16 \text{ bar} \\
\chi_{\text{He}} &= \text{mole fraction of He} = \frac{4}{5} \\
\text{P}_{\text{CH}_4} &= 20 - 16 = 4 \text{ bar} \\
\text{Now applying the formula} \\
\text{n}_{\text{He}} : \text{n}_{\text{CH}_3} &= 8 : 1 \\
\therefore \text{Composition of the mixture (He : CH}_4) \text{ effusing out} = 8 : 1
\end{align*}
\]

17. Calculation of volume of gas:
Weight of cylinder with gas = 29.0 kg
Weight of empty cylinder = 14.8 kg
\( \therefore \) Weight of gas in the cylinder = 14.2 kg
Pressure in cylinder = 2.5 atm
\( \therefore \) No. of moles (n) in 14.2 kg (14.2 \( \times \) 10\(^3\) g) of butane
\[
n = \frac{\text{Wt. of butane}}{\text{Mol. wt. of butane}} = \frac{14.2 \times 10^3}{58} = 244.83 \text{ mol}
\]
Applying gas equation,
\[
V = \frac{nRT}{P} = \frac{244.83 \times 0.0821 \times 300}{2.5} = 2412 \text{ litres}
\]
\([27^\circ \text{C} = 273 + 27 = 300]\)
Calculation of pressure in cylinder after use.
Weight of cylinder after use = 23.2 kg
Weight of empty cylinder = 14.8 kg
\( \therefore \) Wt. of unused gas = 8.4 kg = \( \frac{8.4 \times 10^3}{58} \) moles of butane
Thus \( P = \frac{nRT}{V} = \frac{8.4 \times 10^3 \times 0.0821 \times 300}{58 \times 2412} = 1.478 \text{ atm} \)
\([V=2412 \text{ L} \)]
States of Matter

**Calculation of volume of used gas at 2.5 atm and 27°C.**

Weight of used gas = 14.2 – 8.4 = 5.8 kg

Pressure under normal usage conditions = 1 atm

\[ V = \frac{nRT}{P} \]

\[ = \frac{5.8 \times 10^3}{58} \times \frac{0.0821 \times 300}{1} \]

\[ \therefore n = \frac{5.8}{58} \]

= 2463 litres = **2.463 m³**

18. Let the volume of ethane in mixture = x litre

\[ \therefore \text{Volume of ethene} = (40 - x) \text{litre} \]

Combustion reactions of ethene and ethene are:

(i) \[ \text{C}_2\text{H}_6(g) + \frac{3}{2}\text{O}_2(g) \rightarrow 2\text{CO}_2(g) + 3\text{H}_2\text{O}(l) \]

or \[ 2\text{C}_2\text{H}_6(g) + 7\text{O}_2(g) \rightarrow 4\text{CO}_2(g) + 6\text{H}_2\text{O}(l) \]

(ii) \[ \text{C}_2\text{H}_4(g) + 3\text{O}_2(g) \rightarrow 2\text{CO}_2(g) + 2\text{H}_2\text{O}(l) \]

Volume of \( \text{O}_2 \) required for complete combustion of ethene

\[ \frac{7x}{2} \quad \text{[For x litres]} \]

Volume of \( \text{O}_2 \) required for complete combustion of ethene

\[ = (40 - x) \times 3 \quad \text{[For (40 - x) L]} \]

\[ \therefore \text{Total volume of} \quad \text{O}_2 \text{required} = \frac{7x}{2} + (40 - x)3 \quad \text{L} \]

Calculation of number of moles (n)

\[ P = 1 \text{ atm}, \quad V = \frac{7x}{2} + (40 - x)3 \text{ L} ; \quad R = 0.082 \text{ L atm K}^{-1} \text{ mol}^{-1}; \]

\[ T = 400 \text{ K} \]

Since \( n = \frac{PV}{RT} = \frac{1 \times \left[ \frac{7x}{2} + (40 - x)3 \right]}{0.082 \times 400} = \frac{7x + (40 - x)6}{2 \times 0.082 \times 400} \]

Mass of n moles of \( \text{O}_2 \)

\[ = \left[ \frac{7x + (40 - x)6}{2 \times 0.082 \times 400} \right] \times 32 = 130 \]

or 130 = \[ \left[ \frac{7x + 240 - 6x}{65.6} \right] \times 32 \]

\[ \Rightarrow 8528 = 32x + 240 \times 32 \Rightarrow 32x = 848 \Rightarrow x = \frac{848}{32} = 26.5 \]

Hence mole fraction (%) of ethene = \[ \frac{26.5}{40} \times 100 = \textbf{66.25%} \]

Mole fraction (%) of ethene = \textbf{33.75%}

19. **Mixture**

Krypton

\[ r_{\text{mix}} = 1.16 \]

\[ r_{\text{Kr}} = 1 \]

\[ M_{\text{mix}} = ? \quad M_{\text{Kr}} = 84 \]

We know that

\[ r_{\text{mix}} = \sqrt{\frac{M_{\text{Kr}}}{M_{\text{min}}}} \quad \text{or} \quad \frac{1.16}{1} = \sqrt{\frac{84}{M_{\text{mix}}}} \]

or \( (1.16)^2 = \frac{84}{M_{\text{mix}}} \Rightarrow M_{\text{mix}} = \frac{84}{(1.16)^2} = 62.426 \]

**Determination of the composition of the equilibrium mixture**

Let the fraction of \( \text{Cl}_2 \) molecules dissociated at equilibrium = \( x \)

\[ \text{Cl}_2 \quad \xrightarrow{x} \quad 2\text{Cl} \quad \text{Total} \]

Initially \[ \quad 1 \quad 0 \quad 1 \]

At equilibrium \[ \quad 1-x \quad 2x \quad 1-x+2x = 1+x \]

\[ \therefore \text{Total moles at equilibrium} = 1-x+2x = 1+x \]

\[ \text{Normal molecular mass} \]

\[ \frac{71}{64.426} = 1+x \]

\[ \therefore \alpha = 0.137 = \textbf{13.7%}. \]

20. **TIPS/Formulae:**

(i) He does not react with oxygen.

(ii) KOH absorbs only \( \text{CO}_2 \).

**NOTE:** When the mixture of \( \text{CO}, \text{CH}_4 \) and He gases (20 ml) are exploded by an electric discharge with excess of \( \text{O}_2 \), He gas remains as such and the other reactions involved are:

\[ \text{CO}(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{CO}_2(g) \]  \( \ldots \)(i)

\[ \text{CH}_4(g) + 2\text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(l) \]  \( \ldots \)(ii)

Let the volumes of \( \text{CO} \) and \( \text{CH}_4 \) to be ‘a’ ml and ‘b’ ml in the mixture then

Volume of \( \text{He} \) gas = \[ 20 - (a + b) \] ml

For the initial contraction of 13 ml,

Volume of left hand side in the above reactions = 13 = Volume of right hand side.

\[ \therefore \quad [20 - (a + b)] + \left( a + \frac{1}{2}a \right) + (b + 2b) - 13 \]

\[ = [20 - (a + 2b)] + a + b \quad \text{[neglect the volume of H}_2\text{O}(l)] \]

(Since for gases, volume \( \alpha \) no. of moles)

\[ \therefore \quad \frac{1}{2}a + 2b = 13 \quad \text{or} \quad a + 4b = 26 \] \( \ldots \)(iv)

**NOTE THIS STEP:** The \( \text{CO}_2 \) produced above in reactions (ii) & (iii), \( (a + b) \) ml, reacts with KOH sol for a further contraction of 14 ml.

\[ \text{CO}_2(g) + 2\text{KOH}(l) \rightarrow \text{K}_2\text{CO}_3(l) + \text{H}_2\text{O}(l) \]

\( (a + b) \) ml

\[ \therefore \quad a + b = 14 \] \( \ldots \)(v)

Solving (iv) & (v) we get, \( a = 10 \) ml & \( b = 4 \) ml

\[ \therefore \quad \text{CH}_4 = \frac{4}{20} \times 100 = \textbf{20%}, \quad \text{CO} = \frac{10}{20} \times 100 = \textbf{50%} \]

& \( \text{He} = 100 -(20 + 50) = \textbf{30%} \)

21. **Weight of liquid** = 148 – 50 = 98 g

Volume of liquid = \[ \frac{98}{0.98} = 100 \text{ ml} = \text{volume of vessel} \]

It means, vessel of 100 ml contains ideal gas at 760 mm Hg at 300 K

Weight of gas = 50.5 – 50 = 0.5 g
using, \( PV = nRT \)
\[
\frac{760 \times 100}{760 \times 1000} = 0.5 \times 0.082 \times 300 \quad \left[ n = \frac{0.5}{m} \right]
\]
\[\therefore \text{ Molecular weight of gas (m)} = \frac{123}{m}\]

22. \( \text{POCl}_3 \xrightleftharpoons{} \text{POCl}_3 + \text{Cl}_2 \)

Initial moles = 1

Moles at eq. = 1 - 0.4 = 0.4

\[\therefore \text{ Total mole at equilibrium} = 0.4 + 0.4 = 0.4 \quad \left[ \text{Normal mol wt of POCl}_3 = 1 + \alpha = 1.4 \right] \]

Also, \( \frac{\text{Exp mol wt of POCl}_3}{208.5} = \frac{1 + \alpha}{4} \)

\[\therefore \text{Exp mol wt of POCl}_3 = 1.4 \]

\[\therefore \text{Exp mol wt of POCl}_3 \text{ or m. wt of mixture} = \frac{208.5}{1.4} \]

Now using, \( PV = \frac{w}{m} RT \) for mixture
\[
d = \frac{Vm}{RT} = \frac{1 \times 208.5}{1.4 \times 0.082 \times 400} = 4.53 \text{ g/litre}
\]

23. van der Waals equation for n moles of gas is
\[
\left( P + \frac{n^2 a}{V^2} \right) \left[ V - nb \right] = nRT
\]

Given, \( V = 4 \text{ litre} \), \( P = 110 \text{ atm} \), \( T = 300 \text{ K} \);
\( b = 0.05 \text{ litre mole}^{-1} \cdot n = 2 \)

Thus, \[11 + \frac{2^2 a}{4} \left[ 4 - 2 \times 0.05 \right] = 2 \times 0.082 \times 300 \]
\[\therefore a = 4.64 \text{ atm litre}^{-2} \text{ mol}^{-2} \]

24. \( \text{N}_2\text{O}_5 (g) \xrightleftharpoons{} 2\text{NO}_2 (g) + \frac{1}{2} \text{O}_2 (g) \)

Initial pressure = 600

Final pressure = 600 - P\, P/P2 = 960 mm Hg

\[\therefore \text{mole of \text{N}_2\text{O}_5} = \frac{240}{600} = 0.4 \]

25. We know that
\[
\frac{m_1 \times t_1}{M_1} = \frac{m_2 \times t_2}{M_2}
\]

or \[\frac{M_1}{t_1} \times \frac{t_2}{M_2} = \frac{m_2}{m_1} \times \frac{t_1}{t_2} \]

or \[\frac{1}{38} \times \frac{57}{1} = \frac{M}{28} \times \frac{0.8}{1.6} \quad \therefore M = 252 \]

\[\therefore Xe + \left( F \right)_x = 252 \]

\[\therefore x = 6 \]

Thus compound of xenon with fluorine is \( \text{XeF}_6 \)

26. (I) Given \( P = 1 \text{ atm} \), \( w = 12 \text{ g/mol} \), \( T = (t + 273) \text{ K l/2} \); \( V = \text{V litre} \)

(II) If \( T = t + 10 + 273 = t + 283 \text{ K l/2} \); \( V = \text{V litre} \)

\[P = 1 + \frac{10}{100} = 1.1 \text{ atm} \]

Using gas equation, \( PV = \frac{w}{m} RT \)

Case I. \[1 \times V = \frac{12}{m} \text{ R(t + 273)} \] \( \ldots (1) \)

Case II. \[1.1 \times V = \frac{12}{m} \text{ R(t + 283)} \] \( \ldots (2) \)

From (1) and (2), \( t = -173^\circ \text{C or} \; t = 100 \text{ K} \)

Also from (1), on substituting t and m (120), \( V = 0.82 \text{ litre} \)

27. van der Waals’ equation for one mole of a gas is
\[
\left( P + \frac{a}{V^2} \right) \left( V - b \right) = RT \quad \ldots (1)
\]

Given that volume occupied by CO\(_2\) molecules, \( b = 0 \)

Hence, (1) becomes \[\left( P + \frac{a}{V^2} \right) V = RT \quad \text{or} \quad P = \frac{RT}{V} - \frac{a}{V^2} \]

Using \( R = 0.082, T = 273 \text{K}, V = 22.4 \text{ l for} 1 \text{ mole of an ideal gas} \)

\[\therefore P = \frac{0.082 \times 273}{22.4} - \frac{3.592}{(22.4)^2} = 0.9922 \text{ atm} \]

28. We know that, Compressibility factor, \( Z = \frac{PV}{RT} \)

\[0.5 = \frac{100 \times V}{0.082 \times 273} \quad \therefore V = 0.1119 \text{ L} \]

**NOTE**: Further when volume of a gas molecule is negligible, van der Waal’s equation becomes
\[
\left( P + \frac{a}{V^2} \right) \left( V - 0 \right) = RT
\]

or \[PV = RT - \frac{a}{V} \quad \text{or} \quad a = RTV - PV^2 \]

Substituting the values
\[a = (0.082 \times 0.1119 \times 273) - (100 \times 0.1119 \times 0.1119) \]
\[= 1.253 \text{ atm l}^2 \text{ mol}^{-2} \]

29. (a) \( d = 0.36 \text{ kg m}^{-3} = 0.36 \text{ g/L} \)

(i) From Graham’s Law of diffusion

\[\frac{r_v}{r_{O_2}} = \sqrt{\frac{M_{O_2}}{M_v}} \; \therefore \frac{1.33}{\sqrt{M_v}} = \frac{32}{M_v} \quad \therefore \frac{32}{(1.33)^2} = 18.09 \]

where \( M_v = MW \text{ of the vapour} \)

(ii) Thus, \( 0.36g = \frac{0.36 \text{ mol}}{18.09} \)

\[0.36 \text{ mol occupies 1 L volume, so 1 mol occupies} \]

\[18.09 \text{ L} = 50.25 \text{ L} \]

Thus, molar volume of vapour \( = 50.25 \text{ L} \)

Assuming ideal behaviour the volume of the vapour can be calculated by

\[\frac{V_1}{T_1} = \frac{V_2}{T_2} \quad \therefore V_2 = \frac{22.4 \times 500}{273} = 41.025 \text{L} \]

(iii) Compressibility factor (Z)

\[\frac{(PV)_{\text{obs}}}{(PV)_{\text{ideal}}} = \frac{1 \times 0.36}{1 \times 41.025} = 0.086 \]

\[\therefore \text{Compressibility factor (Z)} = 0.086 \]
(iv) \( Z \) is greater than unity, hence it is the short range repulsive force that would dominate.
\( (\because \text{actual density is less than given density}) \)

(b) \[
E = \frac{3}{2} \frac{3}{2} \frac{8.31}{6.02 \times 10^2} \times 100
\]
\( = 2.07 \times 10^{-20} \text{ J per molecule} \)
\( (\because K, \text{Boltzmann constant} = R/N) \)

30. **TIPS/Formulæ:**

\[
C_{\text{rms}} = \sqrt{\frac{3RT}{M}}, \quad C_{\text{av}} = \sqrt{\frac{8RT}{\pi M}}
\]

\[
\frac{C_{\text{rms}}}{C_{\text{av}}} = \sqrt{\frac{3RT}{M} \times \frac{\pi M}{8RT}} = \sqrt{\frac{3\pi}{8}} = 1.085
\]

\[
C_{\text{rms}} = 1.085 \times C_{\text{av}} = 1.085 \times 400 = 434 \text{ ms}^{-1}
\]

31. The van der Waal equation (for one mole) of a real gas is
\[
\left( P + \frac{a}{V_m^2} \right) (V_m - b) = RT, \quad PV_m - P_b + \frac{a}{V_m} - \frac{ab}{V_m^2} = RT
\]
\[
PV_m = RT + P_b - \frac{a}{V_m} + \frac{ab}{V_m^2} \quad ...(i)
\]

**NOTE THIS STEP:** To calculate the intercept \( P \to 0 \), hence \( V_m \to \infty \) due to which the last two terms on the right side of the equation (i) can be neglected.

\( \therefore PV_m = RT + P_b \)

When \( P = 0 \), intercept = \( RT \)

F. **Match The Following**

1. (A) : (p) and (s)  Because 200 atm pressure is very large. For \( H_2 \) gas, at very high pressure \( Z > 1 \).

(B) : (r)  Since \( P \approx 0 \), it means very low presure, so ideal behaviour is observed.

(C) : (p) and (q)  Since \( P = 1 \text{ atm} \), \( Z \) for \( CO_2 \) would be less than 1.

(D) : (r)  In real gas with very high molar volume, molecules will be very far apart from each other due to which van der Waal’s forces as well as actual volume occupied by molecules will be negligible.

G. **Comprehension Based Questions**

1. (e) According to Graham’s law of diffusion, if all conditions are identical,
\[
r = \frac{1}{\sqrt{M}}
\]

As in this question, all conditions are identical for \( X \) and \( Y \), then
\[
x = \frac{M_y}{M_x}
\]

\( \frac{r_x}{r_y} = \sqrt{\frac{M_y}{M_x}} \)

2. (d) The general formula of mean free path (\( \lambda \)) is
\[
\lambda = \frac{RT}{\sqrt{2} \pi \bar{d}^2 N_A p}
\]
\( (d = \text{diameter of molecule, } p = \text{pressure inside the vessel}) \)

Since \( d \) and \( p \) are same for both gases, ideally their \( \lambda \) are same. Hence it must be the higher drift speed of \( X \) due to which it is facing more collisions per second with the inert gas in comparison to gas \( Y \). Hence \( X \) faces more resistance from inert gas than \( Y \) and hence covers lesser distance than that predicted by Graham’s law.

H. **Assertion & Reason Type Questions**

1. (a) ‘a’ indicates the magnitude of the attractive forces among the gas molecules, which increases in \( NH_3 \) due to \( H\)-bonding.

2. (a) At constant volume, \( P \propto T \) \( \quad (\text{from } PV = nRT) \)
\[
U_{\text{rms}} = \sqrt{\frac{3RT}{M}} \quad \therefore U_{\text{rms}} \propto \sqrt{T} \quad .....(i)
\]

Collision frequency is directly proportional to \( U_{\text{rms}} \).
Thus collision frequency \( \propto \sqrt{T} \)
Hence, on increasing the collisional pressure, increases frequency.

I. **Integer Value Correct Type**

1. \( v_{\text{rms}} \) of \( X = \sqrt{\frac{3RT_x}{M_x}} \); \( v_{\text{mp}} \) of \( Y = \sqrt{\frac{2RT_y}{M_y}} \)

Given \( v_{\text{rms}} = v_{\text{mp}} \), \( \Rightarrow \sqrt{\frac{3RT_x}{M_x}} = \sqrt{\frac{2RT_y}{M_y}} \)

\[\Rightarrow M_y = \frac{2RT_y M_x}{3RT_x} = \frac{2 \times 60 \times 40}{3 \times 400} = 4 \]

2. 7 \( \frac{P_{He}}{1 - 0.68} = 0.32 \text{ atm}, n = 0.1 \)
\[
V = \frac{nRT}{P} = \frac{0.1 \times 0.0821 \times 273}{0.32} = 7
\]

3. (4) Diffusion coefficient \( \propto \lambda \mu \)

Since \( \lambda \propto \frac{T}{P} \) and \( \mu \propto \sqrt{T} \)

\( \therefore \) Diffusion coefficient \( \propto \frac{T \sqrt{T}}{P} \)

Thus \( \frac{D_1}{D_f} = \frac{P}{4T \sqrt{T}} = \frac{1}{(4 \times 2)/2} = \frac{1}{4} \) or \( \frac{D_f}{D_1} = \frac{4}{1} \)
1. (c) \( PV = nRT \) (number of moles = \( n/V \)) \( \cdot \) \( n/V = P/RT \).
2. (c) Value of gas constant
   \( R = 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1} \)
   \( = 8.314 \times 10^7 \text{ ergs K}^{-1} \text{ mol}^{-1} \)
   \( = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} = 1.987 \text{ cal K}^{-1} \text{ mol}^{-1} \)
3. (d) Kinetic theory of gases proves all the given gas laws.
4. (b) According to kinetic theory the gas molecules are in a state of constant rapid motion in all possible directions colliding in a random manner with one another and with the walls of the container and between two successive collisions molecules travel in a straight line path but show haphazard motion due to collisions.
5. (a) K.E. of neon at 40°C \( = \frac{3}{2} \times \frac{K \times 313}{K \times 293} = \frac{313}{293} \)

6. (a) In van der waals equation ‘b’ is for volume correction
7. (c) Distribution of molecular velocities at two different temperature is given shown below.

\[ \text{Fraction of molecules} \]
\[ \text{Molecular velocity} \]
\[ \\
\text{Most probable velocity} \]
\[ 300 \text{ K} \]
\[ 600 \text{ K} \]

\[ Z = 1 + \frac{Pb}{RT} \]
\( Z > 1 \) at high pressure

11. (c) Most probable speed \( (C^*) = \sqrt{\frac{2RT}{M}} \)

Average Speed \( (\bar{C}) = \sqrt{\frac{8RT}{\pi M}} \)

Root mean square velocity \( (c) = \sqrt{\frac{3RT}{M}} \)

\[ C^* : \bar{C} : C = \sqrt{\frac{2RT}{M}} : \sqrt{\frac{8RT}{\pi M}} : \sqrt{\frac{3RT}{M}} \]

\[ = 1 : \sqrt{\frac{4}{\pi}} : \sqrt{\frac{3}{2}} = 1 : 1.128 : 1.225 \]

12. (b) Compressibility factor \( (Z) = \frac{PV}{RT} \)

(For one mole of real gas)

van der Waals equation

\[ (P + \frac{a}{V^2})(V - b) = RT \]

At low pressure, volume is very large and hence correction term \( b \) can be neglected in comparison to very large volume of \( V \).

\[ \left( P + \frac{a}{V^2} \right) V = RT ; \quad PV + \frac{a}{V} = RT \]

\[ PV = RT - \frac{a}{V} \quad ; \quad PV = 1 - \frac{a}{VRT} \]

Hence, \[ Z = 1 - \frac{a}{VRT} \]

13. (b) Number of moles of \( O_2 = \frac{w}{32} \)

Number of moles of \( N_2 = \frac{4w}{28} = \frac{w}{7} \)

\( \therefore \) Ratio = \( \frac{w}{32} : \frac{w}{7} = 7 : 32 \)

14. (b) Hydrogen bond is a type of strong electrostatic dipole-dipole interaction and dependent on the inverse cube of distance between the molecular ion-dipole interaction \( \propto \frac{1}{r^3} \)

15. (a) For a given mass of an ideal gas, the volume and amount (moles) of the gas are directly proportional if the temperature and pressure are constant. i.e \( V \propto n \)

Hence in the given case.

Initial moles and final moles are equal \( (n_f) = (n_f) \)

\[ \frac{PV}{RT_1} + \frac{PV}{RT_1} = \frac{PV}{RT_1} + \frac{PV}{RT_2} \]

\[ \frac{2P}{T_1} = \frac{P_f}{T_1} + \frac{P_f}{T_2} \Rightarrow P_f = \frac{2P_1T_2}{T_1 + T_2} \]
A. Fill in the Blanks

1. isolated
2. endothermic
3. extensive (because its value does not depend on quantity of substance)

B. True/False

1. True; It only tells that if a process occurs the heat gained by one end would be exactly equal to heat lost by the other. It does not predict the direction.

C. MCQs with One Correct Answer

1. (a) TIPS/Formulae:
   Heat capacity at constant volume \( q_v = \Delta E \)
   Heat capacity of constant pressure \( q_p = \Delta H \)
\[ \Delta H = \Delta E + \Delta nRT \] or \[ \Delta H - \Delta E = \Delta nRT \]

\[ \Delta n = \text{no. of moles of gaseous products} \]
\[ - \text{no. of moles of gaseous reactants} \]
\[ = 12 - 15 = -3 \]
\[ \Delta H - \Delta E = -3 \times 8.314 \times 298 \text{ J} = -7.43 \text{ kJ}. \]

2. (d) **TIPS/Formulae:**

\[ \Delta H = \Delta H_i + \Delta nRT \]

For \( \Delta H \neq \Delta E, \Delta n \neq 0 \)

Where \( \Delta n \) = no. of moles of gaseous products – no. of moles of gaseous reactants

(a) \( \Delta n = 2 - 2 = 0 \)
(b) \( \Delta n = 0 \) (\( \therefore \) they are either in solid or liquid state)
(c) \( \Delta n = 1 - 1 = 0 \) (\( \therefore \) C is in solid state)
(d) \( \Delta n = 2 - 4 = -2 \)

\( \therefore \) (d) is correct answer

3. (b) **CO\(_2\)(g) + H\(_2\)(g) \rightarrow CO\(_2\)(g) + H\(_2\)O\(_(g)\), \( \Delta H = ? \)**

\[ \Delta H = \sum \Delta H_f (\text{Product}) - \sum \Delta H_f (\text{reactant}) \]

Given, \( \Delta H_{f \text{CO}2(g)} = -393.5 \text{ kJ/mol} \)
\( \Delta H_{f \text{CO}(g)} = -110.5 \text{ kJ/mol} \)
\( \Delta H_{f \text{H}2\text{O}(g)} = -241.8 \text{ kJ/mol} \)

\[ \therefore \Delta H = \left[ \Delta H_{f \text{CO}(g)} + \Delta H_{f \text{H}2\text{O}(g)} \right] \]
\[ - \left[ \Delta H_{f \text{CO}2(g)} + \Delta H_{f \text{H}2\text{O}(g)} \right] \]
\[ = -110.5 + (-241.8) - (-393.5 + 0) \]
\[ \left[ \therefore \Delta H_{f \text{H}2\text{g}} = 0 \right] \]

\[ = -41.2 \text{ kJ mol}^{-1} \]

4. (c) In a reversible process, the driving and the opposite forces are nearly equal, hence the system and the surroundings always remain in equilibrium with each other.

5. (a) Work is not a state function because it depends upon the path followed.

6. (c) **TIPS/Formulae:**

\[ \Delta H = \Delta U + P_2V_2 - P_1V_1 \]

Given, \( \Delta U = 30.0 \text{ atm} \)
\( P_1 = 2.0 \text{ atm}, V_1 = 3.0 \text{ L}, T_1 = 95 \text{ K} \)
\( P_2 = 4.0 \text{ atm}, V_2 = 5.0 \text{ L}, T_2 = 245 \text{ K} \)
\[ \Delta H = \Delta U + P_2V_2 - P_1V_1 \]
\[ = 30 + (4 \times 5) - (2 \times 3) = 30 + 20 - 6 = 44 \text{ L atm.} \]

7. (b) **TIPS/Formulae:**

\[ \Delta H^o \] is the enthalpy change when 1 mole of the substance is formed from its elements in their standard states.

In (a) carbon is present in diamond however standard state of carbon is graphite. Again, in (d) CO \((g)\) is involved so it can’t be the right option. Further in (c) 2 moles of NH\(_3\) are generated. Hence the correct option is (b).

8. (c) \( \Delta H = nC_p \Delta T \text{solution}; \) since \( \Delta T = 0 \), \( \Delta H = 0 \)

9. (b) \( \Delta S = \frac{\Delta Q_{\text{rev}}}{T}; \]
\[ 75 = \frac{3 \times 10^3}{T} \]
\( \therefore T = 400 \text{ K} \)

10. (a) \( \Delta S_{A \rightarrow B} = \Delta S_{A \rightarrow C} + \Delta S_{C \rightarrow D} - \Delta S_{B \rightarrow D} \)
\[ = 50 + 30 - 20 = 60 \text{ e.u.} \]

11. (b) \( A \rightleftharpoons B \)
\[ \Delta G^o = \Delta H^o - T \Delta S^o \]
\[ \Delta G^o = -2.303 \text{ RTlog}_{10} K \]
\[ -2.303 \text{ RTlog}_{10} K = \Delta H^o - T \Delta S^o \]
\[ \log_{10} K = \frac{T \Delta S^o - \Delta H^o}{2.303RT} \]
\[ \log_{10} K = \frac{298 \times 10 + 54.07 \times 1000}{2.303 \times 298} = 10 \]

12. (a) Since, liquid is passing into gaseous phase so entropy will increase and at 373 K during the phase transformation it remains at equilibrium. So, \( \Delta G = 0 \).

13. (b) The species in its elemental form has zero standard molar enthalpy of formation at 298 K. At 298 K, Cl\(_2\) is gas while Br\(_2\) is liquid.

14. (c) The standard enthalpy of the combustion of glucose can be calculated by the eqn.
\( \text{C}_6\text{H}_{12}\text{O}_6(s) + 6\text{O}_2(g) \rightarrow 6\text{CO}_2(g) + 6\text{H}_2\text{O}(l) \)
\[ \Delta H_f = 6 \times \Delta H_f(\text{CO}_2) + 6 \times \Delta H_f(\text{H}_2\text{O}) - \Delta H_f(\text{C}_6\text{H}_{12}\text{O}_6) \]
\[ \Delta H_f = 6 \times (-400) + 6 \times (-300) - (-1300) = -2900 \text{ kJ/mol} \]

For one gram of glucose, enthalpy of combustion
\[ \Delta H_f = \frac{-2900}{180} = -16.11 \text{ kJ/gm} \]

15. (b) Given conditions are boiling conditions for water due to which
\[ \Delta S_{\text{total}} = 0 \]
\[ \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = 0 \]
\[ \Delta S_{\text{system}} = - \Delta S_{\text{surroundings}} \]

For process, \( \Delta S_{\text{system}} > 0 \)
\[ \Delta S_{\text{surroundings}} < 0 \]

16. (c) From 1st law of thermodynamics
\[ q_{\text{sys}} = \Delta U - w = 0 - \left[ -P_{\text{ext}} \Delta V \right] \]
\[ = 3.0 \text{ atm} \times (2.0 \text{ L} - 1.0 \text{ L}) = 3.0 \text{ L-atm} \]
\[ \therefore \Delta S_{\text{sur}} = \frac{(q_{\text{rev}})_{\text{sur}}}{T} = - \frac{q_{\text{sys}}}{T} \]
\[ = - \frac{3 \times 101.3 \text{ J}}{300 \text{ K}} = -1.013 \text{ J/K} \]

**D. MCQs with One or More Than One Correct**

1. (b, d) Properties independent of mass are intensive properties. Hence (b) and (d) which are independent of mass are the obvious choices.
2. (b, c, d) All combustion reactions are exothermic in nature.
3. (a,d) Internal energy and molar enthalpy are state functions. Work (reversible or irreversible) is a path function.
4. (a, b) Mass independent properties (molar conductivity and electromotive force) are intensive properties. Resistance and heat capacity are mass dependent, hence extensive properties.
5. (a, c) \[ \Delta S_{x\to z} = \Delta S_{x\to y} + \Delta S_{y\to z} \] [Entropy is a state function, hence additive]
   \[ W_{x\to y\to z} = W_{x\to y} \] [Work done in \( y \to z \), is zero because it is an isochoric process].
6. (a, c, d) \( T_1 = T_2 \) because process is isothermal.
   Work done in adiabatic process is less than in isothermal process because area covered by isothermal curve is more than the area covered by the adiabatic curve.
   In adiabatic process expansion occurs by using internal energy, hence, it decreases while in isothermal process temperature remains constant that's why no change in internal energy.
7. (a, b, c) Since the vessel is thermally insulated, \( q = 0 \)
   Further since, \( P_{ext} = 0 \), so \( w = 0 \), hence \( \Delta U = 0 \)
   Since \( \Delta T = 0 \), \( T_1 = T_2 \), and \( P_2 V_2 = P_1 V_1 \)
   However, the process is adiabatic irreversible, so we can't apply \( P_2 V_2 \gamma = P_1 V_1 \gamma \).

E. Subjective Problems
1. The required reaction in terms of dissociation energy is 
   \[ \text{OH}(g) \to \text{O}(g) + \text{H}(g); \quad \Delta H = ? \]
   This equation can be achieved by (a) reversing the equation (i), (b) dividing equation (ii) and (iii) each by 2, and (c) adding the three resulting equations.

   \[ \text{OH}(g) \to \frac{1}{2} \text{H}_2(g) + \frac{1}{2} \text{O}_2(g); \quad \Delta H = +10.06 \text{ kcal} \]

   [Reversing eq (i)]

   \[ \frac{1}{2} \text{H}_2(g) \to \text{H}(g) \]
   \[ \Delta H = -52.09 \text{ kcal} \]

   \[ \frac{1}{2} \text{O}_2(g) \to \text{O}(g); \quad \Delta H = -59.16 \text{ kcal} \]

   \[ \text{OH}(g) \to \text{O}(g) + \text{H}(g); \quad \Delta H = -101.19 \text{ kcal (adding)} \]
   Thus one mole of \( \text{OH}(g) \) needs 101.19 kcal of energy to break into oxygen and hydrogen gaseous atoms. Hence the bond energy of \( \text{O} \text{-H} \) bond is \( \text{101.19 kcal} \).

2. The required equation is:
   \[ 2 \text{C}_2\text{H}_2(g) \to 3 \text{C}_2\text{H}_2; \quad \Delta H = ? \]
   Write the thermochemical equations for the given data
   (i) \[ \text{C}_2\text{H}_2(g) + \frac{5}{2} \text{O}_2(g) \to 2 \text{CO}_2(g) + \text{H}_2\text{O}(l); \quad \Delta H = -310.62 \text{ kcal} \]
   (ii) \[ \text{C}_2\text{H}_2(g) + \frac{5}{2} \text{O}_2(g) \to \text{CO}_2(g) \]
   \[ \Delta H = -94.05 \text{ kcal} \]
   (iii) \[ \text{H}_2(g) + \frac{1}{2} \text{O}_2(g) \to \text{H}_2\text{O}(l); \quad \Delta H = -68.32 \text{ kcal} \]
   For getting the above required reaction, we will have to 
   NOTE:
   (a) Bring \( \text{C}_2\text{H}_2 \) in the product that can be done by reversing the equation (i) to give equation (iv).
   (b) Multiply equation (ii) by 2 to get 2C atoms in the reactants and thus equation (v) is obtained.
   (c) Keep equation (iii) as such.
   (d) Add equations (iv), (v) and (iii).

   (iv) \[ 2\text{CO}_2 + \text{H}_2\text{O} \to 2\text{C}_2\text{H}_2 + \frac{5}{2} \text{O}_2; \quad \Delta H = 310.62 \text{ kcal} \]
   (v) \[ 2\text{C} + 2\text{O}_2 \to 2\text{CO}_2; \quad \Delta H = -188.10 \text{ kcal} \]
   (iii) \[ \text{H}_2 + \frac{1}{2} \text{O}_2 \to \text{H}_2\text{O}; \quad \Delta H = -68.32 \text{ kcal} \]
   On adding, \( 2\text{C} + \text{H}_2 \to 2\text{C}_2\text{H}_2 \quad \Delta H = 54.20 \text{ kcal} \)
   Hence the standard heat of formation of \( \text{C}_2\text{H}_2(g) = 54.20 \text{ kcal} \)

4. The given data can be written as follows
   (i) \[ \text{H}_2(g) + \frac{1}{2} \text{O}_2(g) \to \text{H}_2\text{O}(l); \quad \Delta H = -68.3 \text{ kcal} \]
   (ii) \[ \text{C}_2\text{H}_2(g) + \frac{5}{2} \text{O}_2(g) \to \text{H}_2\text{O}(l) + 2\text{CO}_2(g); \quad \Delta H = -310.6 \text{ kcal} \]
   (iii) \[ \text{C}_2\text{H}_4(g) + 3\text{O}_2 \to 2\text{H}_2\text{O}(l) + 2\text{CO}_2(g); \quad \Delta H = -337.2 \text{ kcal} \]
   The required thermochemical equation is
   \[ \text{C}_2\text{H}_2(g) + \text{H}_2 \to 2\text{H}_2\text{O}(l) + 2\text{CO}_2(g); \quad \Delta H = \] 
   \[ \Delta H = -310.6 \text{ kcal} \]
   The required equation can be obtained by subtracting equation (iii) from the sum of equations (i) and (ii), thus \( \Delta H \) of the required equation can be calculated as below.
   \[ \Delta H = \Delta H - \Delta nRT \]
   Here \( \Delta n = \text{Moles of the gaseous products} - \text{Moles of the gaseous reactants} \)
   \[ \Delta n = 1 - (1 + 1) = 1 \]

   Substituting the values of \( \Delta H, \Delta n, R \) and \( T \) in
   \[ \Delta E = \Delta H - \Delta nRT = -41.7 - (-1 \times 2 \times 10^{-3} \times 298) \]
   \[ \Delta E = 41.104 \text{ kcal} \]
5. Bond
   H – H   Cl–Cl   H – Cl
   \( \Delta H \) disso. 104 kcal 58 kcal 103 kcal

Formation of hydrogen chloride can be represented as
H – H + Cl – Cl \( \rightarrow \) 2H – Cl

Thus the reaction involves
Cleavage of one H – H bond, \( \Delta H = 104 \text{ kcal} \)
Cleavage of one Cl–Cl bond, \( \Delta H = 58 \text{ kcal} \)
Formation of two H – Cl bonds, \( \Delta H = 2 \times -103 \text{ kcal} \)

\[ \Delta H \text{ of the reaction} = (104 + 58) - 2(103) = 162 - 206 = -44 \text{ kcal} \]

Now since the enthalpy of formation of a compound is the change in heat content accompanied in the formation of one mole of the compound, the enthalpy of formation of

HCl gas = \( -\frac{44}{2} = -22 \text{ kcal} \)

6. The required chemical reaction.

\[ 2\text{C}_2\text{H}_4 + 7\text{O}_2 \rightarrow 4\text{CO}_2 + 6\text{H}_2\text{O}; \Delta H = x \]

Note that since 2 moles of ethane are reacting, the \( \Delta H \) of the reaction will be \( \frac{x}{2} \).

The thermochemical equations for the given data are written as below:

(i) \( \text{C}(s) + \text{O}_2(g) \rightarrow \text{CO}_2(g); \Delta H = -94.1 \text{ kcal} \)
(ii) \( \text{H}_2(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{H}_2\text{O}(g); \Delta H = -68.3 \text{ kcal} \)
(iii) \( 2\text{C}(s) + 3\text{H}_2(g) \rightarrow \text{C}_2\text{H}_6(g); \Delta H = -21.1 \text{ kcal} \)

We know that \( \Delta H = H_{\text{products}} - H_{\text{Reactants}} \)

\[ \Delta H = 4\Delta H_{\text{CO}_2} + 6\Delta H_{\text{H}_2\text{O}} - (2\Delta H_{\text{C}_2\text{H}_6} + 7\Delta H_{\text{O}_2}) \]

\[ \Delta H = 4 \times -94.1 + 6 \times -68.3 - (2 \times -21.1 + 0) = -376.4 - 409.8 + 42.2 = -744.0 \text{ kcal/2 mole of ethane} \]

\[ = -372.0 \text{ kcal/mole of ethane} \]

7. \( \text{Fe}_2\text{O}_3 + 2\text{Al} \rightarrow 2\text{Fe} + \text{Al}_2\text{O}_3 \)

\[ 2 \times 56 + 48 = 160 \quad 2 \times 27 = 54 \]

Heat of reaction = 399 - 199 = 200 kcal [Al & Fe are in their standard states]

Total weight of reactants = 160 + 54 = 214 g

\[ \therefore \text{ Fuel value/gram} = \frac{200}{214} = 0.9346 \text{ kcal/g} \]

Volume of Al = 2.7 = 20 cc

Volume of \( \text{Fe}_2\text{O}_3 \) = 160 = 30.77 cc

Total volume = 20 + 30.77 = 50.77 cc

\[ \therefore \text{ Fuel value per cc} = \frac{200}{50.77} = 3.94 \text{ kcal/cc} \]

8. 100 g of glucose = 1560 kJ

Energy utilised in body = \( \frac{50}{100} \times 1560 = 780 \text{ kJ} \)

Energy left unutilised in body = 1560 - 780 = 780 kJ

Energy to be given out = 1560 - 780 = 780 kJ

Enthalpy of evaporation of water = 44 kJ/mole = 44 kJ/18 g of water [1 mole \( \text{H}_2\text{O} = 18 \text{g water} \]

Hence amount water to be perspired to avoid storage of energy = \( \frac{18}{44} \times 780 = 319.1 \text{ g} \)

9. The required reaction is

\[ \text{C}_6\text{H}_{10}(g) + \text{H}_2(g) \rightarrow \text{C}_6\text{H}_{12}(g), \Delta H_1 = ? \]

\[ \text{Cyclohexene} \quad \text{Cyclohexane} \]

The given facts can be written as:

\[ \text{H}_2(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{H}_2\text{O}, \Delta H_2 = -241 \text{ kJ/mol} \]
\[ \text{C}_6\text{H}_{10}(g) + \frac{17}{2}\text{O}_2 \rightarrow 6\text{CO}_2(g) + 5\text{H}_2\text{O}; \Delta H_3 = -3800 \text{ kJ/mol} \]
\[ \text{C}_6\text{H}_{12}(g) + 9\text{O}_2(g) \rightarrow 6\text{CO}_2(g) + 6\text{H}_2\text{O}; \Delta H_4 = -3920 \text{ kJ/mol} \]

The required reaction (1) can be obtained by adding equations (2) and (3) and subtracting (4) from the sum of (2) and (3).

\[ \text{C}_6\text{H}_{10}(g) + \text{H}_2(g) \rightarrow \text{C}_6\text{H}_{12}(g) \]

\[ \Delta H_1 = (\Delta H_2 + \Delta H_3) - \Delta H_4 \]

\[ = -241 + (-3800) - (-3920) \]

\[ = -241 - 3800 + 3920 \]

\[ = -4041 + 3920 = -121 \text{ kJ/mol} \]

10. For \( \text{C}_3\text{H}_8 \):

\[ 3\text{C} + 4\text{H}_2 \rightarrow \text{C}_3\text{H}_6, \Delta H_1 = ? \]

For \( \text{C}_2\text{H}_6 \):

\[ 2\text{C} + 3\text{H}_2 \rightarrow \text{C}_2\text{H}_6, \Delta H_2 = ? \]

\[ \therefore \Delta H_1 = -[2(\text{C} – \text{C}) + 8(\text{C} – \text{H})] + [3\text{C}_2\text{H}_4 + 4(\text{H} – \text{H})] \]

\[ \therefore \Delta H_2 = -[(\text{C} – \text{C}) + 6(\text{C} – \text{H})] + [2\text{C}_2\text{H}_4 + 3(\text{H} – \text{H})] \]

Let bond energy of C–C be \( x \) kcal and bond energy of C–H be \( y \) kcal

\[ \therefore \text{By eq. (1) } \Delta H_1 = -(2x + 8y) + [3 \times 172 + 4 \times 104] \]

\[ \Delta H_1 = -(x + 6y) + [2 \times 172 + 3 \times 104] \]

\[ \Delta H_1 = -(x + 6y) + 538 \]

\[ \therefore \text{Also given } \text{C} + \text{O}_2 \rightarrow \text{CO}_2, \Delta H = -94.0 \text{ k cal} \]

\[ \text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}, \Delta H = -68.0 \text{ kcal} \]

\[ \text{C}_2\text{H}_6 + (7/2)\text{O}_2 \rightarrow 2\text{CO}_2 + 3\text{H}_2\text{O}, \Delta H = -372 \text{ kcal} \]

\[ \text{C}_2\text{H}_4 + 5\text{O}_2 \rightarrow 3\text{CO}_2 + 4\text{H}_2\text{O}, \Delta H = -530 \text{ kcal} \]

\[ \text{By inspection method: } 2 \times (5 + 3 \times 6) - (7) \text{ gives} \]

\[ 2\text{C} + 3\text{H}_2 \rightarrow \text{C}_2\text{H}_6; \Delta H_2 = -20 \text{ kcal} \]

\[ 3\text{C} + 4\text{H}_2 \rightarrow \text{C}_3\text{H}_6; \Delta H_1 = -20 \text{ kcal} \]

\[ \therefore \text{By eq. (3), (4), (9) and (10)} \]

\[ x + 6y = 676 \]

\[ 2x + 8y = 956 \]

\[ \therefore x = 82 \text{ k cal and } y = 99 \text{ k cal} \]

Bond energy of C–C bond = 82 k cal

Bond energy of C–H bond = 99 k cal

11. Combustion of \( \text{C}_2\text{H}_4 \) and \( \text{CH}_4 \) takes place as follows:

\[ \text{C}_2\text{H}_4 + 3\text{O}_2 \rightarrow 2\text{CO}_2 + 2\text{H}_2\text{O} \]

1 vol. 2 vol.

\[ \text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \]

1 vol. 1 vol.

Let the vol. of \( \text{CH}_4 \) in mixture = \( x \)

\[ \therefore \text{Vol. of } \text{C}_2\text{H}_4 \text{ in the mixture} = (3.67 - x) \]
Vol. of CO₂ produced by \( \frac{x}{l} \) of CH₄ = \( \frac{x}{l} \) and
Vol. of CO₂ produced by \( (3.67-x) \) l of C₂H₄ = 2 \( (3.67-x) \) l
\[ \therefore \text{Total vol. of CO}_2 \text{ produced} = x + 2 (3.67 - x) \]
or \[ 6.11 = x + 2 (3.67 - x) \text{ or } x = 1.23 \]
\[ \therefore \text{Vol. of CH}_4 \text{ in the mixture} = 1.23 l \]
and Vol. of C₂H₄ in the mixture = 3.67 - 1.23 = 2.44 l
Vol. of CH₄ per litre of the mixture = \( \frac{1.23}{3.67} \) l = 0.335 l
Vol. of C₂H₄ per litre of the mixture = \( \frac{2.44}{3.67} \) l = 0.665 l
Now we know that volume of 1 mol. of any gas at 25°C (298 K) = \( \frac{22.4 \times 298}{273} \) l = 24.45 l
\[ \therefore \text{Volume at NTP} = 22.4 l \]
Heat evolved due to combustion of 0.335 l of CH₄
\[ = -0.335 \times 891 \times \frac{24.45}{22.4} \text{kJ} = -12.20 \text{kJ} \text{ [given, heat evolved by} \]
combustion of 1 l = 891 kJ]
Similarly, heat evolved due to combustion of 0.665 l of C₂H₄
\[ = -0.665 \times 1423 \times \frac{24.45}{22.4} \text{kJ} = -38.70 \text{kJ} \]
\[ \therefore \text{Total heat evolved} = 12.20 + 38.70 = 50.90 \text{kJ} \]

12. From the given data, we can write:

\( \begin{align*} 
(i) & \quad H_2 + \frac{1}{2} O_2 \rightarrow H_2O, \quad \Delta H_1 = -285.8 \text{kJ/mol} \\
(ii) & \quad CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O, \quad \Delta H_2 = -890 \text{kJ/mol} \\
(iii) & \quad C_2H_6 + \frac{7}{2} O_2 \rightarrow 2CO_2 + 3H_2O, \quad \Delta H_3 = -1560 \text{kJ/mol} \\
(iv) & \quad C(s) + O_2 \rightarrow CO_2, \quad \Delta H_4 = -393.5 \text{kJ/mol} \\
(v) & \quad 3C(s) + 4H_2 \rightarrow C_3H_8(g), \quad \Delta H_5 = -103.8 \text{kJ/mol} 
\end{align*} \)

The required reaction is \( C_3H_8(g) + H_2(g) \rightarrow C_3H_6(g) + CH_4(g), \Delta H = ? \)

It can be obtained by the following calculations.
\[ 3 \times (iv) - (v) + 5(i) - (ii) - (iii) \]
In other words, \( \Delta H = 3\Delta H_4 - \Delta H_5 + 5\Delta H_1 - \Delta H_2 - \Delta H_3 \)
\[ \therefore \Delta H = 3(-393.5) - (-103.8) + 5(-285.8) + 890 + 1560 \]
\[ = -2609.5 + 2553.8 = -55.7 \text{kJ/mol} \]

13. Combustion of CH₄ and C₄H₁₀ takes place as follows
\[ \text{CH}_4 + 2O_2 \rightarrow CO_2 + 2H_2O, \Delta H = -809 \text{kJ mol}^{-1} \]
\[ \text{C}_4\text{H}_{10} + 13/2O_2 \rightarrow 4CO_2 + 5H_2O, \Delta H = -2878 \text{kJ mol}^{-1} \]
In order to get the same calorific output due to C₄H₁₀,
the rate of supply of butane \( = \frac{x \times 809}{2878} \text{ l/hr} \)
Rate of supply of oxygen \( = 0.2803 \times \frac{13}{2} \times 3 = 5.481 \text{ l/hr} \)

14. \( n\text{CH}_4 = \text{CH}_2 \rightarrow (\text{CH}_2 - \text{CH}_2)_n \)
NOTE : During the polymerisation of ethylene, one mole of ethylene breaks i.e. one C = C double bond breaks and the two CH₂ – groups are linked with C – C single bonds thus forming three single bonds (two single bonds are formed when each CH₂ – group of ethylene links with one CH₂ – group of another ethylene molecule). But in the whole unit of polymer, number of single C–C bonds formed/mole of ethylene is 2.

Energy released = Energy due to formation of 2 C–C single bonds
\[ = 2 \times 331 = 662 \text{kJ/mol of ethylene} \]

Energy absorbed = Energy due to dissociation of 1 C=C double bond
\[ = 590 \text{kJ/mol of ethylene} \]
\[ \therefore \text{Enthalpy of polymerisation/mol of ethylene or} \]
\[ \Delta H_{\text{polymerisation}} = 590 - 662 \text{kJ/mol} = -72 \text{kJ/mol} \]

15.

Standard enthalpy of hydrogenation of cyclohexene (-119kJ mol⁻¹) means the enthalpy of hydrogenation of one C = C double bond. Now benzene has three C = C double bonds, the enthalpy of the reaction would be \( 3 \times -119 = -357 \text{kJ mol}^{-1} \)

\[ \text{Actual enthalpy of the reaction can be evaluated as follows.} \]

\[ \Delta H_{\text{Reaction}} = \Delta H_f^\circ (\text{Prduct}) - \Delta H_f^\circ (\text{Reactants}) \]
\[ = -156 - (49 + 0) = -205 \text{kJ mol}^{-1} \]
\[ \therefore \text{Resonance energy} = \Delta H_{\text{Exp}} - \Delta H_{\text{cal}} \]
\[ = -357 - (-205) = -152 \text{kJ mol}^{-1} \]

16. The required thermochemical equation is

\[ \text{C(g) + 4H(g) + O(g) \rightarrow H - C - O - H; \quad \Delta H_f = ?} \]

\[ \text{H} \]

\[ \Delta H_f = \left[ \Delta H_{C\rightarrow H} + 2\Delta H_{H-O} + \frac{1}{2}\Delta H_{O=O} \right] \]
\[ - 3\Delta H_{C-H} + 3\Delta H_{C-O} + \Delta H_{O-H} + \Delta H_{vap\text{CH}_2OH} \]
\[ = [715 + 2 \times 436 + 249] - [3 \times 415 + 356 + 463 + 38] \]
\[ = -266 \text{kJ mol}^{-1} \]

17. TIPS/Formulae:

For ionisation: \( \Delta H_{\text{ionisation}} > \Delta H_{\text{Hydration}} \)
Total hydration energy of Al³⁺ & 3Cl⁻ ions of AlCl₃ (\( \Delta H_{\text{hydration}} \))
\[ = (\text{Hydration energy of Al}^3+ + 3 \times \text{Hydration energy of } Cl^-) \]
\[ = [-4665 + 3 \times (-381)] \text{kJ mole}^{-1} = -5808 \text{kJ mole}^{-1} \]

NOTE : This amount of energy is more than that required for the ionisation of Al into Al³⁺ (ionisation energy of Al to Al³⁺ = 5137 kJ mol⁻¹). Due to this reason, AlCl₃ becomes ionic in aqueous solution. In aqueous solution it exists in ionic form as below
\[ \text{AlCl}_3 + 3H_2O \rightarrow [\text{Al(H}_2\text{O)}_6]^{3+} + 3\text{Cl}^- \]
\[ \text{AlCl}_3 + \text{aq} \rightarrow \text{AlCl}_3^{(aq)}; \Delta H = ? \]

\[ \Delta H = \text{Energy released during hydration} \]
\[ \text{– Energy used during ionisation} \]
\[ = -4665 - 3 \times 381 + 5137 = -671 \text{kJ/mole} \]

Thus formation of ions will take place.
18. \( \text{H}_2\text{C} = \text{CH}_2 \)  \( \text{CH}_2 = \text{CH}_2 \)  \( \text{CH}_3\text{CH} = \text{CH}_2\text{(g)} \);

\[ \Delta H^o = -33.0 \text{kJ} \]  \( \text{C} + \text{O}_2 \rightarrow \text{CO}_2\text{(g)} \); \( \Delta H^o = -393.5 \text{kJ} \)  \( \text{H}_2 + \text{1}/2\text{O}_2 \rightarrow \text{H}_2\text{O}_\text{(g)} \); \( \Delta H^o = -285.8 \text{kJ} \)  \( 3\text{C} + 3\text{H}_2 \rightarrow \text{CH}_3\text{CH} = \text{CH}_2\text{(g)} \); \( \Delta H^o = 20.42 \text{kJ} \)

The required reaction is

\[ \text{H}_2\text{C} = \text{C} + \text{H}_2 + \frac{9}{2}\text{O}_2 \rightarrow 3\text{CO}_2 + 3\text{H}_2\text{O} \]

\( \Delta H^o = ? \)

To calculate the value of \( \Delta H^o \) follow the following steps.

(i) \(- (i) \) yields

\[ 3\text{C} + 3\text{H}_2 \rightarrow \text{H}_2\text{C} = \text{C} + \text{H}_2\text{O} \quad ; \quad \Delta H^o = 53.42 \text{kJ} \]

\[ 3 \times (ii) + 3 \times (iii) - (v) \text{ yields} \]

\[ \text{H}_2\text{C} \quad \text{H}_2\text{C} + (9/2)\text{O}_2 \rightarrow 3\text{CO}_2 + 3\text{H}_2\text{O} \]

\( \Delta H^o = -2091.32 \text{kJ} \)

19. Given \( S_\text{(g)} + 3\text{F}_2\text{(g)} \rightarrow \text{SF}_6\text{(g)} \); \( \Delta H^o = -1100 \text{kJ} \)  \( \text{S}_\text{(g)} \rightarrow \text{S}_\text{(g)} \); \( \Delta H^o = 275 \text{kJ} \)

\[ 1/2 \text{F}_2\text{(g)} \rightarrow \text{F}_\text{(g)} \]; \( \Delta H^o = 80 \text{kJ} \)

To get \( \text{SF}_6\text{(g)} \rightarrow \text{S}_\text{(g)} + 6\text{F}_\text{(g)} \) we can proceed as

(ii) + 6 \times (iii) - (i)

\( \therefore \text{SF}_6\text{(g)} \rightarrow \text{S}_\text{(g)} + 6\text{F}_\text{(g)} \); \( \Delta H^o = 1855 \text{kJ} \)

Thus average bond energy for S-F bond = \( \frac{1855}{6} = 309.16 \text{kJ} \)

20. TIPS/Formulæ : For adiabatic expansion, we have

\[ \frac{\ln T_1}{\ln T_2} = \frac{R}{C_v} \left( \frac{V_1}{V_2} \right) \quad \text{and} \quad \Delta H = nC_p \Delta T. \]

\[ \ln \frac{300}{124.8} = \frac{8.31 \times 2.50}{1.25} \quad \text{Solving, we get} \quad T_2 = 188.5 \text{K} \]

No. of moles of argon gas, \( n = \frac{PV}{RT} = \frac{1 \times 1.25}{0.082 \times 300} = 0.05 \)

Now we know that

\( \Delta H = nC_p \Delta T = 0.05 \times 20.8(188.5 - 300) = 115.41 \text{Joules} \)

\( \therefore C_v = \frac{R \times 12.48 + 8.314}{20.8} = 12.48 + 8.314 = 20.8 \]

21. For following reaction

\[ \text{CO}_\text{(g)} + \frac{1}{2}\text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)} \]

\( \Delta G^o \) can be calculated as follows:

\[ \Delta G^o = \Delta G^o_p - \Delta G^o_R = \left[ \Delta G^o\text{CO}_2 - \left( \Delta G^o\text{CO} + \frac{1}{2} \Delta G^o\text{O}_2 \right) \right] \]

\[ = -394.4 - (-137.2 + \frac{1}{2} \times 0) = -257.2 \text{kJ mol}^{-1} \]

Since,

\[ \Delta G^o = \Delta H^o - T\Delta S^o \]

\[ \therefore \Delta H^o = -257.2 \text{kJ mol}^{-1} \]

Since,

NOTE : \( \therefore \Delta H^o \) is negative, so the reaction is exothermic and since \( \Delta G^o \) is negative so the reaction is spontaneous.

22. The chemical reaction for combustion of diborane is

\[ \text{B}_2\text{H}_6 \text{(g)} + 3\text{O}_2 \text{(g)} \rightarrow \text{B}_2\text{O}_3 \text{(s)} + 3\text{H}_2\text{O(g)} \]

For this the enthalpy change can be calculated in the following way.

\[ \Delta H = [\Delta H_{\text{B}_2\text{O}_3(s)} + 3\Delta H_{\text{H}_2\text{O}(g)}] - \Delta H_{\text{B}_2\text{H}_6(g)} \]

\( \therefore \Delta H^o \text{ of } \text{O}_2 = 0 \)

\( \Delta H_{\text{H}_2\text{O}(g)} \) can be obtained by adding \( \Delta H_{\text{H}_2\text{O}(l)} \) and

\( \Delta H_{\text{H}_2\text{O}(g)} \), i.e. \(-286 + 44 = -242 \text{kJ mol}^{-1} \)

\[ \Delta H = [-1273 + 3 \times -242] = 36 \text{kJ mol}^{-1} = -1273 - 726 - 36 = -2035 \text{kJ mol}^{-1} \]

23. TIPS/Formulæ :

\[ \Delta G^o = -2.303RT \log \left( \frac{[\text{Product}]}{[\text{Reactant}]}) \right) \]

Calculation of \( \Delta G^o \) values:

Thus for the equilibrium \( \text{B} \leftrightarrow \text{A} \)

\[ \Delta G^o_1 = (-2.303 \times 8.314 \times 448) \log \frac{1.3}{95.2} \]

or \( \Delta G^o_1 = 15.992 \text{kJ mole}^{-1} \)

Similarly for the equilibrium \( \text{B} \leftrightarrow \text{C} \)

\[ \Delta G^o_2 = (-2.303 \times 8.314 \times 448) \log \frac{3.5}{95.2} \]

or \( \Delta G^o_2 = 12.312 \text{kJ mole}^{-1} \)

Similarly for equilibrium, \( \text{A} \leftrightarrow \text{C} \)

\[ \Delta G^o = -8.314 \times 448 \times 2.303 \times \log \frac{3.5}{1.3} = -3.688 \text{kJ mole}^{-1} \]

Hence, we have that

\( \text{B} \leftrightarrow \text{A}, \quad \Delta G^o_1 = +15.992 \text{kJ mole}^{-1} \)

\( \text{B} \leftrightarrow \text{C}, \quad \Delta G^o_2 = +12.312 \text{kJ mole}^{-1} \)

\( \text{A} \leftrightarrow \text{C}, \quad \Delta G^o = -3.688 \text{kJ mole}^{-1} \)

Thus, the correct order of stability, \( \text{B} > \text{C} > \text{A} \)
26. **TIPS/Formulae**: For adiabatic process, \( W = P \left( V_2 - V_1 \right) \)
Here \( P_1 = 1 \text{ bar}, P_2 = 100 \text{ bar}, V_1 = 100 \text{ mL}, V_2 = 99 \text{ mL} \); For adiabatic process, \( q = 0 \) \( \therefore \Delta U = w \)
\[ \Delta U = q + W = q - P(V_2 - V_1) = 0 - 100 \times (99 - 100) = 100 \text{ bar mL} \]
\[ \Delta H = \Delta U + \Delta (PV) = \Delta U + (P_2 V_2 - P_1 V_1) = 100 + [(100 \times 99) - (1 \times 100)] \]
\[ = 100 + (9900 - 100) = 9900 \text{ bar mL} \]

27. (i) \( \text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g) \)

Initially \( P_{\text{N}_2\text{O}_4} = P_{\text{NO}_2} = 10 \)

Reaction quotient \( \frac{(P_{\text{NO}_2})^2}{P_{\text{N}_2\text{O}_4}} = \frac{100}{10} = 10 \)

\[ \Delta G^\circ = 2 \Delta G^\circ_{\text{f}(\text{NO}_2)} - \Delta G^\circ_{\text{f}(\text{N}_2\text{O}_4)} = 100 - 100 = 0 \]

\[ \Delta G = \Delta G^\circ - 2.303 \text{ RT} \log K_p = -2.303 \times 298 \times \log 10 = -56.0304 \text{ L atm} \]

(ii) The negative value of \( \Delta G \) indicates that the reaction is spontaneous & will lie in the right direction, (forward).

28. \[ \Delta H = \Delta U + \Delta (PV) = \Delta U + V \Delta P \quad (\because \Delta V = 0) \]

or \( \Delta U = \Delta H - V \Delta P = -560 - [(40 - 70) \times 0.1] \)

\[ = -560 + 3 = -557 \text{ kJ mol}^{-1} \]

So the magnitude is 557 kJ mol\(^{-1}\). 
\( \therefore \Delta G^\circ = -2.303 \text{ RT} \log K_p \) at equilibrium \( \Delta G^\circ = 0 \)

\( \therefore -2.303 \text{ RT} \log K_p = 0 \Rightarrow \log K_p = 0 \) or \( K_p = 1 \)

**F. Match the Following**

1. \( A - p, r, s \); \( B - r, s \); \( C - t \); \( D - p, q, t \)
   (A) \( \text{CO}_2(s) \rightleftharpoons \text{CO}_2(g) \)
   It is phase transition. The process is endothermic (sublimation). Gas is produced, so entropy increases.
   (B) On heating \( \text{CaCO}_3 \) decomposes. So, process is endothermic.
   The entropy increases as gaseous product is formed.
   (C) \( 2\text{H}_2(g) \rightleftharpoons \text{H}_2\text{O}(g) \)
   Entropy decreases as number of gaseous particles decreases.
   (D) It is phase transition.
   White and red P are allotropes. Red P is more stable than white. 
   So \( \Delta H \) is +ve.

2. \( A - (r, t) \); \( B - (p, q, s) \); \( C - (p, q, s) \); \( D - (p, q, s, t) \)
   (A) \( \rightarrow r, t \)
   \( \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{O(s)} \)
   It is at equilibrium at 273 K and 1 atm 
   So \( \Delta S_{\text{sys}} \) is negative
   As it is equilibrium process so \( \Delta G = 0 \)
(D) \( \rightarrow p, q, s \)

Expansion of 1 mole of an ideal gas in vacuum under isolated condition
Hence, \( w = 0 \)
and \( q_p = C_p dT \) \( \therefore dT = 0 \)
\[ \Rightarrow q = 0 \]
\[ \Delta U = C_v dT \] \( \therefore dT = 0 \) \( \Delta U = 0 \)

(C) \( \rightarrow p, q, s \)
Mixing of two ideal gases at constant temperature
Hence, \( \Delta T = 0 \)
\[ \therefore q = 0; \Delta U = 0 \]
also \( w = 0 \) \( (\Delta U = q + w) \)

(D) \( \rightarrow p, q, s, t \)
Reversible heating and cooling of gas follows same path also initial and final position is same.

Hence, \( q = 0 \)
\[ w = 0 \] \( \text{Path same} \)
\[ \Delta U = 0 \] \( \Delta G = 0 \) \( \text{State function} \)

**G. Comprehension Based Questions**

1. (c) Pressure

\[ \begin{array}{c}
\text{K} \\
\downarrow \\
\text{L} \\
\downarrow \\
\text{N} \\
\downarrow \\
\text{M}
\end{array} \]

\( K \rightarrow L \Rightarrow V \text{ increasing at constant } P \)
Hence \( T \text{ increases (Heating)} \)
\( L \rightarrow M \Rightarrow P \text{ decreasing at constant } V \)
Hence \( T \text{ decreases (Cooling)} \)

**H. Assertion & Reason Type Questions**

1. (b) By first law of thermodynamics \( dq = dE + dW \). Under isothermal condition for ideal gas \( dW = 0 \) as volume occupied by the molecules of ideal gas is zero. Also \( (dE)_T = 0 \) as for ideal gas there is no change in internal energy at constant \( T \) due to no force of attraction between the molecules. \( \therefore dq = 0 + 0 = 0 \).

2. (a) Statement 1 is true because it is not possible to convert whole of heat to work. For such a conversion we need an efficiency of 100% but so far we have not been able to get such a machine (carnot engine).
Statement 2 is true because it is not possible to convert the whole of heat absorbed from a reservoir into work. Some of the heat is always given to the sink.
Also statement 2 is correct explanation for statement 1. Thus the correct choice is option (a).

**I. Integer Value Correct Type**

1. Energy released by combustion of 3.5 g gas
\[ = 2.5 \times (298.45 - 298) \text{ kJ} \]
Energy released by 1 mole of gas \( = \frac{2.5 \times 0.45}{3.5/28} = 9 \text{ kJ}\text{mol}^{-1} \)

2. \( w_d = \left( -4 \times \frac{3}{2} \right) + (-1 \times 1) + \left( -\frac{2 \times 5}{2} \right) = - \left( 6 + 1 + \frac{5}{3} \right) \)
\[ w_d = -\frac{26}{3} \text{ L atm} \]
\[ w_s = -2.303 RT \log \frac{5.5}{1/2} = -2.303 \text{ PV log 11} \]
\[ w_s = -4.606 \times 1.04 = -4.8 \text{ L atm} \]
\[ w_{td} = \frac{26}{3} \]
\[ w_{ts} = -\frac{4.8}{1.8} = 2.0 \]
1. (b) TIPS/Formulae:
\[ \Delta G = \Delta H - T \Delta S \]
Since \( \Delta G = \Delta H - T \Delta S \) for an endothermic reaction, \( \Delta H = +ve \) and at low temperature \( \Delta S = +ve \)
Hence \( \Delta G = (+) \Delta H - T (+) \Delta S \)
and if \( \Delta S < \Delta H \) (at low temp)
\( \Delta G = +ve \) (non spontaneous)
But at high temperature, reaction becomes spontaneous i.e. \( \Delta G = -ve \).
because at higher temperature \( T \Delta S > \Delta H \).

2. (a) According to first law of thermodynamics, energy cannot be created nor destroyed although it can be converted from one form to another.
**NOTE**: Carnot cycle is based upon this principle but during the conversion of heat into work some mechanical energy is always converted to other form of energy; hence this data violates 1st law of thermodynamics.

3. (d) \( \Delta H \) negative shows that the reaction is spontaneous. Higher negative value for Zn shows that the reaction is more feasible.

4. (b) The heat required to raise the temperature of body by 1K is called thermal capacity or heat capacity.

5. (c) For a cyclic process, the net change in the internal energy is zero because the change in internal energy does not depend on the path.

6. (c) \( \text{CH}_2 = \text{CH}_2 (g) + \text{H}_2 (g) \rightarrow \text{CH}_3 - \text{CH}_3 \)
Enthalpy change = Bond energy of reactants − Bond energy of products.
\[ \Delta H = 2(\text{C} = \text{C}) + 4(\text{C} = \text{H}) + 1(\text{H} = \text{H}) - 1(\text{C} = \text{C}) - 2(\text{C} = \text{H}) \]
\[ = 2(\text{C} = \text{C}) + 1(\text{H} = \text{H}) - 1(\text{C} = \text{C}) - 2(\text{C} = \text{H}) \]
\[ = 615 + 435 - 347 - 2 \times 141 = 1050 - 1175 = -125 \text{ kJ} \]

7. (a) For spontaneou reaction, \( dS > 0 \) and \( dG \) should be negative i.e. \( < 0 \).

8. (c) \( \Delta G^o = -RT \ln K \) or \( - \Delta G^o = RT \ln K = \Delta G^o \)

9. (b) Enthalpy change for a reaction does not depend upon the nature of intermediate reaction steps.

10. (c) \( w = -P \Delta V = -10^{-5} \times 1 \times 10^{-2} - 1 \times 10^{-3} = -900 \text{ J} \)

11. (d) (i) \( \text{C} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}_2, \Delta H = -393.5 \text{ kJ} \text{mol}^{-1} \)
(ii) \( \text{CO} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}_2, \Delta H = -283.0 \text{ kJ} \text{mol}^{-1} \)
Operating (i) - (ii), we have
\[ \text{C} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}, \Delta H = -110.5 \text{ kJ} \text{mol}^{-1} \]

12. (d) Enthalpy of reaction \( \Delta H = E_{a(b)} - E_{a(b)} \)
for an endothermic reaction \( \Delta H = +ve \) hence for \( \Delta H \) to be negative
\[ E_{a(b)} < E_{a(b)} \]

13. (b) \( \Delta H = \Delta U + \Delta nRT \)
for \( \text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3 \)
\[ \Delta n = 2 - 4 = -2 \]
\[ \therefore \Delta H = \Delta U - 2RT \text{ or } \Delta U = \Delta H + 2RT \therefore \Delta U > \Delta H \]

14. (N) \( \text{X}_2 + \text{Y}_2 \rightarrow 2\text{XY}, \Delta H = 2(-200) \)
Let \( x \) be the bond dissociation energy of \( \text{X}_2 \). Then
\[ \Delta H = -400 = \varepsilon_{x-x} + \varepsilon_{y-y} - 2\varepsilon_{x-y} = x + 0.5x - 2x = -0.5x \]
or \[ x = \frac{400}{0.5} = 800 \text{ kJ} \text{mol}^{-1} \]
(In the question paper, this option was not mentioned. So the answer has been marked 'N')

15. (c) **NOTE**: In a reversible process, the work done is greater than in irreversible process. Hence, the heat absorbed in a reversible process would be greater than in the latter case. So
\[ T_{r(\text{rev})} < T_{r(\text{irr})} \]

16. (c) The standard enthalpy of formation of \( \text{CH}_4 \) is given by the equation:
\[ \text{C(s)} + 2\text{H}_2(g) \rightarrow \text{CH}_4(g) \]
Hence, dissociation energy of hydrogen and enthalpy of sublimation of carbon is required.

17. (a) \( \text{I}_2(s) + \text{Cl}_2(g) \rightarrow 2\text{ICl}(g) \)
\[ \Delta A = [\Delta A_2(s) - \Delta A_1(g) + \Delta H_{\text{Cl}-\text{Cl}} - 2\Delta H_{\text{Cl}-\text{Cl}}] = 151.0 + 242.3 + 62.76 - 2 \times 211.3 = 33.46 \]
\[ \Delta H^0 \text{ (ICl)} = \frac{33.46}{2} = 16.73 \text{ kJ} \text{ mol}^{-1} \]

18. (d) For the reaction, \( \text{C(s)} + \frac{1}{2} \text{O}_2(g) \rightarrow \text{CO} \)
\[ \Delta H = \Delta U + \Delta nRT \text{ or } \Delta H - \Delta U = \Delta nRT \]
\[ \Delta n = 1 \times \frac{1}{2} \times \frac{1}{2} \times 8.314 \times 298 = 1238.78 \text{ J} \text{ mol}^{-1} \]

19. (a) \( \Delta G^0 = \Delta H^0 - T \Delta S^0 \)
For a spontaneous reaction \( \Delta G^0 < 0 \)
or \( \Delta H^0 - T \Delta S^0 < 0 \Rightarrow T > \frac{\Delta H^0}{\Delta S^0} \)
\[ \Rightarrow T > \frac{179.3 \times 10^3}{160.2} > 1117.9 \text{ K} \approx 1118 \text{ K} \]
20. (a) Given \( \Delta H = 41 \text{kJ mol}^{-1} = 41000 \text{J mol}^{-1} \)

\[ T = 100^\circ\text{C} = 273 + 100 = 373 \text{K, } n = 1 \]

\[ \Delta U = \Delta H - \Delta nRT = 41000 - (2 \times 8.314 \times 373) = 37898.88 \text{J mol}^{-1} = 37.9 \text{kJ mol}^{-1} \]

21. (b) Spontaneity of reaction depends on tendency to acquire minimum energy state and maximum randomness. For a spontaneous process in an isolated system the change in entropy is positive.

22. (b) The energy involved in the conversion of

\[ \frac{1}{2} \text{Cl}_2(\text{g}) \text{ to Cl}^{-1}(\text{aq}) \]

is given by

\[ \Delta H = \frac{1}{2} \Delta_{\text{diss}} H_{\text{Cl}_2}^{(\text{c})} + \Delta_{\text{eg}} H_{\text{Cl}}^{(\text{c})} + \Delta_{\text{hyd}} H_{\text{Cl}}^{(\text{c})} \]

Substituting various values from given data, we get

\[ \Delta H = \left( \frac{1}{2} \times 240 \right) + (-349) + (-381) \text{kJ mol}^{-1} = (120 - 349 - 381) \text{kJ mol}^{-1} = -610 \text{kJ mol}^{-1} \]

i.e., the correct answer is (b).

23. (c) For a reaction to be at equilibrium \( \Delta G = 0 \). Since \( \Delta G = \Delta H - T \Delta S \) so at equilibrium \( \Delta H = T \Delta S \) or \( \Delta H = T \Delta S \).

For the reaction

\[ \frac{1}{2} \text{X}_2 + \frac{3}{2} \text{Y}_2 \rightarrow \text{XY}_3 \]

\( \Delta H = -30 \text{kJ} \) (given)

Calculating \( \Delta S \) for the above reaction, we get

\[ \Delta S = 50 - \left[ \frac{1}{2} \times 60 + \frac{3}{2} \times 40 \right] \text{JK}^{-1} \]

\[ = 50 - (30 + 60) \text{JK}^{-1} = -40 \text{JK}^{-1} \]

At equilibrium, \( T \Delta S = \Delta H \)

\[ \therefore T \times (-40) = -30 \times 1000 \]

\[ T = \frac{-30 \times 1000}{-40} \text{ or } 750 \text{ K} \]

24. (a) Given, for reaction

(i) \( \text{H}_2\text{O}(\ell) \rightarrow \text{H}^+(\text{aq}) + \text{OH}^-\text{(aq)}, \Delta H_f = 57.32 \text{kJ} \)

(ii) \( \text{H}_2(\ell) + \frac{1}{2} \text{O}_2(\ell) \rightarrow \text{H}_2\text{O}(\ell), \Delta H_f = -286.20 \text{kJ} \)

For reaction (i)

\[ \Delta H_f^\circ = \Delta H_f^\circ(\text{H}^+ \text{aq}) + \Delta H_f^\circ(\text{OH}^- \text{aq}) - \Delta H_f^\circ(\text{H}_2\text{O}, \ell) \]

\[ 57.32 = 0 + \Delta H_f^\circ(\text{OH}^-, \text{aq}) - \Delta H_f^\circ(\text{H}_2\text{O}, \ell) \]

For reaction (ii)

\[ \Delta H_f = \Delta H_f^\circ(\text{H}_2\text{O}, \ell) - \Delta H_f^\circ(\text{H}_2, \ell) - \frac{1}{2} \Delta H_f^\circ(\text{O}_2, \ell) \]

\[-286.20 = \Delta H_f^\circ(\text{H}_2\text{O}, \ell) \]

25. (b) \( \text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3 \Delta H = 2 \times -46.0 \text{kJ mol}^{-1} \)

Let \( x \) be the bond enthalpy of \( \text{N} - \text{H} \) bond then

[Note: Enthalpy of formation or bond formation enthalpy is given which is negative but the given reaction involves bond breaking hence values should be taken as positive.]

\[ \Delta H = \Sigma \text{Bond energies of products} - \Sigma \text{Bond energies of reactants} \]

\[ 2 \times -46 = 712 + 3 \times (436) - 6x; \]

\[ -92 = 2020 - 6x \]

\[ 6x = 2020 + 92 \Rightarrow 6x = 2112 \Rightarrow x = + 352 \text{kJ/mol} \]

26. (b) At equilibrium \( \Delta G = 0 \).

Hence, \( \Delta G = \Delta H - T \Delta S = 0 \)

\[ \therefore \Delta H = T \Delta S \text{ or } T_e = \frac{\Delta H}{\Delta S} \]

For a spontaneous reaction \( \Delta G \) must be negative which is possible only if \( \Delta H < T \Delta S \)

or \( T > \frac{\Delta H}{\Delta S} \); \( T_e < T \)

27. (a) Entropy change for an isothermal reversible process is given by

\[ \Delta S = nR \ln \frac{V_2}{V_1} = 2 \times 8.314 \times 2.303 \log \frac{100}{10} = 38.3 \text{J mol}^{-1} \text{K}^{-1} \]

28. (c) \( \Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \), \( -RT \ln K = \Delta H^\circ - T \Delta S^\circ \)

\[ \ln K = - \frac{\Delta H^\circ - T \Delta S^\circ}{RT} \]

29. (a) \( \text{C}_2\text{H}_5\text{OH}(\ell) + 3\text{O}_2(\ell) \rightarrow 2\text{CO}_2(\ell) + 3\text{H}_2\text{O}(\ell) \)

Bomb calorimeter gives \( \Delta U \) of the reaction

Given, \( \Delta U = -1364.47 \text{kJ mol}^{-1} \)

\[ \Delta n_g = -1 \]

\[ \Delta H = \Delta U + \Delta n_g RT \]

\[ = -1364.47 - \frac{1 \times 8.314 \times 298}{1000} = -1366.93 \text{kJ mol}^{-1} \]

31. (b) Given

\[ \text{C(s) + O}_2(g) \rightarrow \text{CO}_2(g), \Delta H = -393.5 \text{kJ mol}^{-1} \]

\[ \text{CO}_2(g) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{CO}_2(g), \Delta H = -283.5 \text{kJ mol}^{-1} \]

\[ \therefore \text{Heat of formation of CO = eqn(i) - eqn(ii)} \]

\[ = -393.5 - (-283.5) = -110 \text{kJ} \]
## Equilibrium

**Section-A : JEE Advanced/ IIT-JEE**

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<tbody>
<tr>
<td>A</td>
<td>1. SO\textsubscript{4}\textsuperscript{2–}</td>
<td>2. amphoteric</td>
<td>3. (K_p = K_c (RT)^\Delta n)</td>
<td>4. no change</td>
<td>5. I\textsubscript{2}</td>
</tr>
<tr>
<td>C</td>
<td>1. (b)</td>
<td>2. (a)</td>
<td>3. (d)</td>
<td>4. (b)</td>
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<td>17. (c)</td>
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<td>24. (d)</td>
<td>25. (d)</td>
<td>26. (b)</td>
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<tr>
<td></td>
<td>29. (b)</td>
<td>30. (a)</td>
<td>31. (b)</td>
<td>32. (d)</td>
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<td></td>
<td>36. (d)</td>
<td>37. (b)</td>
<td>38. (e)</td>
<td>39. (b)</td>
<td>40. (a)</td>
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<tr>
<td>D</td>
<td>1. (a, b, c, d)</td>
<td>2. (c, d)</td>
<td>3. (a)</td>
<td>4. (c, d, e)</td>
<td>5. (d)</td>
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<tr>
<td></td>
<td>8. (c, d)</td>
<td>9. (a)</td>
<td>10. (b)</td>
<td>11. (a, b, d)</td>
<td>12. (b)</td>
</tr>
<tr>
<td>E</td>
<td>1. 5.3 g/l, 4.2 g/l</td>
<td>2. (1.5072 \times 10^{-2}) moles, 4.09, 2</td>
<td>3. (1.48 \times 10^{-5}) (P) moles, 3.82 (\times 10^{-3}) litre (M)</td>
<td>4. (4.5686, 4.86) ml</td>
<td>5. (i) (7 \times 10^{-2}), (ii) (4.1549), (iii) (1.43 \times 10^{-10}) mol/l</td>
</tr>
<tr>
<td></td>
<td>8. (i) (N_2 &lt; O_2 &lt; F_2 &lt; Cl_2), (ii) (ClO &lt; ClO_2 &lt; ClO_3 &lt; ClO_4) (iii) (H_2O &lt; CH_3OH &lt; OH^- &lt; CH_3O^-) (iv) (BaO &gt; B_2O_3 &gt; CO_2 &gt; SO_2 &gt; Cl_2O_7)</td>
<td>9. 4.19</td>
<td>10. 1.886</td>
<td>11. (8.7 \times 10^{-4}) g/litre</td>
<td>12. (4.5686, 1)</td>
</tr>
<tr>
<td></td>
<td>13. 1.6 moles, 0.4 moles</td>
<td>14. 0.266 atm, 64%</td>
<td>15. 8.85 (\times 10^{-3}) M</td>
<td></td>
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<tr>
<td></td>
<td>16. (p_{SO_2} = 0.2326) atm, (p_{O_2} = 2.0118) atm, (p_{SO_3} = 0.9764) atm</td>
<td>17. (46.29) mol ion/l, (1.286 \times 10^{-15}) mol ion/l</td>
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<tr>
<td></td>
<td>18. (277.78) mol(^{-2}) (P), (0.1144) atm (^{-2})</td>
<td>19. (2.3724, 2.78 \times 10^9) litres</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>20. (3.794 \times 10^{-12}) mol(^3) (P) (^{-3})</td>
<td>21. (1.828 \times 10^{-5})</td>
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<tr>
<td></td>
<td>22. 743.3 mg</td>
<td>23. (i) (0.05) atm (^{-2}), (187.85) mol(^{-2}) (P), (ii) (12.438) atm</td>
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<tr>
<td></td>
<td>24. 78.36 ml</td>
<td>25. 0.983</td>
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<tr>
<td>26. (\left[\frac{2K_p}{P}\right]^{1/3})</td>
<td>27. (7.5 \times 10^{-18}) M</td>
<td>28. 6.5</td>
<td>29. 11.5</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>30. (1.71 \times 10^{-10})</td>
<td>31. 2</td>
<td>32. (0.0538) M</td>
<td>33. 11.3010</td>
<td></td>
</tr>
<tr>
<td></td>
<td>34. (8.1 \times 10^{-5}) mol(^2) (P) (^{-2}), (4.90 \times 10^{-2}) atm (^{-2})</td>
<td>35. (1.203 \times 10^{-3}) mol litre (^{-1})</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>36. (4.865)</td>
<td>37. (1.75 \times 10^{-4}), 1, 4.75</td>
<td>38. (x = 0.63, y = 0.53, z = 0.98)</td>
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**Section-B : JEE Main/ AIEEE**

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<td>45. (a)</td>
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A. Fill in the Blanks

1. \( \text{SO}_4^{2-} \); Conjugate base = Acid – \( \text{H}^+ \)
   \( \therefore \) Conjugate base of \( \text{HSO}_4^- \) is \( \text{SO}_4^{2-} \)

2. **amphoteric**; because amphoteric substances show properties of both acids and basic.

3. \( k_p = k_c \frac{(RT)^\Delta n}{n} \)
   Here \( \Delta n = \) No. of moles of gaseous products
   \( - \) no. of moles of gaseous reactants
   \( R = \) gas constant, and \( T = \) absolute temperature.

4. **no change**; \( (K_p \) of an equilibrium reaction is independent of the pressure of the system.)

5. \( \text{I}_2 \) \( \therefore \) electron acceptors are Lewis acids.

B. True/False

1. **False** : \( \text{AlCl}_3 \) is a Lewis acid (although they do not have a proton, aprotic) because it accepts electrons (octet being incomplete).

2. **False** : \( K \) for \( A_2 + B_2 \Leftrightarrow 2AB \) is \( \frac{[AB]^2}{[A_2][B_2]} \)
   \( K' \) for \( AB \Leftrightarrow \frac{1}{2} A_2 + \frac{1}{2} B_2 \) is \( \frac{[A_2]^{1/2}[B_2]^{1/2}}{[AB]} \)
   \( \text{or} \quad \frac{[K']^2}{[AB]^2} = \frac{1}{K} \quad \therefore K' = \sqrt[4]{K} \)

3. **True** : Lower the pressure, lower will be boiling point. More liquid will vapourise and temperature decreases.

4. **TIPS/Formulae**:
   Dissolution of \( \text{NaOH} \) is exothermic.
   **False** : When a solute like \( \text{NaOH} \) is added to a solvent exothermic dissolution takes place. An increase in temperature always favour endothermic process. So solutes having exothermic dissolution shows a decrease in their solubility with temperature.

C. MCQs with One Correct Answer

1. **(b)** In molten state the cations and anions become free and flow of current is due to migration of these ions in opposite directions in the electric field.

2. **(a)** **NOTE** : Acidic buffer is mixture of weak acid and its salt with common anion.
   (a) \( \text{CH}_3\text{COOH} + \text{CH}_3\text{COONH}_4 \) is acidic buffer.
   (b) \( \text{NH}_4\text{Cl} + \text{NH}_3\text{OH} \) is basic buffer.
   (c) \( \text{H}_3\text{SO}_4 \) + \( \text{Na}_2\text{SO}_4 \) is not buffer because both the compounds are strong electrolytes.
   (d) \( \text{NaCl} + \text{NaOH} \) is not buffer solution because both compounds are strong electrolytes.

3. **(d)** **TIPS/Formulae** :
   (i) pH of acid cannot be more than 7.
   (ii) While calculating pH in such case, consider contribution \( [\text{H}^+] \) from water also.
   Molar conc. of \( \text{HCl} = 10^{-8} \). (given)
   \( \therefore \) pH = 8. But this cannot be possible as pH of an acidic solution can not be more than 7. So we have to consider \( [\text{H}^+] \) coming from \( \text{H}_2\text{O} \).
   Total [\( \text{H}^+ \)] = [\( \text{H}^+ \)\( \text{HCl} \)] + [\( \text{H}^+ \)\( \text{H}_2\text{O} \)]
   **Ionisation of \( \text{H}_2\text{O} \) : \( \text{H}_2\text{O} \Leftrightarrow \text{H}^+ + \text{OH}^- \)**
   \( K_w = 10^{-14} = [\text{H}^+] [\text{OH}^-] \)
   Let \( x \) be the conc. of \( [\text{H}^+] \) from \( \text{H}_2\text{O} \)
   or \( [\text{H}^+] = x = [\text{OH}^-] \) \( \therefore [\text{H}^+] = [\text{OH}^-] \) in water
   \( 10^{-14} = (x + 10^{-8}) (x) \) or \( x = 9.5 \times 10^{-8} \) M
   \( [\text{For quadratic equation } x = \frac{-b \pm \sqrt{4ac}}{2a}] \)
   \( \therefore \) Total [\( \text{H}^+ \)] = \( 10^{-8} + 9.5 \times 10^{-8} = 10.5 \times 10^{-8} \) or pH \( = -\log (10.5 \times 10^{-8}) = 6.98 \)
   It is between 6 and 7.

4. **(b)** **TIPS/Formulae** :
   (i) According is Le-Chateliers principle, exothermic, reactions are favoured at low temperature.
   (ii) According to Le-Chateliers principle, the reaction in which \( n < 0 \), are favoured at high pressure.

   **Given** \( 2\text{SO}_2 + \text{O}_2 \Leftrightarrow 2\text{SO}_3 + \text{Heat} \)
   \( \therefore \) It is exothermic reaction
   \( \therefore \) Yield of \( \text{SO}_3 \) is maximum at low temperature
   \( n = 2 - 2 = 0 \) so there is no change in \( K_p \) when total pressure changes.

5. **(d)** Only temperature affects the equilibrium constant. Since here \( \Delta H = 2 - 2 = 0 \), so there is no change in \( K_p \) when total pressure changes.

6. **(a)** **TIPS/Formulae**:
   (i) Lower the oxidation state of central atom, weaker will be oxy acid.
   (ii) Weaker the acid, stronger will be its conjugate base.
   Oxidation state of \( \text{Cl} \) in \( \text{HClO} \) is + 1, in \( \text{HClO}_2 \) is + 3, in \( \text{HClO}_3 \) is + 5, and in \( \text{HClO}_4 \) is + 7
   \( \therefore \) \( \text{HClO} \) is the weakest acid and so its conjugate base \( \text{ClO}^- \) is the strongest B ronnsted base.

7. **(b)** For pure water, \([\text{H}_2\text{O}^+] = [\text{OH}^-] \)
   \( \Rightarrow K_w = 10^{-6} \times 10^{-6} = 10^{-12} \)

8. **(b)** **TIPS/Formulae**:
   For precipitation to occur ionic product > solubility products
Given, $K_{spCaF_2} = 1.7 \times 10^{-10}$

$$CaF_2 \rightleftharpoons Ca^{2+} + 2F^-$$

Ionic product of $CaF_2 = [Ca^{2+}] [F^-]^2$

Calculate I.P. in each case

(a) I.P. of $CaF_2 = (10^{-4}) \times (10^{-4})^2 = 10^{-12}$

(b) I.P. of $CaF_2 = (10^{-2}) \times (10^{-3})^2 = 10^{-8}$

(c) I.P. of $CaF_2 = (10^{-5}) \times (10^{-3})^2 = 10^{-11}$

(d) I.P. of $CaF_2 = (10^{-3}) \times (10^{-5})^2 = 10^{-13}$

$\therefore$ I.P $> \text{solubility in choice (b) only.}$

$\therefore$ ppt of $CaF_2$ is obtained in case of choice (b) only.

9. (c) Vapours and liquid are at the same temperature.

10. (a) Statement (a) is correct and the rest statements are wrong. $K_p$ depends only on temperature hence at constant temp. $K_p$ will not change.

11. (a) For a basic buffer, $pH = 14 - pK_b - \log \frac{[\text{salt}]}{[\text{base}]}$

$$pH = 14 - pK_b - \log \frac{[\text{salt}]}{[\text{base}]} = 14 - (-\log 10^{-10}) - \log 1$$

$\Rightarrow pH = 4$

12. (c) TIPS/Formulae:

The equilibrium constant for the neutralization of a weak acid with a strong base is given by

$$K = K_a/K_w = \frac{1.0 \times 10^{-4}}{1.0 \times 10^{-14}} = 1.0 \times 10^{10}$$

13. (d) As all the reactants and products are present in aqueous form in (d) so it is a reversible reaction. In others either solid or gas is generated which is insoluble or volatile and hence makes the reaction unidirectional.

14. (d) TIPS/Formulae:

The pH of the solution at the equivalence point will be greater than 7 due to salt hydrolysis. So an indicator giving colour in basic medium will be suitable. Phenolphthalein is a good indicator if the base is strong because strong base immediately changes the pH at end point.

15. (a) Base $+ H^+ \rightarrow$ (conjugate acid)

$NH_2$ (base) $+ H^+ \rightarrow NH_4$ (conjugate acid)

16. (d) NOTE: Electron acceptors or elements having incomplete octet are Lewis acids.

(i) $BF_3$ (B has 6 e- in valence shell), $AlCl_3$ (Al has 6 electrons in valence shell), $BeCl_2$ (Be has 4 e- in valence shell) are electron deficient compounds and hence Lewis acids.

(ii) $SnCl_4$ has complete octet so it is Lewis base.

17. (c) $CaO$, $CaCO_3$ and $Ca(OH)_2$ dissolve in $CH_3COOH$ due to formation of $(CH_3COO)_2Ca$. But $CaC_2O_4$ does not dissolve as $CH_3COO^-$ is a stronger conjugate base than $C_2O_4^{2-}$.

18. (d) (a) is a neutral solution due to both cationic and anionic hydrolysis ($K_a = K_b = 1.8 \times 10^{-5}$); (b) is acidic solution due to cationic hydrolysis; (c) is acidic solution due to cationic hydrolysis; (d) is basic solution due to anionic hydrolysis.

Alternate solution. Step-1.

19. (a) For a precipitation to occur, Solubility product $< \text{Ionic product}$

Given $K_{sp} = 1.8 \times 10^{-10}$

Calculating ionic products in each

Ionic product $= [Ag^+] [Cl^-] = \frac{10^{-4}}{2} \times \frac{10^{-4}}{2}$

$= 2.5 \times 10^{-9}$

which is greater than $K_{sp}$ ($1.8 \times 10^{-10}$).

$\therefore$ equal volumes are mixed,

so $[Ag^+] = \frac{10^{-4}}{2}$ and $[Cl^-] = \frac{10^{-4}}{2}$

Step-2

20. (d) TIPS/Formulae:

In acidic medium weak acids are unionized due to common ion effect and they are completely ionised in alkaline medium.

Aspirin (or acetyl salicylic acid) is unionised in stomach (where pH is 2-3) and is completely ionised in small intestine (when pH is 8).

21. (a) TIPS/Formulae:

(i) Higher the electronegativity of central atom higher will be the acidic strength.

(ii) In case of same atom higher the value of oxidation state of the metal, higher will be its acidic strength.

The electronegativity of Cl > S.

Oxidation no. of Cl in $ClO_3(OH) = + 7$

Oxidation no. of Cl in $ClO_4(OH) = + 5$

Oxidation no. of S in $SO_3H_2 = + 4$

Oxidation no. of S in $SO_2(OH)_2 = + 6$

$\therefore$ $ClO_3(OH)$ is the strongest acid.

22. (d) NOTE: In case of alkaline earth hydroxides solubility increases on moving down the group. Be(OH)$_2$ has lowest solubility and hence lowest solubility product. [Be at tip of the group]

23. (a) Due to absence of hydrolyisation of $FeCl_3$, backward reaction will not take place.
24. (d) Since HCl is stronger than CH₃COOH hence acts as acid. On the other hand Cl⁻ is a stronger base than CH₃COOH⁺, and is the conjugate base of HCl.

\[
\text{HCl} + \text{CH}_3\text{COOH} \rightleftharpoons \text{Cl}^- + \text{CH}_3\text{COOH}^+ \\
\text{acid}_1 \quad \text{base}_2 \quad \text{base}_1 \quad \text{acid}_2
\]

25. (d) (a) It is not a correct answer because 100 ml M/10 HCl will completely neutralize 100 ml M/10 NaOH and the solution will be neutral.

(b) After neutralisation resultant solution will be acidic due to presence of excess of HCl.

(c) After neutralisation resultant solution will be basic due to presence of excess of NaOH.

(d) M. eq. of HCl = 75 N/5 = 15 Meq

\[
\text{M.eq. of NaOH} = 25 \times \frac{1}{5} = 5 \text{ Meq}
\]

\[
\therefore \quad \text{M. eq. of HCl left} = 10, \quad [\text{HCl}] = \frac{10}{100} = \text{M/10}
\]

\[
\therefore \quad \text{pH} = -\log [\text{H}^+] = -\log \left(\frac{1}{10}\right) = 1
\]

26. (b) **TIPS/Formulæ:**

\[
\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^- \\
(1 - \alpha) \quad \alpha \quad \alpha \quad \alpha
\]

\[
\alpha = 1.9 \times 10^{-7}; \quad \text{Density of water} = \frac{1.0 \text{ gm}}{\text{cm}^3}
\]

\[
\therefore \quad c = \frac{1}{18} \times 1000 = 55.56 \text{ moles/l}
\]

\[
\therefore \quad [\text{H}^+] = 55.56 \times 1.9 \times 10^{-9} = 1.055 \times 10^{-7}
\]

\[
\therefore \quad K_w = [\text{H}^+] [\text{OH}^-] = (1.055 \times 10^{-7})^2 = 1.0 \times 10^{-14}
\]

27. (c) Salts of weak base and strong acid get hydrolysed in aqueous solution forming an acidic solution.

\[
\text{AlCl}_3 + 3\text{H}_2\text{O} \rightarrow \text{Al(OH)}_3 + 3\text{HCl}
\]

(weak) \quad (strong) \quad (acetic)

28. (a) Among oxyacids of the same type formed by different elements, acidic nature increases with increasing electronegativity. In general, the strength of oxyacids decreases as we go down the family in the periodic table.

\[
\text{HOCl (I)} > \text{HOB (II)} > \text{HOI (III)}
\]

[In halogen groups Cl is above Br and I]

29. (b) The characteristics of the given solutions are:

- NaCl - neutral solution
- NH₄Cl - slightly acidic due to the following reaction
  \[
  \text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3\text{OH} + \text{H}^+ 
  \]
- NaCN - slightly alkaline due to the following reaction
  \[
  \text{CN}^- + \text{H}_2\text{O} \rightleftharpoons \text{HCN} + \text{OH}^- 
  \]

30. (a) The given reaction will be exothermic in nature due to the formation of three X - Y bonds from the gaseous atoms. The reaction is also accompanied with the decrease in the gaseous species (i.e. \(\Delta n\) is negative).

Hence, the reaction will be affected by both temperature and pressure. The use of catalyst does not affect the equilibrium concentrations of the species in the chemical reaction.

\[
K_b = K_c (RT)^{\Delta n}
\]

\[
\Delta n = 2 - 4 = -2 \quad K_c = \frac{K_p}{(RT)^{\Delta n}} = \frac{1.44 \times 10^{-5}}{(0.082 \times 773)^{-2}}
\]

(R in L.atm.K⁻¹.mole⁻¹).

32. (d) At initial stage of reaction, concentration of each product will increase and hence Q will increase.

33. (a) **TIPS/Formulæ:**

For oxyacids containing similar central atom, the acid strength increases with the increase in the number of oxygen atom attached to the central atom and not attached to any other atom.

**TIPS/Formulæ:**

Higher the oxidation number of the central atom, higher is the acidity of the species. Thus acidity follows the order

\[
\text{Oxi. No. of Cl} \quad \text{HClO} < \text{HClO}_2 < \text{HClO}_3 < \text{HClO}_4
\]

\[
+1 \quad +3 \quad +5 \quad +7
\]

34. (a) \[
A_pB_q(s) \rightleftharpoons pA^{+q} + qB^{-p}
\]

\[
L_s = (pS)^p (qS)^q
\]

35. (d) At constant temperature \(K_p\) or \(K_c\) remains constant.

With change of pressure, \(x\) will change in such a way that \(K_p\) remains a constant.

36. (d) **TIPS/Formulæ:**

At constant temperature \(K_p\) or \(K_c\) remains constant.

For the equilibria:

\[
\text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g)
\]

**NOTE:** \(K_p = K_c\) because here \(\Delta n = 1\)

\[
[\text{K}_p = K_c \times (RT)^{\Delta n}] \quad \text{Since temperature is constant so } K_c \text{ or } K_p \text{ will remain constant. Further since volume is halved, the pressure will be doubled so } \alpha \text{ will decrease so as to maintain the constancy of } K_c \text{ or } K_p.
\]

\[
\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2
\]

\[
\text{initial} \quad 1 \quad 0
\]

at equilibrium \(1 - \alpha\) \(2\alpha\)

\[
\therefore \quad \text{T. mole} = 1 - \alpha + 2\alpha = 1 + \alpha
\]

Let total pressure = P

\[
\therefore \quad p\text{N}_2\text{O}_4 = \frac{1 - \alpha}{1 + \alpha} \quad p\text{NO}_2 = \frac{2\alpha}{1 - \alpha} \quad p
\]
\[ K_p = \left( \frac{pNO_2}{pN_2O_4} \right)^2 = \frac{4\alpha^2 \times p}{(1-\alpha)(1+\alpha)} = \frac{4\alpha^2 p}{1 - \alpha^2} \]

Since \( K_p \) is constant, so \( \alpha \propto \frac{1}{\sqrt{p}} \)

So when volume is halved, pressure gets doubled and thus \( \alpha \) will decrease.

37. (b) \[ h = \frac{K_w}{K_a \times c} = \sqrt{\frac{10^{-14}}{10^{-5} \times 0.1}} = 10^{-4} \]

Hence, % hydrolysis = 10^{-4} \times 100 = 0.01

38. (c) \textbf{NOTE:} For isotonic solutions, osmotic pressure is same.

\[ \text{Na}_2\text{SO}_4 \quad \overset{(0.004-x)}{\underset{2x}{\rightleftharpoons}} \quad 2\text{Na}^+ + \text{SO}_4^{2-} \]

Since both solutions are isotonic, therefore, 0.004 + 2x = 0.01 \; ; \; x = 3 \times 10^{-3}

\[ \therefore \; \% \text{ Dissociation} = \frac{3 \times 10^{-3}}{0.004} \times 100 = 75\% \]

\textbf{Alternate eqn.} Total no. of moles = 0.004 \times x + 2x + x

39. (b) \textbf{NOTE:}

For basic buffer pH is more than 7.

\[
\begin{align*}
\text{CH}_3\text{NH}_2 + \text{HCl} & \rightarrow \text{CH}_3\text{NH}_3^+ \text{Cl}^- \\
\text{Initial moles} & \quad 0.1 \quad 0.08 \quad 0 \\
\text{Moles after} & \quad 0.02 \quad 0.08 \\
\text{mixing} & \quad 0.02 \quad 0.08 \\
\text{As it is a basic buffer solution.} & \\
\rho OH & = \rho \text{NH}_3 + \log \frac{0.08}{0.02} = -\log 5 \times 10^{-4} + \log 4 \\
& = 3.30 + 0.602 = 3.902 \\
\text{pH} & = 14 - 3.902 = 10.09; [H^+] = 7.99 \times 10^{-11} \approx 8 \times 10^{-11} \text{ M} \\
\end{align*}
\]

40. (a) In a reversible reaction, catalyst speeds up both the forward and backward reactions to the same extent, so (c) is wrong. At equilibrium,

\[ \Delta G = G_{products} - G_{reactants} = 0 \]

\[ \Rightarrow 2G_{NH_3} - (G_{N_2} + 3G_{H_2}) = 0 \]

or \( 2G_{NH_3} = G_{N_2} + 3G_{H_2} \)

41. (d) Let the weak monoacidic base be BOH, then the reaction that occurs during titration is

\[ \text{BOH} + \text{HCl} \rightarrow \text{BCl} + \text{H}_2\text{O} \]

\text{Equilibrium:} \quad \text{B}^+ \quad + \quad \text{H}_2\text{O} \quad \overset{C(h)}{\rightleftharpoons} \quad \text{BOH} + \text{H}^+ \quad \overset{C(h)}{\rightleftharpoons} \quad \text{C}_h \\

\text{Using the normality equation,} \; N_1V_1 = N_2V_2 \\
\text{Substituting various given values, we get} \]

\[
\frac{2}{15} \times V_1 = 2.5 \times \frac{2}{5} \]

or \( V_1 = 2.5 \times \frac{2}{5} \times \frac{15}{2} = 2.5 \times 3 = 7.5 \text{ ml} \)

Then the concentration of BCl in resulting solution is given by

\[
[\text{BCl}] = \frac{2 \times 2.5}{10} = \frac{2}{10} = 0.1 \text{ M} \\
\]

Since \( K_h = \frac{K_w}{K_b} \; \therefore \; K_h = \frac{10^{-14}}{10^{-12}} = 10^{-2} \)

Thus \( K_h = \frac{0.1h^2}{(1-h)} \) or \( 10^{-2} = \frac{0.1h^2}{(1-h)} \)

or \( 10^{-2} - 10^{-2}h = 0.1h^2 \) or \( 0.1h^2 + 10^{-2}h - 10^{-2} = 0 \)

(Solving this quadratic equation for \( h \), we get)

\[
\frac{-0.01 \pm \sqrt{0.001 + 0.004}}{0.2} = \frac{-0.01 \pm 0.0041}{0.2} = 0.27 \\
\text{[Neglecting the negative term]}
\]

\( \therefore \; [H^+] = 0.27 \times 10^{-2} \text{ M} \)

Thus the correct answer is [d].

42. (d) \textbf{MX} \rightarrow \textbf{M}^+ + \textbf{X}^- \quad \text{(Where s is the solubility)}

Then \( K_{sp} = s^2 \) or \( s = \sqrt{K_{sp}} \)

Similarly for \textbf{MX}_2 \rightarrow \textbf{M}^{2+} + 2\textbf{X}^-

\[
K_{sp} = s \times (2s)^2 = 4s^3 \quad \text{or} \quad s = \left[ \frac{K_{sp}}{4} \right]^{\frac{1}{3}} \\
\]

and for \textbf{MX}_3 \rightarrow 3\textbf{M}^+ + 3\textbf{X}^- \quad \text{3s}^3

\[
K_{sp} = (3s)^3 \times s = 27s^4 \quad \text{or} \quad s = \left[ \frac{K_{sp}}{27} \right]^{\frac{1}{4}} \\
\]

From the given values of \( K_{sp} \) for \textbf{MX}, \textbf{MX}_2 and \textbf{MX}_3, we can find the solubilities of those salts at temperature, \( T \).

Solubility of \textbf{MX} = \sqrt{4 \times 10^{-8}} = 2 \times 10^{-4}
Solubility of $MX_2 \approx \left[ \frac{3.2 \times 10^{-14}}{4} \right]^\frac{1}{3}$ or $\left[ \frac{32}{4} \times 10^{-15} \right]^\frac{1}{3}$

$= \left[ 8 \times 10^{-15} \right]^\frac{1}{3}$ or $2 \times 10^{-15}$

Solubility of $M_3X = \left[ \frac{2.7 \times 10^{-15}}{27} \right]^\frac{1}{4}$

$= \left[ 10^{-16} \right]^\frac{1}{4}$ or $10^{-4}$

Thus the solubilities are in the order $MX > M_3X > MX_2$

i.e the correct answer is (d).

**D. MCQs with One or More Than One Correct**

1. **(a, b, c, d)** The reaction is exothermic, hence increasing temperature will favour backward reaction (i.e. conc. of $C_2H_4$ increases) removing $H_2$ and adding $C_2H_6$ favours backward reaction.

2. **(c, d)** $2NaNO_3 \rightarrow 2NaNO_2 + O_2$

   According to Le Chatelier principle an increase in pressure always favours the reaction, where volume or moles decrease (i.e. reverse direction). As heat is added, i.e. reaction is endothermic and is supported in forward direction with increase in temperature.

3. **(a)** At constant volume, concentrations do not change.

4. **(c, d, e)** Introduction of an inert gas at constant pressure causes the equilibrium to shift in a direction in which number of moles increases. The forward reaction is further accelerated by increase in the quantity of substrate, i.e., PCl_3 and by the increase of space, i.e., volume of container.

5. **(d)** $CO_{(g)} + H_2O_{(g)} \leftrightarrow CO_{2(g)} + H_2(g)$

   $K_C = \frac{[CO_2][H_2]}{[CO][H_2O]}$

   A catalyst simply helps in attaining the equilibrium earlier.

   Addition of inert gas has no effect on a reaction because in it $\Delta n = 0$.

   This equilibrium is not based upon volume because in it $\Delta n = 0$.

   On increasing the amount of CO, $K_C$ will decrease but it is constant at constant temperature, so for maintaining the constant value of $K_C$, the amount of CO$_2$ increases.

6. **(b, c)** $pH$ of $1 \times 10^{-8}$ M is below 7 because it is an acid.

   $H_2PO_4^- + H_2O \leftrightarrow HPO_4^{2-} + H_3O^+$

   $K$ (Auto protolysis constant of water i.e. ionic product of water) increases with temperature. For half neutralisation of a weak acid by a weak base,

   $pH = pK_a + \log \frac{[Salt]}{[Acid]}$

   $[Salt] = [Acid], \therefore pH = pK_a$

   **7. (a, c)** A buffer solution is prepared by mixing a weak acid/base with salt of its conjugate base/acide.

   **8. (c, d)** Any solution of a weak acid and its salt with strong base acts as an acidic buffer solution.

   If volume of HNO_3 solution added is less as compared to that of CH$_3$COONa solution, it results in the formation of an acidic buffer solution.

   $CH_3COONa + HNO_3 \rightarrow CH_3COOH + NaNO_3$

   **9. (a)** As ester hydrolysis is first order with respect $[H^+]$.

   $\frac{R_{HA}}{R_{HX}} = \frac{[H^+]_{HA}}{[H^+]_{HX}}$ ; $\frac{1}{100} = [H^+]_{HA}$ = 0.01

   $\frac{HA}{H^+ + A^-}$

   $K_a = \frac{0.01 \times 0.01}{1} = 10^{-4}$

   **10. (b)** $Ag_2CrO_4 \Leftrightarrow 2Ag^+ + CrO_4^{2-}$

   $K_{sp} = 1.1 \times 10^{-12} = [Ag^+]^2 \cdot [CrO_4^{2-}]$

   $1.1 \times 10^{-12} = [0.1]^2 \cdot s = 1.1 \times 10^{-10}$

   **11. (a, b, d)**

   (A) $\Delta H = C_p \Delta T$

   Hence enthalpy depends on temperature.

   (B) $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$ $K_p = P_{CO_2}$

   (C) $K_{eq}$ depends only on temperature and not on pressure.

   (D) Enthalpy of reaction is independent of the catalyst. Catalyst generally changes activation energy.

   **12. (b)** Initially on increasing temperature rate of reaction will increase, so % yield will also increase with time. But at equilibrium % yield at high temperature ($T_2$) would be less than at $T_1$ as reaction is exothermic so the graph is
E. Subjective Problems

1. Phenolphthalein indicates half neutralization.

\[ \text{Na}_2\text{CO}_3 + \text{H}^+ \rightarrow \text{NaHCO}_3 + \text{Na}^+ \]  \hspace{1cm} \text{(i)}

Methyl orange indicates complete neutralisation

\[ \text{NaHCO}_3 + \text{H}^+ \rightarrow \text{Na}^+ + \text{H}_2\text{O} + \text{CO}_2 \]  \hspace{1cm} \text{(ii)}

\[ \therefore \text{Volume of} \ 0.1 \text{M H}_2\text{SO}_4 \text{ required for complete neutralisation} = 2 \times 2.5 = 5.0 \text{ ml} \]

\[ 0.1 \text{ M H}_2\text{SO}_4 = 0.2 \text{ NH}_2\text{SO}_4 \]

[For H_2SO_4 molarity = 2 × normality]

\[ (\therefore \text{ Mol. wt. of} \ H_2\text{SO}_4 = 98, \text{ and eq. wt. of} \ H_2\text{SO}_4 = 49) \]

\[ \therefore 0.2 \text{ M H}_2\text{SO}_4 = 0.4 \text{ NH}_2\text{SO}_4 \]

\[ N_1 = \text{normality of} \text{Na}_2\text{CO}_3, \quad V_1 = \text{volume of} \text{Na}_2\text{CO}_3 = 10 \text{ ml}, \]

\[ N_2 = \text{normality of} \text{H}_2\text{SO}_4 = 0.2, \quad V_2 = \text{volume of} \text{H}_2\text{SO}_4 = 5.0 \text{ ml} \]

\[ \therefore N_1V_1 = N_2V_2 \Rightarrow N_1 \times 10 = 0.2 \times 5 \]

\[ \therefore N_1 = \frac{0.2 \times 5}{10} = 0.1 \text{ N} \]

\[ \therefore \text{ Eq. wt. of Na}_2\text{CO}_3 = \frac{1}{2} \times \text{ molecular weight} = \frac{106}{2} = 53 \]

Strength of Na_2CO_3 = 53 × 0.1 = 5.3 g/l

[:: strength = normality × Eq. wt]

For neutralization with methyl orange, volume of 0.2 M H_2SO_4 used = 2.5 ml = 2.5 ml of 0.4 N H_2SO_4

\[ = 5 \text{ ml of} \ 0.2 \text{ N H}_2\text{SO}_4 \] \hspace{1cm} [:: N_1V_1 = N_2V_2]

From 5 ml of 0.2 N H_2SO_4, 2.5 ml is used for neutralising NaHCO_3 formed during first half neutralization Na_2CO_3

Volume of 0.2N H_2SO_4 used for neutralisation of NaHCO_3 present in original solution = 5.0 - 2.5 = 2.5 ml

\[ \therefore N_1V_1 = N_2V_2 \]

where \( \quad N_1 = \text{Normality of NaHCO}_3, \]

\[ N_2 = \text{Normality of} \text{H}_2\text{SO}_4 = 0.2, \]

\[ V_1 = \text{Volume of} \text{NaHCO}_3 = 10 \text{ ml}, \quad V_2 = \text{Volume of} \text{H}_2\text{SO}_4 = 2.5 \text{ ml} \]

\[ N_1V_1 = N_2V_2 \Rightarrow N_1 \times 10 = 0.2 \times 2.5 \]

\[ N_1 = \frac{0.2 \times 2.5}{10} = 0.05 \text{ N} \]

Eq. wt. of NaHCO_3 = 84

\[ \therefore \text{ Strength of NaHCO}_3 = 84 \times 0.05 = 4.2 \text{ g/l} \]

2. Suppose the number of moles of sodium propionate = \( x \)

Then \( \text{pH} = pK_a + \log \left( \frac{\text{[Salt]}}{\text{[Acid]}} \right) \)

\[ 4.75 = -\log (1.34 \times 10^{-5}) + \log \left( \frac{x}{0.02} \right) \]

or \[ 4.75 = 5 - 0.1271 + \log \frac{x}{0.02} \]

or \[ 4.75 = 4.8729 + \log \frac{x}{0.02} \]

\[ \log \frac{x}{0.02} = -0.1229 \]

or \[ \frac{x}{0.02} = \text{Antilog} [-0.1229] \text{ or } \frac{x}{0.02} = 0.7536 \]

\[ x = 0.7536 \times 0.02 = 1.5072 \times 10^{-2} \text{ mol} \]

\[ \text{HCl} \quad \Longleftrightarrow \quad \text{H}^+ + \text{Cl}^- \]

\[ 0.01 \text{ mole} \quad 0.01 \text{ mole} \]

When 0.01 mole of HCl is added, there is (0.01 + 0.02) M of propionic acid and (0.015 - 0.010) M of propionate. Therefore

\[ p\text{H} = -\log (1.34 \times 10^{-5}) + \log \left( \frac{0.005}{0.03} \right) = 4.09 \]

The p\text{H} of a 0.010 molar HCl solution = -log 10^{-2} = 2

3. Initial moles \[ \begin{array}{ccc} 1 & 3 & 0 \\ \text{N}_2\text{(g)} & + & \text{H}_2\text{(g)} & \Longleftrightarrow & \text{2NH}_3\text{(g)} \end{array} \]

Eq. moles \[ \begin{array}{ccc} 1 - 0.0025 & 3 - 0.0075 & 2 \times 0.0025 \\ \text{Eq. conc.} & \frac{1 - 0.0025}{4} & \frac{3 - 0.0075}{4} & \frac{2 \times 0.0025}{4} \end{array} \]

Now we know that \( K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2]^1[\text{H}_2]^3} \)

Since 0.0025 and 0.0075 are very small, 1 - 0.0025 and 3 - 0.0075 may be taken as 1 and 3 respectively.

Substitute the various values

\[ K_c = \frac{\left( \frac{2 \times 0.0025}{4} \right)^2}{\left( \frac{1}{4} \right)^3 \left( \frac{3}{4} \right)^3} = \frac{0.0025 \times 0.0025}{\frac{4}{3 \times 3 \times 3}} \times \frac{4 \times 4 \times 4}{4} \]

\[ = 1.48 \times 10^{-5} \text{ litre}^2 \text{ mol}^{-2} \]

For the equilibrium,

\[ \frac{1}{2} \text{N}_2\text{(g)} + \frac{3}{2} \text{H}_2\text{(g)} \Longleftrightarrow \text{NH}_3\text{(g)} \]

\[ K_c' = \frac{[\text{NH}_3]}{[\text{N}_2]^{1/2}[\text{H}_2]^{3/2}} = \sqrt{K_c} \]

\[ = \sqrt{(1.48 \times 10^{-5} \text{ litre}^2 \text{ mol}^{-2})} \]

\[ = 3.82 \times 10^{-3} \text{ litre} \text{ mol}^{-1} \]

4. TIPS/Formulae:

(i) Find the moles of each species after reaction.

(ii) \[ \text{pH} = -\log K_a + \log \left( \frac{\text{[salt]}}{\text{[Acid]}} \right) \]

Given, \( \text{NaOH} \ 0.2 \text{ M, } 20 \text{ ml} \); \( \text{CH}_3\text{COOH} \ 0.2 \text{ M, } 50 \text{ ml} \)

\( K_a = 1.8 \times 10^{-5} \)
V of 0.2M NaOH required to make pH = 4.74 = ?

From the chemical reaction

$$
\text{CH}_3\text{COOH} + \text{NaOH} \rightarrow \text{CH}_3\text{COONa} + \text{H}_2\text{O}
$$

It is evident that 70 ml of the product will contain

(i) 30 ml of 0.2 M unused CH$_3$COOH

[unused CH$_3$COOH = 50 – 20 = 30 ml]

(ii) 20 ml of CH$_3$COONa.

\[
\text{No. of moles of CH}_3\text{COOH in solution} = \frac{0.2}{1000} \times 30 = 0.006 \text{ mole}
\]

Similarly, No. of moles of CH$_3$COONa solution

\[
= \frac{0.2}{1000} \times 20 = 0.004 \text{ moles}
\]

\[
\text{pH} = -\log K_a + \log \left(\frac{\text{[Salt]}}{\text{[Acid]}}\right)
\]

Substituting the values of the various values

\[
\text{pH} = -\log 1.8 \times 10^{-5} + \log \frac{0.004}{0.006}
\]

\[
= 4.7447 - 0.1761 = 4.5686
\]

Calculation of the additional volume of 0.2 M NaOH required to make pH of solution 4.74.

\[
\text{pH} = -\log K_a + \log \left(\frac{\text{[Salt]}}{\text{[Acid]}}\right)
\]

or 4.74 = -\log 1.8 \times 10^{-5} + \log \left(\frac{\text{[Salt]}}{\text{[Acid]}}\right)

or 4.74 = 4.7447 + \log \left(\frac{\text{[Salt]}}{\text{[Acid]}}\right)

\[
\therefore \log \left(\frac{\text{[Salt]}}{\text{[Acid]}}\right) = 0.0047 \text{ or } \frac{\text{[Salt]}}{\text{[Acid]}} = \frac{1}{1.011}
\]

NOTE THIS STEP: Let x ml. be the volume of additional 0.2 M NaOH added to make the pH of the solution 4.74. This will further neutralise x ml. of 0.2 M CH$_3$COOH and produce x ml. of 0.2 M sodium acetate. The resulting solution (70 + x) will now contain

(i) (30 – x) ml of 0.2 M acetic acid.

(ii) (20 + x) ml of 0.2 M sodium acetate.

Number of moles of acetic acid in (70 + x) ml. solution

\[
= \frac{0.2}{1000} \times (30 – x) = 2 \times 10^{-4} (30 – x)
\]

Number of moles of CH$_3$COONa in (70 + x) ml. solution

\[
= \frac{0.2}{1000} \times (20 + x) = 2 \times 10^{-4} (20 + x)
\]

Therefore,

\[
\frac{\text{[Salt]}}{\text{[Acid]}} = \frac{2 \times 10^{-4} (20 + x)}{2 \times 10^{-4} (30 – x)} = \frac{20 + x}{30 – x}
\]

5. (i) From the dissociation of weak acid HA,

HA $\Leftrightarrow$ H$^+$ + A$^-$

It is the degree of ionization of the acid HA, then

$[\text{H}^+] = 0.1 \alpha$ \quad [\because \text{the acid is decimolar}]

$[\text{A}^-] = 0.1 \alpha$; \quad [\text{HA}] = 0.1 (1 – $\alpha$)

Therefore,

\[
K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{0.1 \alpha \times 0.1 \alpha}{0.1 (1 – \alpha)}
\]

\[
= \frac{0.1 \alpha \times 0.1 \alpha}{0.1} \quad \text{(since acid is weak, 1 – $\alpha$ = 1)}
\]

$K_a = 0.1 \alpha^2$ or $4.9 \times 10^{-8} = 0.1 \alpha^2$

or $\alpha^2 = \frac{4.9 \times 10^{-8}}{0.1}$ or $\alpha = 7 \times 10^{-4}$

\[
\therefore \text{Percentage ionization} = 100 \times \frac{7 \times 10^{-4}}{7} = 7 \times 10^{-2}\%
\]

(ii) Calculation of pH

$[\text{H}^+] = 0.1 \alpha = 0.1 \times 7 \times 10^{-4}$ mole/litre \quad [\because \lambda = 7 \times 10^{-4}]

= $7 \times 10^{-5}$ mole/litre

Now since pH = $-\log [\text{H}^+] = -\log [7 \times 10^{-5}]$

= $5 - \log 7 = 5 - 0.8451 = 4.1549$

(iii) Concentration of OH$^-$ in decimolar solution

$[\text{H}^+] = 7 \times 10^{-5}$ mole per litre

Now, \quad $K_w = [\text{H}^+][\text{OH}^-]$ or $1.0 \times 10^{-14} = 7 \times 10^{-5} \times [\text{OH}^-]$

\[
\therefore [\text{OH}^-] = \frac{1 \times 10^{-14}}{7 \times 10^{-5}} = 1.43 \times 10^{-10} \text{ mole per litre}
\]

6. TIPS/Formulae:

For precipitation to occur ionic product > $K_{sp}$.

Mixture solution contains 0.1 M Ag$^+$ and 0.1 Mg Hg$_2^{2+}$.

$K_{sp}$ of Hg$_2$I$_2$ = $2.5 \times 10^{-26}$ is much smaller than $K_{sp}$ of AgI which is $8.5 \times 10^{-17}$.

[I$^-]$ concentration needed to precipitate Hg$_2$I$_2$ is calculated as:

\[
\text{Hg}_2\text{I}_2 \Leftrightarrow \text{Hg}_2^{2+} + 2\text{I}^-\]

\[
[I^-] = \sqrt{\frac{K_{sp}}{[\text{Hg}_2^{2+}]}} = \sqrt{\frac{2.5 \times 10^{-26}}{0.1}} = 5.0 \times 10^{-13} \text{ M}
\]

Similarly, [I$^-]$ concentration needed to precipitate AgI is:

\[
\text{AgI} \Leftrightarrow \text{Ag}^+ + \text{I}^-
\]

\[
[I^-] = \frac{K_{sp}}{[\text{Ag}^+]} = \frac{8.5 \times 10^{-17}}{0.1} = 8.5 \times 10^{-16} \text{ M}
\]
**Equilibrium**

**NOTE:** Since $[\Gamma^{-}]$ concentration needed to ppt. Agl is smaller than that needed to ppt. Hg$_2$I$_2$, Agl is completely precipitated first. Agl starts precipitation with $[\Gamma^{-}] = 8.5 \times 10^{-16}$ M. However, Hg$_2$I$_2$ starts precipitating with Agl only when molar concentration of $[\Gamma^{-}]$ reaches $5.0 \times 10^{-13}$ M. [Ag$^+$] left when Hg$_2$I$_2$ begins to ppt. is given by

$$K_{sp} \text{ of Agl} \left[\Gamma^{-}\right]_{Hg_2I_2} = \frac{8.5 \times 10^{-17}}{5.0 \times 10^{-13}} = 1.7 \times 10^{-4} \text{ M}$$

Thus $\%$ [Ag$^+$] left unprecipitated = $\frac{1.7 \times 10^{-4}}{0.1} \times 100 = 0.17\%$

Hence $\%$ Ag$^+$ precipitated = $99.83\%$

7. Let $x$ be the degree of dissociation of PCl$_5$(g), then

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

Initial $\begin{array}{c} \text{3} \\ \text{0} \\ \text{1} \end{array}$

At equilibrium $\begin{array}{c} 3(1-x) \\ 3x \\ 1 + 3x \end{array}$

:. Total number of moles at equilibrium

$= 3(1-x) + 3x + 1 + 3x = 3(1+x) + 1$

Using the gas equation: $PV = nRT$

$$n = \frac{PV}{RT}$$

Here, $P = 2.05$ atm., $V = 100$ litres, $R = 0.082$ atm.deg., $T = 273 + 227 = 500$ K

$$n = \frac{2.05 \times 100}{0.082 \times 500} = 5 \Rightarrow 3(1+x) + 1 = 5$$

or $3 + 3x + 1 = 5$ or $3x = 5 - 4$ or $x = \frac{1}{3} = 0.333$

Hence percentage dissociation of PCl$_5$ = $0.333 \times 100 = 33.3\%$

Calculation of $K_p$ for the reaction:

$$K_p = \left[\frac{[PCl_3][Cl_2]}{[PCl_5]}\right] \approx \left[\frac{3xP}{3(1 + x) + 1}\right] \left[\frac{(1 + 3x)P}{3(1 + x) + 1}\right]$$

$$= \frac{3x(3x + 1)}{3(1 - x)} \times \frac{1P}{3(1 + x) + 1}$$

$$= \frac{(3x^2 + x) \times P}{(4 + 3x)(1 - x)} = \frac{x(3x + 1) \times P}{(4 + 3x)(1 - x)}$$

Substituting, $x = 1/3$ and $P = 2.05$ atm., we get

$$K_p = \frac{\frac{1}{3} \left(3 \times \frac{1}{3} + 1\right)}{4 + 3\left(\frac{1}{3}\right)} \times 2.05 = 4.1 \text{ atm} = 0.41$$

8. (i) $N_2 < O_2 < F_2 < Cl_2$

i.e., $N \equiv N < O = O < F = F < Cl = Cl$

**NOTE:**

As the number of bonds increases the bond length decreases.

So $N_2 < O_2 <$ halogens. Among $F_2$ and $Cl_2$ bond length of $Cl_2$ will be higher because of higher atomic radii.

(ii) Among oxyacids of the same element, acidic nature increases with its oxidation number, e.g.,

$$HOCl < HOCIO < HOCIO_2 < HOCIO_3$$

O.N. of $Cl$ +1 +3 +5 +7

(iii) $H_2O < CH_3 - OH = OH^- < OCH_3$

Weaker the base stronger is its conjugate acids

$H_2O^+ > CH_3 O^+ > H_2O > CH_3OH$ (Decreasing acidic order of the conjugate bases.)

(iv) $BaO > B_{2}O_3 > CO_2 > SO_2 > Cl_2O_7$

Basicity increases with increase in oxidation state

(Ba = +2, B = +3, C = +4, S = +6, Cl = +7).

9. **TIPS/Formulæ:**

For acidic buffer $pH = -\log K_a + \log \left[\frac{[Salt]}{[Acid]}\right]$

Calculation of concentration of $HCOOH$.

Here, $c = 0.2$ M, $[H^+] = 6.4 \times 10^{-3}$

$$[H^+] = c \alpha \Rightarrow \alpha = \frac{[H^+]}{c} = \frac{6.4 \times 10^{-3}}{0.2} = 3.2 \times 10^{-2}$$

**NOTE:** Thus the degree of dissociation of $HCOOH$ is very low which on addition of sodium formate is further suppressed due to common ion effect.

Since the degree of dissociation is very low ($3.2 \times 10^{-2}$), it can be neglected and hence $[HCOOH]$ can be taken as $0.2$ M.

**Calculation of concentration of $HCOO^-$, $[HCOO^-]$**

It can be obtained in the following manner:

$$HCOONa \rightleftharpoons HCOO^- + Na^+$$

At start $\begin{array}{c} \text{1} \\ \text{0} \\ \text{0} \end{array}$

At equ. $0.25 \begin{array}{c} \text{0.75} \\ \text{0.75} \end{array}$

:. $[HCOO^-] = 0.75$

For acidic buffer $pH = -\log K_a + \log \left[\frac{[Salt]}{[Acid]}\right]$

$$=-\log 2.4 \times 10^{-4} + \log 0.75 = 4.19$$

10. $A_2(g) + B_2(g) \rightleftharpoons 2AB(g)$

At start $\begin{array}{c} \text{1} \\ \text{2} \end{array}$

At equ. $\begin{array}{c} 1-x \\ 2-x \end{array}$

:. $[A_2] = \frac{1-x}{3}$, $[B_2] = \frac{2-x}{3}$, $[AB] = \frac{2x}{3}$

:. $K = \frac{(2x/3)^2}{[(1-x)/3][2-x/3]} = 50$
On solving we get, \( 23x^2 - 75x + 50 = 0; x = 2.317 \) or 0.943
The value 2.317 is inadmissible because initial concentration of reactants is 2 moles and so \( x = 0.943 \)
\[ \therefore \text{Moles of AB formed} = 2 \times 0.943 = 1.886 \]

11. **Solubility of Mg(OH)\(_2\) in water**

\[
S = 9.57 \times 10^{-3} \text{ g/litre} = \frac{9.57 \times 10^{-3}}{58} = 1.65 \times 10^{-4} \text{ mole/litre}
\]

\[ \therefore \text{M for Mg(OH)\(_2\)} = 58 \]

\[
\text{Mg(OH)}_2 \iff \text{Mg}^{2+} + 2\text{OH}^- \\
K_{sp} = (S)(2S)^2 = 4S^3 = 4(1.65 \times 10^{-4})^3 = 1.8 \times 10^{-11} \text{ approx.}
\]

Calculation of solubility of Mg(NO\(_3\))\(_2\), say, \(x\), in Mg(NO\(_3\))\(_2\)

\[ [\text{Mg}^{2+}] = x + 0.02, [\text{OH}^-] = -x \\
K_{sp} = [\text{Mg}^{2+}][\text{OH}^-]^2 \times 1.8 \times 10^{-11} = (x + 0.02)(2x)^2
\]

Neglecting \(x\) in comparison to 0.02 (common ion effect)

\[ 4x^2 = 1.8 \times 10^{-11} \\
\]

\[ 0.02 = 9 \times 10^{-10} \text{ or } 2x = 3 \times 10^{-5}
\]

\[ x = 1.5 \times 10^{-5} \text{ moles/litres} \\
= 1.5 \times 58 \times 10^{-2} = 8.7 \times 10^{-4} \text{ g/litre.}
\]

12. (i) **Amount of HCl added** = 0.20 mole

\[ [\text{H}^+] = 0.2 \text{ g litre}^{-1} \]

**NOTE**: Added H\(^+\) ions will combine with the acetic acid ions forming acetic acid with the result concentration of acetic acid ions will decrease while that of acetic acid will increase.

\[ \text{CH}_3\text{COO}^- + \text{H}^+ \rightarrow \text{CH}_3\text{COOH} + \text{Cl}^- \]

- Before reaction: 1 0.2 1 0
- After reaction: 0.8 0 1.2 0.2

\[ \therefore \text{Concentration of acetate ions after adding 0.20 mole of HCl.} \]

\[ [\text{CH}_3\text{COO}^-] = 1.0 - 0.2 = 0.8 \text{ mole} \]

Similarly, concentration of acetic acid,

\[ [\text{CH}_3\text{COOH}] = 1.0 + 0.2 = 1.2 \text{ mole} \]

Now, \(pH = -\log K_a + \log \left(\frac{\left[\text{Salt}\right]}{\left[\text{Acid}\right]}\right)\)

\[ = -\log 1.8 \times 10^{-5} + \log \frac{0.8}{1.2}
\]

\[ pH = 4.7447 + 0.3010 - 0.4771 = 4.5686 \]

(ii) **Amount of HCl added** = 0.20 mole

Out of 0.2 mole of [H\(^+\)] added, 0.1 mole will combine with 0.1 mole of CH\(_3\)COO\(^-\) forming 0 mole of CH\(_3\)COOH.

\[ \text{CH}_3\text{COO}^- + \text{H}^+ \rightarrow \text{CH}_3\text{COOH} + \text{Cl}^- \]

- Before reaction: 0.1 0.2 0.1 0
- After reaction: 0.1 0.2 0.1 0

\[ \therefore \text{Total concentration of acetic acid} [\text{CH}_3\text{COOH}] = 0.1 + 0.1 = 0.2 \text{ mole} \]

In presence of [H\(^+\)], CH\(_3\)COOH will not ionize. Therefore, pH of the solution will be due to the presence of H\(^+\) of HCl, i.e., 0.2 - 0.1 = 0.1 mole HCl

\[ pH = -\log [\text{H}^+] = -\log [0.1] = 1 \]

13. **Initial concentration of each gas** = 1 mole

Let the No. of moles of NO\(_2\) reacted at equilibrium = \(x\)

Then, \( \text{SO}_3(g) + \text{NO}_2(g) \iff \text{SO}_2(g) + \text{NO}(g) \)

At equilibrium \( (1-x) \) \( (1-x) \) \( (1+x) \) \( (1+x) \)

Now we know that, \[
\frac{[\text{SO}_3][\text{NO}]}{[\text{SO}_2][\text{NO}_2]} = K_c
\]

\[ \frac{(1+x)(1+x)}{(1-x)(1-x)} = 16 \text{ or } \frac{(1+x)^2}{(1-x)^2} = 16 \quad (\because V = 1L) \]

\[ \frac{1+x}{1-x} = 4 \text{ or } 1 + x = 4 - 4x \text{ or } 5x = 3 \]

\[ x = \frac{3}{5} = 0.6 \]

\[ \therefore \text{Thus the concentration of NO at equilibrium} \]

\[ = 1 + x = 1 + 0.6 = 1.6 \text{ moles} \]

Concentration of NO\(_2\) at equilibrium

\[ = 1 - x = 1 - 0.6 = 0.4 \text{ moles} \]

14. (i) **N\(_2\)O\(_4\)** \( \iff \) 2NO\(_2\)

Before dissociation

\[ 1 \quad 0 \]

After dissociation

\[ 1 - \alpha \quad \alpha \]

\[ \therefore \text{Total moles} = 1 - \alpha + 2\alpha = 1 + \alpha \]

\[ K_p = \frac{(\text{P}_{\text{NO}_2})^2}{\text{P}_{\text{N}_2\text{O}_4}} = \left(\frac{2\alpha}{1 + \alpha}\right) \times \frac{P}{(1 + \alpha)} \]

Where \(P\) is total pressure

\[ K_p = \left(\frac{2 \times 0.25 \times 1}{1 + 0.25}\right) = 0.266 \text{ atm} \quad (\because \alpha = 0.25) \]

\[ (ii) \quad K_p = \frac{4\alpha^2 P}{(1 + \alpha)^2 (1 - \alpha) \times P} = \frac{4\alpha^2 P}{(1 + \alpha)(1 - \alpha)} \]

\[ \Rightarrow 0.266 = \frac{4\alpha^2 \times 0.1}{1 - \alpha^2} \Rightarrow \alpha = 0.64 \]

\[ \therefore \text{Percentage dissociation} = 63\% \]

15. **TIPS/Formulae**:

\[ pH = pK_a + \log \left(\frac{\left[\text{Salt}\right]}{\left[\text{Acid}\right]}\right) \]

If \(x\) moles of HCl are added then they will combine with NaCN to form \(x\) moles of very weak acid HCN.

\[ \text{NaCN} + \text{HCl} \rightarrow \text{NaCl} + \text{HCN} \]

At equilibrium \( (0.01-x) \) \( x \) \( x \) \( x \)

For an acidic buffer,
\[ \text{pH} = \log K_a + \log \left( \frac{\text{Salt}}{\text{Acid}} \right) \]

\[ \therefore 8.5 = -\log 4.1 \times 10^{-10} + \log \left( \frac{0.01 - x}{x} \right) \]

or \[ 8.5 = (10 - \log 4.1) + \log \left( \frac{0.01 - x}{x} \right) \]

\[ \log \left( \frac{0.01 - x}{x} \right) = -0.8872 \quad [\log 4.1 = 0.6128] \]

\[ \frac{0.01 - x}{x} = 0.1296 \]

\[ x = 8.85 \times 10^{-3} \text{ M} = 8.85 \times 10^{-3} \text{ moles of HCl} \]

16. **NOTE:** Since the reaction is carried out at constant volume, change in partial pressure of a species will be directly proportional to the change in its amount. Hence, we can write

\[ 2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g}) \]

Initial pressure \[ \begin{array}{c} 0 \\ 2 \text{ atm} \\ 1 \text{ atm} \end{array} \]

Equilibrium pressure \[ \begin{array}{c} 2x \\ 2 \text{ atm} + x \\ 1 \text{ atm} - 2x \end{array} \]

Where \( 2x \) is the change in partial pressure of \( \text{SO}_3 \) at equilibrium.

Substituting the expression of partial pressure in the expression. For \( K_p \), we get

\[ K_p = \frac{(p_{\text{SO}_3})^2}{(p_{\text{SO}_2})^2 (p_{\text{O}_2})} \]

or \[ 900 \text{ atm}^{-1} = \frac{(1 \text{ atm} - 2x)^2}{(2x)^2 (2 \text{ atm} + x)} \]

Assuming \( x \) is very small as compared to 1

\[ 900 \text{ atm}^{-1} = \frac{1 \text{ atm}^2}{(4x^2) (2 \text{ atm})} \]

On usual calculations, \( x = 0.0118 \text{ atm} \)

Thus \( p_{\text{SO}_2} = 2x = 2 \times 0.0118 \text{ atm} = 0.0236 \text{ atm} \)

\( p_{\text{O}_2} = 2 \text{ atm} + x = 2 + 0.0118 = 2.0118 \text{ atm} \)

\( p_{\text{SO}_3} = 1 \text{ atm} - 2x = 1 - 0.0236 = 0.9764 \text{ atm} \)

17. **TIPS/Formulae:**

\[ p(\text{OH}) \text{ for basic buffer} = pK_b + \log \left( \frac{\text{Salt}}{\text{Base}} \right) \]

We know that

\[ p\text{OH} = pK_b + \log \left( \frac{\text{Salt}}{\text{Base}} \right) \quad \text{or} \quad -\log 1.8 \times 10^{-5} + \log \frac{0.25}{0.05} \]

\[ p\text{OH} = 5 - \log 1.8 + \log 5 = 5.6989 - 0.2552 \]

\[ -\log [\text{H}^+] = 5.4437; \quad \log [\text{OH}^-] = -5.4437 \]

\[ [\text{H}^+] = 3.5999 \times 10^{-6} \quad [\text{Taking antilog]} \]

\[ K_{sp} \text{ for Mg(OH)}_2 = [\text{Mg}^{2+}] [\text{OH}^-]^2 \]

\[ 6 \times 10^{-10} = [\text{Mg}^{2+}] (3.5999 \times 10^{-6})^2 \]

\[ [\text{Mg}^{2+}] = \frac{6 \times 10^{-10}}{12.9598 \times 10^{-12}} = 0.4629 \times 10^2 \]

\[ = 46.29 \text{ mole ion per litre} \]

\[ K_{sp} \text{ for Al(OH)}_3 = [\text{Al}^{3+}] [\text{OH}^-]^3 \]

\[ 6 \times 10^{-32} = [\text{Al}^{3+}] (3.5999 \times 10^{-6})^3 \]

\[ [\text{Al}^{3+}] = \frac{6 \times 10^{-32}}{(3.5999 \times 10^{-6})^3} = 1.286 \times 10^{-15} \text{ mol ion/l} \]

18. Let the total number of moles of all gases at equilibrium point = \( n \)

\[ P = 4.92 \text{ atm}; \quad T = 273 + 327 = 600K \]

By applying the formula \( PV = nRT \)

\[ \frac{PV}{RT} = \frac{4.92 \times 5}{0.0821 \times 600} = 0.5 \text{ moles} \]

(i) **Calculation of the number of moles of the individual gases at equilibrium point.**

No. of moles of \( \text{CH}_3\text{OH} \) formed = 0.1 (Given)

\[ \therefore \text{No. of moles of } \text{CO (also)} = 0.1 \]

\[ \therefore \text{ moles of CO = moles of } \text{CH}_3\text{OH} \text{ formed} \]

Hence No. of moles of \( \text{H}_2 = 0.5 - (0.1 + 0.1) = 0.3 \)

\[ \therefore \text{ Molar concentration of various species will be} \]

\[ [\text{CH}_3\text{OH}] = [\text{CO}] = \frac{0.1}{5} = 0.02; \quad [\text{H}_2] = \frac{0.3}{5} = 0.06 \]

\[ \therefore \]

\[ K_c = \frac{[\text{CH}_3\text{OH}]}{[\text{CO}] [\text{H}_2]^2} = \frac{0.02}{(0.02 \times 0.06)^2} = 277.78 \text{ mol}^{-2} \]

(ii) **Calculation of \( K_p \).** We know that

\[ K_p = K_c \times (RT)^{\Delta n} = 277.78 \times (0.0821 \times 600)^{2} \]

\[ = \frac{277.78}{2426.54} = 0.1144 \text{ atm}^{-2} \]

19. **Case I.** \( \text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+ \)

At start \[ \begin{array}{c} 1 \\ 0 \\ 0 \end{array} \]

At equilib. \[ \begin{array}{c} 1 - \alpha \\ \alpha \\ \alpha \end{array} \]

\[ [\text{H}^+] = c \alpha = c \sqrt{\frac{K_a}{c}} = \sqrt{K_a c} \]

\[ \therefore [\text{H}^+] = \sqrt{1.8 \times 10^{-5} \times 1} = 4.24 \times 10^{-3} \text{ M} \]

Thus \( p\text{H} = -\log \text{H}^+ = -\log 4.24 \times 10^{-3} = 2.3724 \)

**Case II.** \( p\text{H} \text{ after dilution} = 2 \times \text{ original } p\text{H} \)

\[ = 2 \times 2.3724 = 4.7448 \]

Let conc. after dilution = \( c_1 \)

and degree of dissociation = \( \alpha \)

Since \( p\text{H} = -\log [\text{H}^+] \)

\[ 4.7448 = -\log [\text{H}^+] \]
Since the solution represents a basic buffer, following Hendersen equation can be applied.

\[
pOH = -\log K_b + \log \frac{[\text{Salt}]}{[\text{Base}]} \]

\[
14 - 10.04 = -\log K_b + \log \frac{0.5}{(x - 0.5)} \quad \ldots (i)
\]

**Case II.**

<table>
<thead>
<tr>
<th>BOH</th>
<th>HCl</th>
<th>(\rightarrow)</th>
<th>BCl</th>
<th>H(_2)O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moles at start</td>
<td>(x)</td>
<td>0.1 \times 20 = 2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Moles after adding 20 ml. of 0.1N HCl</td>
<td>((x - 2))</td>
<td>2</td>
<td>2</td>
<td></td>
</tr>
</tbody>
</table>

\[
\therefore \text{Molar concentration} = \frac{x - 2}{V_1} \quad \frac{2}{V_1} \quad \frac{2}{V_1}
\]

Again the solution is acting as basic buffer

\[
\therefore \text{pOH} = -\log K_b + \log \frac{0.5}{(x - 0.5)} \quad \ldots (ii)
\]

Divide \((i)\) by \((ii)\).

\[
\frac{3.96}{4.86} = \frac{0.5}{(x - 0.5)} \times \frac{(x - 2)}{2} \Rightarrow x = 0.088 \text{ mol l}^{-1}
\]

Substituting \(x\) in \((i)\) and solving for \(K_b\)

\[
3.96 = -\log K_b + \log \frac{0.5}{0.088 - 0.5}
\]

\[
K_b = 1.828 \times 10^{-5}
\]

**22.** Let the solubility of Ca(OH)\(_2\) in pure water = \(S\) moles/litre

\[
\text{Ca(OH)}_2 \quad \Leftrightarrow \quad \text{Ca}^{2+} + \ 2\text{OH}^{-}
\]

Now \(K_{sp} = [\text{Ca}^{2+}] [\text{OH}^-]^2\)

\[
4.42 \times 10^{-5} = S (2S)^2 \quad 4.42 \times 10^{-5} = 4S^3
\]

\[
S = 2.224 \times 10^{-2} = 0.0223 \text{ moles litre}^{-1}
\]

\[
\therefore \text{No. of moles of Ca}^{2+} \text{ ions in 500 ml. of solution} = \lambda = \frac{0.0223 \times 500}{4000} = 0.01115
\]

**NOTE THIS STEP:** Now when 500 ml. of saturated solution is mixed with 500 ml of 0.4M NaOH, the resultant volume is 1000 ml. The molarity of OH\(^-\) ions in the resultant solution would therefore be 0.2 M.

\[
\therefore [\text{Ca}^{2+}] = \frac{K_{sp}}{[\text{OH}^-]^2} = \frac{4.42 \times 10^{-5}}{(0.2)^2} = 0.001105 \text{ M}
\]

Thus, No. of moles of Ca\(^{2+}\) or Ca(OH)\(_2\) precipitated

\[
= 0.01115 - 0.001105 = 0.010045
\]

Mass of Ca(OH)\(_2\) precipitated

\[
= 0.010045 \times 74 = 0.7433 \text{ g} = 743.3 \text{ mg}
\]

[mole wt. of Ca(OH)\(_2\) = 74]
23. (i) \[ \text{CO(g)} + 2 \text{H}_2\text{(g)} \rightleftharpoons \text{CH}_3\text{OH} \]

Moles at start: \(0.15\ a\ 0\)
Moles at equil: \((0.15 - x)\ (a - 2x)\ 0.08\)
or \((0.15 - 0.08)\ (a - 0.16)\ 0.08\)
\[\text{:. Total moles at equil.} = 0.15 - 0.08 + a - 0.16 + 0.08 = a - 0.01\]

Total moles at equilibrium can also be calculated from the following relation
\[
n = \frac{PV}{RT} = \frac{8.5 \times 2.5}{0.0821 \times 750} = 0.345
\]
\[\text{:. 0.345} = a - 0.01 \quad [\text{Comparing (i) and (ii)}]
\]

or \(a = 0.355\)

Thus, Moles of CO at equilibrium = 0.15 - 0.08 = 0.07
Moles of H\(_2\) at equilibrium = 0.355 - 0.16 = 0.195
Moles of CH\(_3\)OH at equilibrium = 0.08

Substituting the values in the relation,
\[
K_c = \frac{[\text{CH}_3\text{OH}]}{[\text{H}_2\text{S}]^2[\text{CO}]} = \frac{0.08/2.5}{(0.195/2.5)^2 \times (0.07/2.5)} = 187.85 \text{ mole}^{-2} \text{ litre}^2
\]
\[\text{[: } V = 2.5 \text{ L]}
\]

Calculation of \(K_p\)
\[
K_p = K_c(RT)^n = 187.85 \times (0.0821 \times 750)^2 = 0.05 \text{ atm}^{-2}
\]
\[\text{[: } \Delta n = -2\]

(ii) Calculation of final pressure when there is no reaction
Moles of CO = 0.15; Moles of H\(_2\) = 0.355
\[\therefore \text{ Total moles} = 0.15 + 0.355 = 0.505\]

\[P\times V = nRT\]

\[P \times 2.5 = 0.505 \times 0.0821 \times 750 \Rightarrow P = 12.438 \text{ atm}.
\]

24. Volume of blood = 10 ml. (given)

[\text{H}_2\text{CO}_3\text{]} \text{ in blood} = 2 \text{ M} \quad \text{(given)}

[\text{NaHCO}_3\text{]} \text{ to be added} = 5 \text{ M} \quad \text{(given)}

Let volume of NaHCO\(_3\) added in 10 ml blood = V ml
\[\therefore [\text{H}_2\text{CO}_3\text{]} \text{ in blood mixture} = \frac{2 \times 10}{(V + 10)}\]

[NaHCO\(_3\)] in blood mixture = \(\frac{5 \times V}{(V + 10)}\)

\[\therefore \text{ pH} = pK_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}
\]
or 7.4 = -log 7.8 \times 10^{-7} + \log \frac{5V/(V + 10)}{20/(V + 10)} \therefore V = 78.36 \text{ ml}

25. \(\text{H}_2\text{S} \rightleftharpoons \text{H}^+ + \text{HS}^-\) \quad \(\therefore K_1 = \frac{[\text{H}^+][\text{HS}^-]}{[\text{H}_2\text{S}]}\)

Further, \(\text{HS}^- \rightleftharpoons \text{H}^+ + \text{S}^{2-}\) \quad \(\therefore K_2 = \frac{[\text{H}^+][\text{S}^{2-}]}{[\text{HS}^-]}\)

Dissociation constant of \(\text{H}_2\text{S}, K = K_1 \times K_2\)
\[\i.e. K = 1 \times 10^{-7} \times 1.3 \times 10^{-13} = 1.3 \times 10^{-20}\]

Now we know that
\[
K_{sp} = [\text{M}^{2+}][\text{S}^{2-}] \quad \Rightarrow 6 \times 10^{-21} = 0.05 \times [\text{S}^{2-}]
\]
\[\text{[S}^{2-}] = \frac{6 \times 10^{-21}}{0.05} = 1.2 \times 10^{-19}
\]

Substituting the various values in the following relation
\[
K = \frac{[\text{H}^+]^2[\text{S}^{2-}]}{[\text{H}_2\text{S}]}\]
\[1.3 \times 10^{-20} = \frac{[\text{H}^+]^2[1.2 \times 10^{-19}]}{0.1}
\]
\[\text{:. } [\text{H}_2\text{S}] = 0.1 \text{ M}
\]

\[\text{[H}^+] = \frac{1.3 \times 10^{-20} \times 0.1}{1.2 \times 10^{-19}} = 1.04 \times 10^{-1}
\]

\[\text{pH} = -\log [\text{H}^+]; p\text{H} = -\log (1.04 \times 10^{-1})
\]
\[= 1.0 - \log 1.04 = 1.0 - 0.017 = 0.983
\]

26. \(2\text{AB}(g) \rightleftharpoons 2\text{AB}(g) + B_2(g)\)

Initial mole 1 0 0
Moles at equil 1 - x x \(\frac{x}{2}\)

Total moles at equil. = 1 - x + x + \(\frac{x}{2}\) = 1 + \(\frac{x}{2}\) = \(\frac{2 + x}{2}\)

\[p_{\text{AB}_2} = \frac{(1 - x)}{2 + x/2} = \frac{2(1 - x)}{2 + x} P
\]
\[p_{\text{AB}} = \frac{x}{2 + x / 2} = \frac{2x}{2 + x} P
\]
\[p_{B_2} = \frac{x}{2} = \frac{x}{2 + x} P
\]
\[\therefore K_p = \frac{(p_{\text{AB}})^2(p_{B_2})}{(p_{\text{AB}_2})^2} = \frac{(\frac{2x}{2 + x}P)^2(\frac{x}{2 + x}P)}{\left(\frac{1}{2 + x}P\right)^2}
\]
\[= \frac{x^3P}{(2 + x)(1 - x)^2}
\]
\[K_p \approx \frac{x^3}{2} P \quad \text{or} \quad x = \left[\frac{2K_p}{P}\right]^{1/3}
\]

27. TIPS/Formulæ:
Consider common ion effect
Conc. of Ag\(^+\) ions = Conc. of AgNO\(_3\) = 0.03 M
Most of these Ag\(^+\) ions will be present in the form of [Ag(CN)\(_2\)^-]:
0.03 MAgNO\(_3\) requires 2 \times 0.03 M
= 0.06 M CN\(^-\) to form [Ag(CN)\(_2\)^-]
28. For ammonium formate which is a salt of weak acid with weak base, we know that
\[ pK_b = \frac{1}{2} [pK_w + pK_a - pK_b] = \frac{1}{2} [14 + 3.8 - 4.8] = 6.5 \]

29. \( pK_b = 4.70 \), \( K_b = 10^{-4.7} \)

Now we know that
\[ [OH^-] = \sqrt{K_b \times c} \]
\[ [OH^-] = \sqrt{10^{-4.7} \times 0.5} = 3.158 \times 10^{-3} \text{ M} \]

Now we know that
\[ pOH = -\log[OH^-] = -\log 3.158 \times 10^{-3} = 2.5 \]
or, \( pH = 14 - 2.5 = 11.5 \)

30. The concerned chemical reaction is
\[ 2AgCl + Na_2CO_3 \rightarrow Ag_2CO_3 + 2NaCl \]

Calculation of \([Ag^+]\) left in the solution:
\[ K_{sp}(Ag_2CO_3) = [Ag^+]^2 [CO_3^{2-}] \]
\[ [Ag^+] = \sqrt{\frac{8.2 \times 10^{-12}}{1.5}} = 2.34 \times 10^{-6} \text{ M} \]

Concentration of Cl\(^{-}\) left = \( 0.0026 \text{ g/l} \)
\[ = \frac{0.0026}{35.5} \text{ mol/l} = 7.33 \times 10^{-5} \text{ M} \]

\[ K_{sp}(AgCl) = [Ag^+] [Cl^-] = (2.34 \times 10^{-6}) (7.33 \times 10^{-5}) = 1.71 \times 10^{-10} \]

31. Given \( K_c = 1 \times 10^{-5} \)
\[ pK_a = 5 \]
The two conditions when color indicator will be visible are derived by
\[ pH = pK_a + \log \left[ \frac{[In^-]}{[HIn]} \right] \]
(i) \( pH = 5 + \log 10 = 6 \)
(ii) \( pH = 5 + \log 0.1 = 4 \)
Thus minimum change in \( pH \) is 2

32. For AgCl; \( AgCl \rightleftharpoons Ag^+ + Cl^- \)
\[ K_{sp} = [Ag^+] [Cl^-] \]
Again it is given that
\[ [Ag(NH_3)_2]^+ \rightleftharpoons Ag^+ + 2NH_3; K_c = 6.2 \times 10^{-8} \]
or \( Ag^+ + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+ \)

33. \( HCl + NaOH \rightarrow NaCl + H_2O \)
Meq before reaction [HCl] = \( 2 \times 10^{-2} \text{ M} \), [NaOH] = \( 12 \times 10^{-2} \text{ M} \)
\[ \text{pH before reaction} = \frac{100 \times 10^{-2}}{200 \times 10^{-2}} = 0.5 \]
\[ \text{pOH after reaction} = -\log 2 \times 10^{-3} = 2.5 \]
\[ \text{pH of solution} = 14 - 2.5 = 11.5 \]

34. \( NH_3HS_s \rightleftharpoons NH_3(g) + H_2S(g) \)
Initial moles \( \frac{3.06}{51} 0 0 \)
Moles at eq. \( \frac{3.06}{51} \times \frac{70}{100} \frac{3.06}{51} \times \frac{30}{100} \frac{3.06}{51} \times \frac{30}{100} \)
Given \( V' = 2 \text{ litre} \), \( T' = 300K \), \( n = 2 - 0 = 2 \)
\[ K_c = [NH_3][H_2S] = \frac{3.06 \times 30}{51 \times 100} \times \frac{3.06 \times 30}{51 \times 100} = 8.1 \times 10^{-5} \text{ mole/litre}^2 \]

35. \( Pb(OH)_2 \rightleftharpoons Pb^{2+} + 2OH^- \)
\[ K_f = \frac{[Pb^{2+}][OH^-]^2}{[Pb(OH)_2]} = 6.7 \times 10^{-6} \times 2 \times 6.7 \times 10^{-6} = 1.203 \times 10^{-15} \]
Thus in this buffer we have, \[ [Pb^{2+}][OH^-]^2 = 1.203 \times 10^{-15} \]
\[ [Pb^{2+}] = 1.203 \times 10^{-3} \text{ mole/litre}^{-1} \]
36. Amount of SO₂ in atmosphere = \( \frac{10}{10^5} = 10 \times 10^{-6} \)

Molar concentration of SO₂ present in water
= Amount of SO₂ \times \text{Solubility of SO₂ in water}
= 10 \times 10^{-6} \times 1.3653 \text{ mole L}^{-1} = 1.3653 \times 10^{-5} \text{ M}

Writing the concerned chemical equation

\[
\text{H}_2\text{SO}_3 \rightarrow \text{H}^+ + \text{HSO}_3^-
\]

Initial conc. \( 1.3653 \times 10^{-5} \) \( 0 \) \( 0 \)

Molar conc. at eqm. \( 1.3653 \times 10^{-5} - x \) \( \text{x} \) \( \text{x} \)

Therefore \( K_a = \frac{\text{x}^2}{(1.3653 \times 10^{-5} - \text{x})} \)

\( 10^{-1.92} = \frac{\text{x}^2}{(1.3653 \times 10^{-5} - \text{x})} \)

\( pK_a = 1.92 \Rightarrow K_a = 10^{-1.92} \)

\( \Rightarrow 1.2 \times 10^{-2} = \frac{\text{x}^2}{(1.3653 \times 10^{-5} - \text{x})} \)

\( x^2 = 1.2 \times 10^{-2} (1.3653 \times 10^{-5} - x) \)

On solving, \( x = 1.364 \times 10^{-5} \)

Therefore, \( pH = -\log (1.364 \times 10^{-5}) = 4.865 \)

37. (i) The volume being doubled by mixing the two solutions, the molarity of each component will be halved i.e. [CH₃COOH] = 0.1 M, [HCl] = 0.1 M.

**NOTE:**
HCl being a strong acid will remain completely ionised and hence H⁺ ion concentration furnished by it will be 0.1 M. This would exert common ion effect on the dissociation of acetic acid, (a weak acid.)

\[
\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+
\]

At start
\[
\begin{array}{cccc}
\text{C} & 0 & 0 & 0 \\
\text{C}_1 & \text{C} & \text{C} & 0.1 \\
\end{array}
\]

\[ K_a = \frac{C\alpha(C\alpha + 0.1)}{C(1 - \alpha)} = \frac{C\alpha^2 + 0.1\alpha}{1 - \alpha} \]

Since \( \alpha \) is very very small, \( C\alpha^2 \) can be neglected and \( 1 - \alpha \) can be taken as unity

\( \therefore K_a = 0.1 \alpha \)

or \( \alpha = \frac{K_a}{0.1} = \frac{1.75 \times 10^{-5}}{0.1} = 1.75 \times 10^{-4} \)

\[ [\text{H}^+]_{\text{Total}} = 0.1 + C\alpha \]

\( C\alpha \) is negligible as compared to 0.1.

\( \therefore [\text{H}^+]_{\text{Total}} = 0.1 \)

\( \therefore pH = 1 \)

(ii) 6g NaOH = \( \frac{6}{40} = 0.15\text{mol} \)

0.1 mole of NaOH will be consumed by 0.1 mole of HCl. Thus, 0.05 mole of NaOH will react with acetic acid according to the equation.

\[
\text{CH}_3\text{COOH} + \text{NaOH} \rightarrow \text{CH}_3\text{COO}^- + \text{H}_2\text{O}
\]

Initial moles : 0.1 mol 0.05 mol 0
At equilibrium : 0.05 mol 0 mol 0.05 mol 0.05 mol

Thus, solution of acetic acid and sodium acetate will become acidic buffer. So pH of the buffer will be

\[ pH = pK_a + \log \left(\frac{\text{salt}}{\text{acid}}\right) = -\log (1.75 \times 10^{-5}) + \log 1 = 4.75 \]

38. **TIPS/Formulae:**
Higher the value of dipole-dipole interaction higher is b.p. Higher value of \( K_b \) of a solvent suggests larger polarity of solvent molecules which in turn leads to higher dipole – dipole interaction implies higher boiling point due to dipole – dipole interaction. Therefore, the correct order of \( K_b \) values of the three given solvents is

Mathematically \( K_b = \frac{M_A R T_b^2}{\Delta H_{\text{vap}} \times 1000} \)

or \( K_b \propto T_b \) (b.pt.)

<table>
<thead>
<tr>
<th>Solvents</th>
<th>Boiling point</th>
<th>( K_b ) values</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>100°C</td>
<td>0.63</td>
</tr>
<tr>
<td>Y</td>
<td>27°C</td>
<td>0.53</td>
</tr>
<tr>
<td>Z</td>
<td>283°C</td>
<td>0.98</td>
</tr>
</tbody>
</table>

**G. Comprehension Based Questions**

1. **(a)** Let the heat capacity of insulated beaker be C.

Mass of aqueous content in exp. 1 = (100 + 100) \times 1 = 200 \text{ g}

\( \Rightarrow \pm \text{Total heat capacity} = (C + 200 \times 4.2) \text{ J/K} \)

Moles of acid, base neutralised in exp. 1 = 0.1 \times 1 = 0.1

\( \Rightarrow \text{Heat released in exp. 1} = 0.1 \times 57 = 5.7 \text{ KJ} \)

\( = 5.7 \times 1000 \text{ J} \)

\( = 5.7 \times 1000 = (C + 200 \times 4.2) \times \Delta T \)

\( 5.7 \times 1000 = (C + 200 \times 4.2) \times 5.7 \)

\( \Rightarrow (C + 200 \times 4.2) = 1000 \)

In second experiment, \( n_{\text{CH}_3\text{COOH}} = 0.2 \), \( n_{\text{NaOH}} = 0.1 \)

Total mass of aqueous content = 200 g

\( \Rightarrow \text{Total heat capacity} = (C + 200 \times 4.2) = 1000 \)

\( \Rightarrow \text{Heat released} = 1000 \times 5.6 = 5600 \text{ J} \)

Overall, only 0.1 mol of \( \text{CH}_3\text{COOH} \) undergo neutralization.

\( \Rightarrow \Delta H_{\text{neutralisation}} \text{of} \text{CH}_3\text{COOH} = \frac{-5600}{0.1} \)

\( = -56000 \text{ J/mol} \)

\( \Rightarrow \Delta H_{\text{neutralisation}} \text{of} \text{CH}_3\text{COOH} = 57 - 56 = 1 \text{ KJ/mol} \)

2. **(b)** Final solution contain 0.1 mole of \( \text{CH}_3\text{COOH} \) and \( \text{CH}_3\text{COONa} \) each.

Hence it is a buffer solution.

\[ pH = pK_a + \log \left(\frac{[\text{CH}_3\text{COOH}^-]}{[\text{CH}_3\text{COOH}]}\right) \]

\[ = 5 - \log 2 + \log \frac{0.1}{0.1} = 4.7 \]
3. (b) \[ X_2(g) \rightleftharpoons 2X(g) \]

Initial mole: 1 0

moles at equilibrium: \(\left(1 - \frac{\beta_{eqbm}}{2}\right) \beta_{eqbm}\)

Partial pressure:
\[
\left(\frac{1 - \frac{\beta_{eqbm}}{2}}{1 + \frac{\beta_{eqbm}}{2}}\right) \cdot P = \left(\frac{\beta_{eqbm}}{1 + \frac{\beta_{eqbm}}{2}}\right) \cdot P
\]

\[
\therefore \quad K_p = \frac{(P_x)^2}{P_x^2} = \frac{\beta_{eqbm}^2 P}{\frac{\beta_{eqbm}^2}{4}}
\]

\[
\therefore \quad K_p = \frac{4\beta_{eqbm}^2 P}{4 - \beta_{eqbm}^2}
\]

Since \(P = 2\) bar

\[
\therefore \quad K_p = \frac{8\beta_{eqbm}^2}{4 - \beta_{eqbm}^2}
\]

\[\text{4. (c)}\]

(A) Correct statement.

As on decrease in pressure reaction move in direction where no. of gaseous molecules increase.

(B) Correct statement

At the start of reaction \(Q_p < K_p\) so dissociation of \(X_2\) take place spontaneously.

(C) Incorrect statement as

\[
K_p = \frac{8\beta_{eqbm}^2}{4 - \beta_{eqbm}^2} = \frac{8 \times (0.7)^2}{4 - (0.7)^2} > 1
\]

H. Assertion & Reason Type Questions

1. (d) The statement-1 is clearly wrong in context to LeChatelieris principle, which states that “increase in temperature shifts the equilibrium in the forward direction of those reactions which proceed with absorption of heat (endothermic reactions), and in the backward direction of those reactions which proceed with the evolution of heat (exothermic reactions).”

Statement -2 is clearly true again according to LeChatelier principle.

2. (e) TIPS/Formulae:

Among oxacids, the acidic character increases with increase in oxidation state of the central atom.

O.S. of N in HNO₃ = +5

O.S. of N in HNO₂ = +3


3. (d) We know that for every chemical reaction at equilibrium, Gibb's free energy (\(\Delta G = 0\)) is zero. However standard Gibb's free energy (\(\Delta G^\circ\)) may or may not be zero. Thus statement 1 is False.

For a spontaneous reaction, at constant temperature and pressure, the reaction proceeds in the direction in which \(\Delta G\) is < 0 i.e. in the direction of decreasing Gibb's energy (G) so the statement 2 is True.

Thus the only such option is (d) which is correct answer.
1. (a) **NOTE**: A buffer is a solution of weak acid and its salt with strong base and vice versa. HCl is a strong acid and NaCl is its salt with a strong base. pH is less than 7 due to HCl.

2. (a) \((\text{HSO}_4^-)^-\) can accept and donate a proton: \((\text{HSO}_4^-)^- + \text{H}^+ \rightarrow \text{H}_2\text{SO}_4^-\) (acting as base) \((\text{HSO}_4^-)^- - \text{H}^+ \rightarrow \text{SO}_4^{2-}\) (acting as acid)

3. (a) \(\text{Mg(OH)}_2 \rightarrow [\text{Mg}^{2+}] + [2\text{OH}^-] \times 2x\)

\[ K_{sp} = [\text{Mg}][\text{OH}]^2 = [x][2x]^2 = 4x^3 \]

4. (a) In this reaction the ratio of number of moles of reactants to products is same i.e. 2 : 2, hence change in volume will not alter the number of moles.

5. (c) \(K_p = K_c (RT)^\Delta n\)

\[ \Delta n = 1 - \left(1 + \frac{1}{2}\right) = \frac{1 - 3}{2} = -1/2 \quad \therefore \quad \frac{K_p}{K_c} = (RT)^{-1/2} \]

6. (b) pH of an acidic solution should be less than 7. The reason is that from \(\text{H}_2\text{O}, [\text{H}^+] = 10^{-8}\) which cannot be neglected in comparison to \(10^{-4}\). The pH can be calculated as:

from acid, \([\text{H}^+] = 10^{-8}\) from \(\text{H}_2\text{O}, [\text{H}^+] = 10^{-7}\)

\[ \therefore \text{Total} [\text{H}^+] = 10^{-8} + 10^{-7} = 10^{-8}(1 + 10) = 11 \times 10^{-8} \]

\[ \therefore \text{pH} = -\log [\text{H}^+] = -\log 11 \times 10^{-8} = -\log 1.0414 = 7.9586 \]

7. (d) \(\text{AB}_2 \rightarrow \text{A}^{2+} + 2\text{B}^-\)

\([A] = 1.0 \times 10^{-5}, [B] = 2.0 \times 10^{-5}\)，

\[ K_{sp} = [B]^2[A] = [2 \times 10^{-5}]^2[1 \times 10^{-5}] = 4 \times 10^{-15} \]

8. (b) \(K_c = \frac{[\text{NO}_2^-]^2}{[\text{N}_2\text{O}_4]} = \frac{[1.2 \times 10^{-2}]^2}{4.8 \times 10^{-8}} = 3 \times 10^{-3} \text{ mol/L} \)

9. (b) Due to exothermicity of reaction low or optimum temperature will be required. Since 3 moles are changing to 2 moles.

\(\therefore\) High pressure will be required.

10. (d) The rain water after thunderstorm contains dissolved acid and therefore the pH is less than rain water without thunderstorm.

11. (d) **NOTE**: Conjugate acid-base differ by \(\text{H}^+\)

\(\text{H}_2\text{PO}_4^- \rightarrow \text{H}^+ \rightarrow \text{HPO}_4^{2-}\)

12. (d) For \(P_4(s) + 5\text{O}_2(g) \leftrightarrow P_4\text{O}_{10}(s)\)

\[ K_c = \frac{1}{(\text{O}_2)^5}. \text{ The solids have concentration unity} \]

13. (c) \(K_p = K_c (RT)^\Delta n\); Here \(\Delta n = 1 - 2 = -1\)

\[ \therefore \frac{K_p}{K_c} = \frac{1}{RT} \]

14. (b) \(K_c = \frac{[\text{NO}_2^-]^2}{[\text{N}_2\text{O}_4]} = 4 \times 10^{-4}\)

\[ K_c' = \frac{[\text{N}_2\text{O}_4]^{1/2}[\text{O}_2]^{1/2}}{[\text{NO}]} = \frac{1}{\sqrt{K_c}} = \frac{1}{\sqrt{4 \times 10^{-4}}} = 50 \]

15. (d) \(\text{MX}_4 \rightarrow \text{M}^{4+} + 4\text{X}^-\)

\[ K_{sp} = [s][4s]^4 = 256s^5 \quad \therefore \quad s = \left(\frac{K_{sp}}{256}\right)^{1/5} \]

16. (b) \(\text{Na}_2\text{SO}_4 \rightarrow 2\text{Na}^+ + \text{SO}_4^{2-}\)

\[ 1 - \alpha \]

\[ 2\alpha \]

\[ \text{Vant. Hoff's factor} \quad i = \frac{1 - \alpha + 2\alpha + \alpha}{1} = 1 + 2\alpha \]

17. (c) \(\text{MX}_2 \rightarrow \text{M}^{++} + 2\text{X}^-\)

Where \(s\) is the solubility of \(\text{MX}_4\)
then \(K_{sp} = 4s^3\), \(s \times (2s)^2 = 4 \times 10^{-12} = 4s^3\), \(s = 1 \times 10^{-4}\)

\[ \therefore \quad [\text{M}^{++}] = s = 1[\text{M}^{++}] = 10^{-4} \]

18. (a) The reaction given is an exothermic reaction thus accordingly to Lechatalier's principle lowering of temperature, addition of \(\text{F}_2\) and \(\text{Cl}_2\) favour the forward direction and hence the production of \(\text{ClF}_3\).

19. (d) For the reaction:\(2\text{NO}_2(g) \rightarrow 2\text{NO}(g) + \text{O}_2(g)\)

Given \(K_c = 1.8 \times 10^{-6}\) at 184 °C

\[ R = 0.0831 \text{ kJ/mol k} \]

\[ K_p = 1.8 \times 10^{-6} \times 0.0831 \times 457 = 6.836 \times 10^{-6} \]

\[ \therefore \quad 184^\circ C = (273 + 184) = 457 k, \Delta n = (2 + 1, -1) = 1 \]

Hence it is clear that \(K_p > K_c\).

20. (a) \(\text{pH} = -\log [\text{H}^+] = \log \frac{1}{[\text{H}^+]} \quad 5.4 = \log \frac{1}{[\text{H}^+]} \)

On solving, \([\text{H}^+] = 3.98 \times 10^{-6}\)

21. (a) Conjugate acid-base pair differ by only one proton.

\(\text{OH}^- \rightarrow \text{H}^+ + \text{O}^2-\) Conjugate base of \(\text{OH}^-\) is \(\text{O}^2-\)

22. (a) \(\text{NH}_4\text{HS(s)} \rightarrow \text{NH}_3\text{(s)} + \text{H}_2\text{S(s)}\)

\[ \begin{array}{c|c|c}
\text{start} & 0.5 \text{ atm} & 0 \text{ atm} \\
\text{At equib.} & 0.5 + x \text{ atm} & x \text{ atm.}
\end{array} \]
Then $0.5 + x + x = 2x + 0.5 = 0.84$ (given) 
$\Rightarrow x = 0.17$ atm.

$p_{NH_3} = 0.5 + 0.17 = 0.67$ atm; $p_{H_2S} = 0.17$ atm

$K = p_{NH_3} \times p_{H_2S} = 0.67 \times 0.17 = 0.1139 \approx 0.11$

23. (c) $\text{PCl}_3(g) \rightleftharpoons \text{PCl}_3(g) + \text{Cl}_2(g)$

Total moles after dissociation $1 - x + x + x = 1 + x$

$p_{\text{PCl}_3} = \text{mole fraction of } \text{PCl}_3 \times \text{Total pressure}$

$= \left( \frac{x}{1+x} \right) p$

24. (e) $\text{SO}_3(g) \rightleftharpoons \text{SO}_2(g) + \frac{1}{2} \text{O}_2(g)$

$K_c = \left[ \frac{[\text{SO}_2]^\frac{1}{2}}{[\text{SO}_3]} \right] = 4.9 \times 10^{-2};$

On taking the square of the above reaction

$\frac{[\text{SO}_2]^2}{[\text{SO}_3]^2} = 24.01 \times 10^{-4}$

Now $K'_c$ for $2\text{SO}_2(g) + \frac{1}{2} \text{O}_2(g) \rightleftharpoons 2\text{SO}_3$

$= \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2 [\text{O}_2]} = \frac{1}{24.01 \times 10^{-4}} = 416$

25. (b) (i) $\text{Ag} \rightarrow \text{Ag}^+ + e^- \quad E^o = -0.800 \text{ V}$

(ii) $\text{Ag} + \text{I}^- \rightarrow \text{AgI} + e^- \quad E^o = 0.152 \text{ V}$

From (i) and (ii) we have,

$\text{AgI} \rightarrow \text{Ag}^+ + \text{I}^- \quad E^o = -0.952 \text{ V}$

$E^o_{\text{cell}} = \frac{0.059}{n} \log K$

$\therefore -0.952 = - \frac{0.059}{1} \log [\text{Ag}^+] [\text{I}^-] \quad [\because k = [\text{Ag}^+] [\text{I}^-]]$

or $\frac{0.952}{0.059} = \log K_{sp} \quad \therefore -16.13 = \log K_{sp}$

26. (d) $\text{H}_2\text{A} \rightarrow \text{H}^+ + \text{HA}^-$

$\therefore K_1 = 1.0 \times 10^{-5} = \frac{[\text{H}^+][\text{HA}^-]}{[\text{H}_2\text{A}]} \quad \text{(Given)}$

$\text{HA}^- \rightarrow \text{H}^+ + \text{A}^-$

$\therefore K_2 = 5.0 \times 10^{-10} = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}^-]} \quad \text{(Given)}$

$K = \frac{[\text{H}^+]^2 [\text{A}^-]}{[\text{H}_2\text{A}]} = K_1 \times K_2$

$= (1.0 \times 10^{-5}) \times (5 \times 10^{-10}) = 5 \times 10^{-15}$

27. (d) For acidic buffer $pH = pK_a + \log \left[ \frac{\text{salt}}{\text{acid}} \right]$

or $pH = pK_a + \log \left[ \frac{[\text{A}^-]}{[\text{HA}]} \right]$

Given $pK_a = 4.5$ and acid is 50% ionised.

$\therefore pH = pK_a + \log 1 \quad \therefore pH = pK_a = 4.5$

$pOH = 14 - pH = 14 - 4.5 = 9.5$

28. (c) Let $s = \text{solubility}$

$\text{AgI}_3 \rightleftharpoons \text{Ag}^+ + 3\text{I}^-$

$K_{sp} = [\text{Ag}^+] [\text{I}^-]^3 = s \times s = s^2$

Given $K_{sp} = 1 \times 10^{-8}$

$\therefore s = \sqrt{K_{sp}} = \sqrt{1 \times 10^{-8}}$

$= 1.0 \times 10^{-4} \text{ mol/lit} = 1.0 \times 10^{-4} \times 283 \text{ g/lit}$

(: Molecular mass of $\text{AgI}_3 = 283$)

$= \frac{1.0 \times 10^{-4} \times 283 \times 100}{1000} \text{ gm/100ml}$

$= 2.83 \times 10^{-3} \text{ gm/100ml}$

29. (a) Let the initial moles of X be ‘a’ and that of Z be ‘b’ then for the given reactions, we have

$X \rightleftharpoons 2Y$

Initial $\quad a \quad 0$

At equi. $a(1-\alpha) \quad 2a\alpha$

Total no. of moles $= a(1-\alpha) + 2a\alpha$

$= a - a\alpha + 2a\alpha = a(1+\alpha)$

Now, $K_{P_1} = \left( \frac{n_y}{n_X} \right)^2 \times \left( \frac{P_{T_1}}{\sum n} \right)^{\Delta n}$

or, $K_{P_1} = \frac{(2a\alpha)^2 P_{T_1}}{[a(1-\alpha)][a(1+\alpha)]}$

$Z \rightleftharpoons P + Q$

Initial $\quad b \quad 0 \quad 0$

At equi. $b(1-\alpha) \quad b\alpha \quad b\alpha$

(moles)
Equilibrium

Total no. of moles = \( b(1 - \alpha) + b\alpha + b\alpha \)
\[ = b - b\alpha + b\alpha + b\alpha = b(1 + \alpha) \]

Now \( K_p_2 = \frac{n_Q \times n_p}{n_z} \left[ \frac{P_{T_2}^n}{\Sigma_n} \right] \)

or \( K_p_2 = \frac{(b\alpha)(b\alpha)P_{T_2}}{[b(1-\alpha)][b(1+\alpha)]} \)

or \( \frac{K_p_1}{K_p_2} = \frac{4\alpha^2}{(1-\alpha)^2} \times \frac{(1-\alpha)^2}{P_{T_1}P_{T_2}\alpha^2} = \frac{4P_{T_1}}{P_{T_2}} \)

or \( \frac{P_{T_1}}{P_{T_2}} = \frac{1}{9} \quad \therefore \quad \frac{K_p_1}{K_p_2} = \frac{1}{9} \quad \text{given} \)

or \( \frac{P_{T_1}}{P_{T_2}} = \frac{1}{36} \) or \( 1 : 36 \)

i.e., (a) is the correct answer.

30. (c) Reaction (c) can be obtained by adding reactions (a) and (b) therefore \( K_1 = K_1, K_2 \)
Hence (c) is the correct answer.

31. (e) The correct order of acidic strength of the given species
in \( \text{HSO}_4^- > \text{H}_2\text{O}^+ > \text{SO}_4^{2-} > \text{HC}_2\text{O}_3^- \)

or (i) < (iii) < (ii) < (iv)
It corresponds to choice (c) which is correct answer.

32. (e) In aqueous solution BA(salt) hydrolyses to give
\( BA + H_2O \rightarrow \text{BOH} + HA \)
Base acid
Now pH is given by
\[ pH = \frac{1}{2}pK_w + \frac{1}{2}pK_a - \frac{1}{2}pK_b \]

Substituting given values, we get
\[ pH = \frac{1}{2}(14 + 4.80 - 4.78) = 7.01 \]

33. (a) \( Na_2\text{CO}_3 \rightarrow 2Na^+ + \text{CO}_3^{2-} \)
\[ 1x10^{-8}M \quad 1x10^{-8}M \quad 1x10^{-8}M \]

\( K_{SP}(\text{BaCO}_3) = [\text{Ba}^{2+}][\text{CO}_3^{2-}] \)

\[ [\text{Ba}^{2+}] = \frac{5.1 \times 10^{-9}}{1 \times 10^{-4}} = 5.1 \times 10^{-5} \quad \text{M} \]

34. (a) (i) \( \text{H}_3\text{PO}_4 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}^+ + \text{H}_2\text{PO}_4^- \)
\( \text{acid}_1 \quad \text{base}_2 \quad \text{acid}_2 \quad \text{base}_1 \)

(ii) \( \text{H}_2\text{PO}_4^- + \text{H}_2\text{O} \rightarrow \text{HPO}_4^{2-} + \text{H}_3\text{O}^+ \)
\( \text{acid}_1 \quad \text{base}_2 \quad \text{base}_1 \quad \text{acid}_2 \)

(iii) \( \text{H}_3\text{PO}_4^- + \text{OH}^- \rightarrow \text{H}_2\text{PO}_4^- + \text{O}^- \)
\( \text{acid}_1 \quad \text{base}_1 \quad \text{acid}_2 \quad \text{base}_2 \)

Hence only in (ii) reaction \( \text{H}_2\text{PO}_4^- \) is acting as an acid.

35. (c) \( \text{H}_2\text{CO}_3(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HCO}_3^-(aq) + \text{H}_3\text{O}^+(aq) \)
\[ 0.034-x \quad x \quad y \]

\[ K_1 = \frac{[\text{HCO}_3^-][\text{H}_3\text{O}^+]}{[\text{H}_2\text{CO}_3]} = \frac{x \times x}{0.034 - x} \]

\[ \Rightarrow 4.2 \times 10^{-7} = \frac{x^2}{0.034} \Rightarrow x = 1.195 \times 10^{-4} \]

As \( \text{H}_2\text{CO}_3 \) is a weak acid so the concentration of \( \text{H}_2\text{CO}_3 \) will remain 0.034 as 0.034 >> x.

\( x = [\text{H}^+] = [\text{HCO}_3^-] = 1.195 \times 10^{-4} \)

Now, \( \text{HCO}_3^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{CO}_2^2-(aq) + \text{H}_3\text{O}^+(aq) \)
\[ x-y \quad y \quad y \]

As \( \text{HCO}_3^- \) is again a weak acid (weaker than \( \text{H}_2\text{CO}_3 \)) with \( x >> y \).

\[ K_2 = \frac{[\text{CO}_2^2-][\text{H}_3\text{O}^+]}{[\text{HCO}_3^-]} = \frac{y \times (x+y)}{(x-y)} \]

Note: \( [\text{H}_3\text{O}^+] = [\text{H}^+] \) from first step \( x \) and from second step \( y = (x+y) \)

[As \( x >> y \) so \( x+y = x \) and \( x-y = x \)]

So, \( K_2 = \frac{y \times x}{x} = y \)

\[ \Rightarrow K_2 = 4.8 \times 10^{-11} = y = [\text{CO}_2^2-] \]

So the concentration of \( [\text{H}^+] = [\text{HCO}_3^-] = \) concentrations obtained from the first step. As the dissociation will be very low in second step so there will be no change in these concentrations.
Thus the final concentrations are
\[ [\text{H}^+] = [\text{HCO}_3^-] = 1.195 \times 10^{-4} \quad \text{&} \quad [\text{CO}_2^2-] = 4.8 \times 10^{-11} \]

36. (b) \( \text{AgBr} \rightarrow \text{Ag}^+ + \text{Br}^- \)

\( K_{sp} = [\text{Ag}^+][\text{Br}^-] \)

For precipitation to occur
Ionic product > Solubility product

\[ [\text{Br}^-] = \frac{K_{sp}}{[\text{Ag}^+] = \frac{5 \times 10^{-13}}{0.05} = 10^{-11} \]

i.e., precipitation just starts when \( 10^{-11} \) moles of \( \text{KBr} \)

\[ \therefore \text{Number of moles of} \quad \text{Br}^- \quad \text{needed from} \quad \text{KBr} = 10^{-11} \]
\[ \therefore \text{Mass of} \quad \text{KBr} = 10^{-11} \times 120 = 1.2 \times 10^{-9} \quad \text{g} \]
37. (b) \( \text{Mg(OH)}_2 \rightleftharpoons \text{Mg}^{2+} + 2\text{OH}^- \)

\[
K_{sp} = [\text{Mg}^{2+}][\text{OH}^-]^2 = 1.0 \times 10^{-11} = 10^{-3} \times [\text{OH}^-]^2
\]

\[ [\text{OH}^-] = \sqrt{\frac{10^{-11}}{10^{-3}}} = 10^{-4} \]

\( \therefore \) pH \( \approx 4 \) \( \therefore \) pH + pOH \( = 14 \) \( \therefore \) pH = 10

38. (a) \( \text{CO}_2 + \text{C}(\text{graphite}) \rightleftharpoons 2\text{CO} \)

\[
P_{\text{initial}} = 0.5 \text{ atm}
\]

\[
P_{\text{final}} = (0.5 - x) \text{ atm} \quad x \text{ atm}
\]

Total \( P \) at equilibrium = \( 0.5 - x + 2x = 0.5 + x \text{ atm} \)

\[
0.8 = 0.5 + x
\]

\( \therefore x = 0.8 - 0.5 = 0.3 \text{ atm} \)

Now \( k_p = \frac{(P_{\text{CO}})^2}{P_{\text{CO}_2}} = \frac{(2 \times 0.3)^2}{(0.5 - 0.3)} = \frac{(0.6)^2}{0.2} = 1.8 \text{ atm}^{-1} \)

39. (d) For the reaction

\( \text{N}_2 + \text{O}_2 \rightleftharpoons 2\text{NO} \quad K = 4 \times 10^{-4} \)

Hence for the reaction

\( \text{NO} \rightleftharpoons \frac{1}{2} \text{N}_2 + \frac{1}{2} \text{O}_2 \quad K' = \frac{1}{\sqrt{K}} = \frac{1}{\sqrt{4 \times 10^{-4}}} = 50 \)

40. (c) \( \text{H}^+ = C\alpha; \alpha = \frac{[\text{H}^+]}{C} \) or \( \alpha = \frac{10^{-3}}{0.1} = 10^{-2} \)

\[ K_d = C\alpha^2 = 0.1 \times 10^{-2} \times 10^{-2} = 10^{-5} \]

41. (d) \( \therefore \) pH \( = 1 \); \( H^+ = 10^{-1} = 0.1 \text{ M} \)

\( \text{pH} = 2 \); \( H^+ = 10^{-2} = 0.01 \text{ M} \)

\( \therefore M_1 = 0.1 \); \( V_1 = 1 \); \( M_2 = 0.01 \); \( V_2 = ? \)

From

\[
M_1V_1 = M_2V_2 \quad 0.1 \times 1 = 0.01 \times V_2
\]

\( V_2 = 10 \text{ litre} \)

\( \therefore \) volume of water added = 10 - 1 = 9 litre.

42. (b) \( \text{SO}_2(g) + \frac{1}{2}\text{O}_2(g) \rightleftharpoons \text{SO}_3(g) \)

\( K_p = K_C(RT)^x \)

where \( x = \Delta n_g = \) number of gaseous moles in product

\( - \) number of gaseous moles in reactant

\( = 1 - \left(1 + \frac{1}{2}\right) = 1 - \frac{3}{2} = -\frac{1}{2} \)

43. (d) \( \Delta G^o = 2494.2 \text{ J} \)

\( 2\text{A} \rightleftharpoons \text{B} + \text{C} \)

\( R = 8.314 \text{ J/K/mole} \)

\( e = 2.718 \)

\[
[A] = \frac{1}{2}, \quad [B] = 2, \quad [C] = \frac{1}{2}; \quad Q = \frac{[B][C]}{[A]^2} = \frac{2 \times 1/2}{(1/2)}^2 = 4
\]

\( \Delta G^o = -2.303 \text{ RT} \log K_c \)

\( 2494.2 \text{ J} = -2.303 \times (8.314 \text{ J/K/mole}) \times (300 \text{ K}) \log K_c \)

\( \Rightarrow \log K_c = -\frac{2494.2}{2.303 \times 8.314 \times 300} \)

\( \Rightarrow \log K_c = -0.4341; \quad K_c = 0.37; \quad Q > K_c \)

44. (b) \( \Delta G^o_{\text{NO}_2} = 86.6 \text{ J/mole} = 86600 \text{ J/mol} \) \( T \) \( = 298 \) \( K_0 = 1.6 \times 10^{12} \)

\( \Delta G^o = -RT \ln K_p \)

Given equation,

\( 2\text{NO}(g) + \frac{1}{2}\text{O}_2(g) \rightleftharpoons 2\text{NO}_2(g) \)

\( \therefore 2\Delta G^o_{\text{NO}_2} - 2\Delta G^o_{\text{NO}} = -R \text{ (298) ln (1.6 \times 10^{12})} \)

\( 2\Delta G^o_{\text{NO}_2} - 2 \times 86600 = -R \text{ (298) ln (1.6 \times 10^{12})} \)

\( 2\Delta G^o_{\text{NO}_2} = 2 \times 86600 - R \text{ (298) ln (1.6 \times 10^{12})} \)

\( \Delta G^o_{\text{NO}_2} = \frac{1}{2} \left[ 2 \times 86600 - R \text{ (298) ln (1.6 \times 10^{12})} \right] \)

\( = 0.5 \left[ 2 \times 86600 - R \text{ (298) ln (1.6 \times 10^{12})} \right] \)

45. (a) \( \text{A} + \text{B} \rightleftharpoons \text{C} + \text{D} \)

Given,

\( \quad \text{A} + \text{B} \rightleftharpoons \text{C} + \text{D} \)

No. of moles initially \( 1 \quad 1 \quad 1 \quad 1 \)

At equilibrium \( 1-a \quad 1-a \quad 1+a \quad 1+a \)

\( \therefore \) \( K_c = \left( \frac{1+a}{1-a} \right)^2 = 100 \)

\( \therefore \) \( \frac{1+a}{1-a} = 10 \)

On solving

\( a = 0.81 \)

\( [D]_{\text{At eq}} = 1 + a = 1 + 0.81 = 1.81 \)
The s-Block Elements

Section-A : JEE Advanced/ IIT-JEE


B 1. F 2. T 3. F
C 1. (b) 2. (c) 3. (a) 4. (d) 5. (c) 6. (b) 7. (b)
   8. (d) 9. (d) 10. (a) 11. (b) 12. (b) 13. (b) 14. (b)
   15. (a) 16. (a)
D 1. (b, d) 2. (a, c) 3. (a, b) 4. (a) 5. (a) 6. (a, b) 7. (b, c, d)
E 6. 4.48 volumes 8. 1.344
   10. Ba, Ba\(_2\)N\(_2\), Ba(OH)\(_2\), BaCO\(_3\) 11. SrSO\(_4\) > CaSO\(_4\) > MgSO\(_4\) > BeSO\(_4\)
H 1. (a) 2. (b)

Section-B : JEE Main/ AIEEE

1. (a) 2. (a) 3. (d) 4. (a) 5. (a) 6. (a) 7. (b)
8. (a) 9. (c) 10. (c) 11. (a) 12. (d) 13. (d) 14. (c)
15. (d) 16. (d) 17. (d) 18. (b) 19. (c) 20. (a) 21. (b)
22. (b)

Section-A

JEE Advanced/ IIT-JEE

A. Fill in the Blanks

1. Anhydrous HCl  
   ∴ All the water of crystallisation cannot be removed by heating hydrated MgCl\(_2\).
2. occlusion.
3. of solvated electrons.

\[
\text{NaH} \xrightarrow{\text{electricity}} \text{Na}^{+} + 2\text{H}^{+} \\
\downarrow +e^{-} \downarrow -2e^{-}
\]
5. higher effective nuclear charge.

B. True/False

1. False : Although 4 molecules of water of crystallisation are removed by heating, the remaining two react with MgCl\(_2\) as per the equation given below:
   MgCl\(_2\) + 2H\(_2\)O → MgO + 2HCl + H\(_2\)O
   NOTE : In order to avoid this to happen, MgCl\(_2\)2H\(_2\)O is dehydrated in presence of HCl gas, which checks, (being in excess) the hydrolysis of MgCl\(_2\) by its own water of crystallisation.
2. True : The metallic bonding decreases with increase in atomic size and thus the tendency to show metallic bonding among alkali metals decreases from Li to Cs and thus close packing of atoms in crystal lattice decreases from Li to Cs resulting in an increase in softness.
3. False : Sodium when burnt in excess of oxygen gives mono-oxide and sodium peroxide (Na\(_2\)O\(_2\)) and not sodium oxide.
   4Na + O\(_2\) → 2Na\(_2\)O, 2Na + O\(_2\) → Na\(_2\)O\(_2\)

C. MCQs with One Correct Answer

1. (b) CaO + H\(_2\)O → Ca(OH)\(_2\) + Heat  
   CaO + CO\(_2\) → CaCO\(_3\)
2. (c) BaO\(_2\) + 8H\(_2\)O + H\(_2\)SO\(_4\) → BaSO\(_4\) + H\(_2\)O\(_2\) + 8H\(_2\)O
3. (a) Ca is obtained by electrolysis of molten mixture of CaCl\(_2\) mixed with CaF\(_2\).
4. (d) The free ammoniated molten mixture of CaCl\(_2\) mixed with CaF\(_2\).

NOTE : The ammonical solution of an alkali metal is rather favoured as a reducing agent than its aqueous solution because in aqueous solution the alkali metal being highly electropositive evolves hydrogen from water (thus H\(_2\)O acts as an oxidising agent) while its solution in ammonia is quite stable, provided no catalyst (transition metal) is present.
5. (c) Heavy water is D₂O, deuterium oxide.
6. (b) Na⁺ ion has larger size than Mg²⁺ ion and hence hydration energy of Mg²⁺ is larger than that of Na⁺.
7. (b) Na₂O₂ + H₂SO₄ (20% ice cold) → Na₂SO₄ + H₂O₂
8. (d) Glauber’s salt is Na₂SO₄. 10 H₂O.
9. (d) NOTE: The more electropositive metal will not be reduced by hydrogen.
   Among given choices only Al is more electropositive than hydrogen.
   :; It will not be reduced by hydrogen.
10. (a) NOTE: Acidic and basic salts cannot exist together.
   Since NaHCO₃ is an acid salt of H₂CO₃, it reacts with NaOH to form Na₂CO₃ and H₂O.
   NaHCO₃ + NaOH → Na₂CO₃ + H₂O
11. (b) Oscillation of loose electrons.
12. (b) Volume strength = Normality × 5.6 = 1.5 × 5.6 = 8.4 L
13. (b) The increasing thermal stability is BeCO₃ < MgCO₃ < CaCO₃ < K₂CO₃
   (IV) (II) (III) (I)
   NOTE: Increasing size of cation decreases its polarization ability towards carbonate, making the compound more stable.
14. (b) In going from top to bottom in a group, the first ionization potential decreases, thus
   Be > Mg > Ca
15. (a) MgCl₂ + 2NaHCO₃ → MgHCO₃ + 2NaCl
   (soluble)
16. (a) KIO₃ + H₂O₂ → KIO₂ + H₂O + O₂
    Thus H₂O₂ is acting as a reducing agent
    2NH₄OH + H₂O₂ → N₂ + 4H₂O
    Here H₂O₂ is acting as an oxidising agent

D. MCQs with One or More Than One Correct
1. (b, d) Na₂Al₂Si₂O₈ · xH₂O + Ca²⁺ → CaAl₂Si₂O₈ · xH₂O + 2Na⁺
   Na₂Al₂Si₂O₈ · xH₂O + Mg²⁺ → MgAl₂Si₂O₈ · xH₂O + 2Na⁺
2. (a, c) Only H₂O₂ (hydrogen peroxide) and BaO₂ (Barium peroxide) contain peroxide ions. So (a) and (c) are the correct choices.
3. (a, b) Blue colour is due to the presence of solvated (ammoniated) electrons, while electrical conductance is due to the presence of ions.

   M → M⁺ + e⁻
   M⁺ + xNH₃ → [M(NH₃)ₓ]⁺
   e⁻ + yNH₃ → [e(NH₃)ₓ]⁻

   on adding M + (x + y)NH₃ → [M(NH₃)ₓ]⁺ + [e(NH₃)ₓ]⁻

   Ammoniated cation
   Ammoniated electron
   NOTE: Sodium in liquid ammonia forms NaNH₂ only in presence of a catalyst like Pt black, iron oxide etc.
   [e(NH₃)ₓ]⁻ → Fe₂O₃ → NH₂ + H₂ + (y - 1)NH₃.
4. (a) CO₂ + H₂O ↔ H₂CO₃
    ↔ H⁺ + HCO₃⁻ ↔ H⁺ + CO₃²⁻

5. (a) Mg²⁺ + NH₃ + HPO₄²⁻ → Mg(NH₄)PO₄
6. (a,b) 4Na + O₂ (limited) → 2Na₂O
   2Na + O₂ (excess) → Na₂O₂
7. (b,c,d) Temporary hardness is due to bicarbonates of calcium and magnesium. Temporary hardness can be removed by Clark’s process, which involves the addition of slaked lime, Ca(OH)₂. Washing soda (Na₂CO₃) removes both the temporary and permanent hardness by converting soluble calcium and magnesium compounds into insoluble carbonates.
   Ca(HCO₃) + Ca(OH)₂ → 2CaCO₃↓ + 2H₂O
   Ca(HCO₃) + Na₂CO₃ → CaCO₃↓ + 2NaHCO₃
   2OC₁⁻ + 2H₂O ↔ 2HOCI + 2OH⁻
   Ca(HCO₃)₂ + 2OH⁻ → CaCO₃↓ + CO₃²⁻ + 2H₂O

E. Subjective Problems
1. (i) Potassium carbonate cannot be manufactured by Solvay process, since, unlike sodium hydrogen carbonate, potassium hydrogen carbonate is rather too soluble in water to be precipitated like NaHCO₃.
   (ii) H₂O₂ is a better oxidizing agent than H₂O because oxidation number of oxygen in H₂O₂ is -1 and that in water it is -2. So H₂O₂ easily reduces to -2 oxidation number.
   (iii) MgO is used for the lining of steel making furnace because it acts as basic flux and facilitates the removal of acidic impurities of Si, P and S from steel through slag formation.
   (iv) The anhydrous magnesium chloride is fused with NaCl to provide conductivity to the electrolyte and to lower the fusion temperature of anhydrous MgCl₂.
   NOTE: NaCl prevents hydrolysis of MgCl₂.
   (v) The oxidation state of oxygen in H₂O₂ (i.e. -1) can be changed to 0 or -2 i.e. oxygen in H₂O₂ exists in an intermediate oxidation state with respect to O₂ and O²⁻. Hence it acts both as an oxidising and reducing agent.
   (vi) NOTE: Smaller the size of cation, higher will be hydration tendency because hydration energy of cation is inversely proportional to size of cation.
   The size of alkaline earth metal ions are smaller than the size of alkali metal ions. So in crystalline form the salts of alkaline earth metals have more water molecules than those of alkali metals.
   (vii) BeCl₂ is hydrolysed due to high polarising power and presence of vacant p-orbitals in Be-atom.
   \[ Be = 1s^2, 2s^2, 2p^1 \]
   \[ 2p_0^2 \]

2. Bleaching powder, Ca(ClO)₂, can be prepared by passing chlorine through Ca(OH)₂ solution.
   \[ 3Ca(OH)₂ + 2Cl₂ \quad \text{below} \quad 35^°C \quad \rightarrow \quad \text{Ca(ClO)₂, CaCl₂, Ca(OH)₂, 2H₂O} \]
   Slaked Lime
   Bleaching Powder
   (a mixture of Ca(ClO) and basic chloride)
The s-Block Elements

3. (i) \[ 2\text{Ca}_3(\text{PO}_4)_2 + 6\text{SiO}_2 + 10\text{C} \rightarrow \text{6CaSiO}_3 + 10\text{CO} + \text{P}_4 \]

This is the electrothermal process to extract phosphorus from phosphorite or bone ash [\( \text{Ca}_3(\text{PO}_4)_2 \)].

(ii) Ferricyanide is oxidised to ferrocyanide on treatment with alkali
\[ 2\text{K}_3[\text{Fe(CN)}_6]_3 + \text{H}_2\text{O} + 2\text{KOH} \rightarrow 2\text{K}_4[\text{Fe(CN)}_6]_2 + 2\text{H}_2\text{O} + \text{O}_2 \]

(iii) \[ \text{NaCl} + \text{NH}_3 + \text{H}_2\text{O} + \text{CO}_2 \rightarrow \text{NH}_4\text{Cl} + \text{NaHCO}_3 \]

(iv) \[ 2\text{K}_3[\text{Fe(CN)}_6]_3 + \text{H}_2\text{O} + 2\text{KOH} \rightarrow 2\text{K}_4[\text{Fe(CN)}_6]_2 + 2\text{H}_2\text{O} + \text{O}_2 \]

(v) \[ \text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{Ca(HCO}_3)_2 \]

Calcium bicarbonate

NOTE: Suspension of lime stone is CaCO_3.

4. In sea water Mg exists as MgCl_2.

On treating sea water with slaked lime Mg(OH)_2 is obtained.
\[ \text{MgCl}_2 + \text{Ca(OH)}_2 \rightarrow \text{Mg(OH)}_2 \downarrow + \text{CaCl}_2 \]

in sea water

slaked lime

On reacting Mg(OH)_2 with HCl, MgCl_2 is obtained.
\[ \text{Mg(OH)}_2 + 2\text{HCl} \rightarrow \text{MgCl}_2 + \text{H}_2\text{O} \]

From MgCl_2, Mg is obtained by reduction of MgCl_2 with CaC_2.
\[ \text{MgCl}_2 + \text{CaC}_2 \rightarrow \text{Mg} + \text{CaCl}_2 + 2\text{C} \]

5. \[ \text{Ca}_3(\text{PO}_4)_2 + 5\text{H}_2\text{SO}_4 + 10\text{H}_2\text{O} \rightarrow \text{3H}_2\text{PO}_4 + 5\text{CaSO}_4 + 2\text{H}_2\text{O} + \text{HF} \]

6. \[ \text{H}_2\text{O}_2 + 2\text{H}_2\text{SO}_4 + 2\text{KI} \rightarrow \text{K}_2\text{SO}_4 + \text{I}_2 + 2\text{H}_2\text{O} \]

\[ \text{K}_2\text{SO}_4 + 2\text{H}_2\text{O} \]

i.e. 254 gm of I_2 is released by 34 gm H_2O_2
\[ \therefore 0.508 \text{ gm of I}_2 \text{ will be released by} \]
\[ \frac{34}{254} \times 0.508 = 0.068 \text{ gm} \]

5 ml of H_2O_2 sol. contains 0.068 gm of H_2O_2.
\[ \therefore 1 \text{ ml of H}_2\text{O}_2 \text{ sol contains} \]
\[ \frac{0.068}{5} = 0.0136 \text{ gm H}_2\text{O}_2 \]

NOTE: The strength of H_2O_2 is generally calculated in terms of volume strength. According to which 10 volume of H_2O_2 means that 1 ml of H_2O_2 sol gives 10 ml of O_2 at STP.

\[ 2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2 \]

\[ 2\times 34 \frac{32}{2} \text{ gm or} \]

22,400 ml at STP

\[ \text{i.e.,} \]

68 gm of H_2O_2 gives 22,400 ml of O_2 at STP

or 1 ml of H_2O_2 sol

\[ \frac{0.068}{5} \text{ gm of H}_2\text{O}_2 \text{ gives} \]

22,400 \times \frac{0.068}{5} = 4.48 \text{ ml}

or 1 ml of H_2O_2 sol gives 4.48 ml of O_2 i.e. strength of H_2O_2 sol is 4.48 volumes

7. LiF has more ionic character while LiI has more covalent character. The latter is due to the greater polarizability of larger iodide ion than the fluoride ion.

8. Meq. of H_2O_2 = Meq. of Na_2S_2O_3
\[ \frac{w}{1000} = \frac{20 \times 0.3}{17} \]
\[ w = 0.102 \text{ g} \]
\[ \text{Volume of } \frac{11200 \times 0.102}{34} = 33.6 \text{ mL} \]

\[ \therefore \text{ Volume strength } = \frac{33.6}{25} = 1.344 \]

9. \[ 2\text{KMnO}_4 + 3\text{H}_2\text{SO}_4 \rightarrow \text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 3\text{H}_2\text{O} + 5 \text{[O]} \]
\[ \begin{array}{c}
\text{[H}_2\text{O}_2 + \text{[O]} \rightarrow \text{H}_2\text{O} + \text{O}_2 \}
\end{array} \]
\[ 2\text{KMnO}_4 + 5\text{H}_2\text{O}_2 \rightarrow \text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 8\text{H}_2\text{O} + 5\text{O}_2 \]

10. 3\text{M} + \text{N}_2 \rightarrow 2\text{Mg} + \text{N}_2

\[ \text{A} \]

\[ \text{B} \]

\[ \text{C} \]

\[ \text{D} \]

M may be either Ca or Ba.

NOTE: It is not magnesium because Mg(OH)_2 has very low solubility in water.

If we consider Ba as M then A is Ba, B is Ba_3N_2, C is Ba(OH)_2, D is BaCO_3.

11. SrSO_4 > CaSO_4 > MgSO_4 > BeSO_4 (Based upon size of cation or ionic character)

12. 3Ca(OH)_2 + 2Cl_2 \rightarrow Ca(ClO)_2 + Ca(OH)_2 + CaCl_2.H_2O

Bleaching powder

(a mixture of Ca(ClO)_2 and basic chloride)

13. When H_2O_2 acts as oxidising agent, following reaction takes place:
\[ \text{H}_2\text{O}_2 + 2\text{e}^- \rightarrow 2\text{OH}^- \]

While regarding its action as reducing agent, the following reaction takes place:
\[ \text{H}_2\text{O}_2 + 2\text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 2\text{e}^- \]

Examples of oxidising character of H_2O_2 in alkaline medium
\[ 2\text{Cr(OH)}_3 + 4\text{NaOH} + 3\text{H}_2\text{O}_2 \rightarrow 2\text{Na}_2\text{CrO}_4 + 8\text{H}_2\text{O} \]

Here Cr^{3+} (Cr is a first row transition metal) is oxidised to Cr^{6+}.

Example of reducing character of H_2O_2 in alkaline medium
\[ 2\text{K}_3[\text{Fe(CN)}_6] + 2\text{KOH} + \text{H}_2\text{O}_2 \rightarrow 2\text{K}_4[\text{Fe(CN)}_6]^+ + 2\text{H}_2\text{O} + \text{O}_2 \]

Here Fe^{3+} (Fe is a first row transition metal) is reduced to Fe^{2+}.

H. Assertion & Reason Type Questions

1. (a) Both S & E are true and E is the correct explanation of S.

2. (b) Statement-I is correct. Statement-II is also correct but not the correct explanation because blue colour of the solution is due to the solvated electrons.
1. (a) \(2\text{KO}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{KOH} + \text{H}_2\text{O}_2 + \text{O}_2\).

\(\text{KO}_2\) is used as an oxidising agent. It is used as air purifier in space capsules. Submarines and breathing masks as it produces oxygen and remove carbon dioxide.

2. (a) The alkali metals dissolve in liquid ammonia without evolution of hydrogen. The metal loses electrons and combine with ammonia molecule.

\[\text{M} \rightarrow \text{M}^+ \text{ (in liquid ammonia)} + e^- \text{ (ammoniated)}\]

\[\text{M} + (x + y) \text{NH}_3 \rightarrow [\text{M} \text{(NH}_3)_x]^+ + e^- \text{(NH}_3)_y\]

Solvated electron

It is ammoniated electron which is responsible for colour.

3. (d) Sulphate of alkaline earth metal are sparingly soluble or almost not soluble in water whereas BeSO_4 is soluble in water due to high degree of solvation. Be(OH)_2 is insoluble in water but soluble in NaOH.

\[\text{BeO} + 2\text{NaOH} \rightarrow \text{Na}_2\text{BeO}_2 + \text{H}_2\text{O}\]

4. (a) Setting of cement is exothermic process which develops interlocking crystals of hydrated silicates.

5. (a) Gypsum is CaSO_4 \cdot 2\text{H}_2\text{O}

6. (a) As we move down the group, the lattice energies of carbonates remain approximately the same. However the hydration energies of the metal cation decreases from Be\(^{++}\) to Ba\(^{++}\), hence the solubilities of carbonates of the alkaline earth metal decrease down the group mainly due to decreasing hydration energies of the cations from Be\(^{++}\) to Ba\(^{++}\).

7. (b) Permanent hardness of water is due to chlorides and sulphates of calcium and magnesium i.e CaCl_2, CaSO_4, MgCl_2 and MgSO_4.

8. (a) Mg_3N_2 + 6\text{H}_2\text{O} \rightarrow 3\text{Mg(OH)}_2 + 2\text{NH}_3

9. (c) **TIPS/Formulae**:

A diamagnetic substance contains no unpaired electron.

\[\text{H}_2 = \sigma^2, \quad \text{H}_2^+ = \sigma^1, \quad \text{H}_2^- = \sigma^2,\]

(diamagnetic) (paramagnetic) (paramagnetic)

\[\sigma^1; \quad \text{He}_2^+ = \sigma^2, \quad \sigma^1\]

(paramagnetic) (paramagnetic)

10. (c) LiCl has partly covalent character. Other halides are ionic in nature. Lattice energy decreases with increase of ionic radius of cation, anion being the same. Larger is the lattice energy, the higher will be m. pt. hence NaCl will have highest lattice energy.

11. (a) **NOTE**: In one electron species, such as H-atom, the energy of orbital depends only on the principal quantum number, n.

Hence answer (d)

i.e. is \(< 2s = 2p < 3s = 3p = 3d < 4s = 4p \Rightarrow 4d = 4g\)

12. (d) Smaller the size of cation higher is its hydration energy and greater is its ionic mobility hence the correct order is Li\(^+\) < Na\(^+\) < K\(^+\) < Rb\(^+\)

13. (d) On the industrial scale hydrogen is prepared from water gas according to following reaction sequence

\[\text{CO} + \text{H}_2 + \text{H}_2\text{O} \xrightarrow{\text{catalyst}} \text{CO}_2 + 2\text{H}_2 \text{ (steam)}\]

\[2\text{NaOH} \xrightarrow{\text{alkali}} \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}\]

From the above it is clear that CO is first oxidised to CO\(_2\) which is then absorbed in NaOH.

14. (c) Calcium carbonate on thermal decomposition gives CaO (Basic oxide) and CO\(_2\) (Acidic oxide)

\[\text{CaCO}_3 \xrightarrow{\Delta} \text{CaO} + \text{CO}_2\]

Basic oxide Acidic oxide

15. (d) Very pure hydrogen can be prepared by the action of water on sodium hydride.

\[\text{NaH} + \text{H}_2\text{O} \rightarrow \text{NaOH} + \text{H}_2\]

(very pure Hydrogen)

16. (d) The reducing agent loses electron during redox reaction i.e. oxidises itself.

(a) \(\text{H}_2\text{O}_2 + 2\text{H}^+ + 2e^- \rightarrow 2\text{H}_2\text{O} \text{ (Red.)}\)

(b) \(\text{H}_2\text{O}_2 \rightarrow \text{O}_2 + 2\text{H}^+ + 2e^- \text{(Ox.)}\)

(c) \(\text{H}_2\text{O}_2 + 2e^- \rightarrow 2\text{OH}^- \text{ (Red.)}\)

(d) \(\text{H}_2\text{O}_2 + 2\text{OH}^- \rightarrow \text{O}_2 + \text{H}_2\text{O} + 2e^- \text{(Ox.)}\)

17. (d) In alkaline earth metals, ionic size increases down the group. The lattice energy remains constant because sulphate ion is so large, so that small change in cationic size does not make any difference. On moving down the group the degree of hydration of metal ions decreases very much leading to decrease in solubility.

\[\text{BeSO}_4 > \text{MgSO}_4 > \text{CaSO}_4 > \text{SrSO}_4 > \text{BaSO}_4\]

18. (b) 2 mole of water softener require 1 mole of Ca\(^{2+}\) ion

So, 1 mole of water softener require \(\frac{1}{2}\) mole of Ca\(^{2+}\) ion

Thus, \(\frac{1}{2} \times 206 = \frac{1}{412}\) mol/g will be maximum uptake,

19. (c) \(\text{H}_2\text{O}_2\) has oxidizing and reducing properties both.

20. (a) There is extensive intermolecular hydrogen bonding in the condensed phase instead of intramolecular H-bonding.

21. (b) Alkali metals have the lowest ionization energy in each period on the other hand Sc is a d – block element. Transition metals have smaller atomic radii and higher nuclear charge leading to high ionisation energy.

22. (b) On heating with excess of air Li, Na and K forms following oxides

\[4\text{Li} + \text{O}_2 \rightarrow 2\text{Li}_2\text{O} \quad \text{Lithium monoxide}\]

\[2\text{Na} + \text{O}_2 \xrightarrow{\text{Sodium peroxide}} \text{Na}_2\text{O}_2\]

\[\text{K} + \text{O}_2 \rightarrow \text{KO}_2 \quad \text{Potassium superoxide}\]
Organic Chemistry — Some Basic Principles & Techniques

**Section-A : JEE Advanced/ IIT-JEE**

A 1. tert-butyl carbonion ion 2. propadiene 3. cyclopropane 4. $sp^3$

5. vicinal, adjacent 6. non-superimposable, enantiomers 7. $sp$

8. hyperconjugation 9. butane-1, 4-dioic acid


C 1. (c) 2. (a) 3. (d) 4. (c) 5. (d) 6. (a) 7. (c) 8. (d) 9. (c) 10. (c)

11. (b) 12. (b) 13. (a) 14. (d) 15. (c) 16. (c) 17. (b) 18. (b) 19. (c) 20. (b)

21. (a) 22. (b) 23. (c) 24. (c) 25. (d) 26. (d) 27. (b) 28. (b) 29. (d) 30. (c)

31. (a) 32. (c) 33. (d) 34. (b) 35. (d) 36. (d) 37. (d) 38. (c) 39. (b) 40. (c)

41. (b) 42. (a) 43. (a) 44. (c) 45. (c) 46. (a) 47. (b) 48. (b) 49. (a) 50. (a)

51. (b) 52. (d) 53. (b) 54. (d) 55. (c) 56. (b)

D 1. (a,b,c) 2. (a,c) 3. (b,d) 4. (a,d) 5. (c,d) 6. (a) 7. (a,c) 8. (d) 9. (a,c,d) 10. (b,c,d)

11. (b,c,d) 12. (a,d) 13. (a,d) 14. (b,d) 15. (b,c) 16. (b,c) 17. (a,b,c) 18. (a)

E 1. (i) $\text{C}_2\text{H}_5\text{COCH}_3 < \text{CH}_2\text{COCH}_3 < \text{CH}_2\text{CHO} < \text{HCHO}$ (ii) isobutane $< n$-butane $< n$-butyl chloride $< n$-butanol

(iii) chlorobenzene $<$ benzene $<$ toluene $<$ methoxybenzene (iv) IV $<$ II $<$ III $<$ V $<$ I

(v) $\text{CH}_3\text{F} < \text{CH}_3\text{Cl} < \text{CH}_3\text{Br} < \text{CH}_3\text{I}$

2. (i) Pent-2-en-1-oic acid or 2-Pentenoic acid (ii) 5, 6-diethyl-3-methyl-4-decene

(iii) 3-(N, N dimethylamino)-3-methylpentane

5. $\text{CH}_3\text{CH} = \text{CH} - \text{CH} = \text{CH}_3$ 9. enantionmers – I & III; diastereomers – I & II and II & III.

10. Anyhydrous $\text{AlCl}_3$ 14. (i) $\mu_{(\text{gauche})} = 5.55 \text{ D}$

F 1. (A) - (q), (B) - (p, s), (C) - (r, s), (D) - (q) 2. (A) - (p, s), (B) - (q), (C) - (q, r, s), (D) - (q, r)

3. (A) - (p,q,t), (B) - (p,s,t), (C) - (r,s), (D) - (p) 4. (A) - (r,s,t), (B) - (p,s), (C) - (r,s), (D) - (q,r)

H 1. (d) 2. (a) 3. (c)

I 1. 7 2. 5 3. 8 4. 6 5. 3 6. 2

**Section-B : JEE Main/ AIEEE**

1. (b) 2. (c) 3. (c) 4. (d) 5. (c) 6. (c) 7. (b) 8. (d) 9. (d) 10. (b)

11. (d) 12. (a) 13. (a) 14. (d) 15. (a) 16. (a) 17. (b) 18. (c) 19. (a) 20. (d)

21. (d) 22. (c) 23. (d) 24. (a) 25. (d) 26. (a) 27. (b) 28. (c) 29. (b) 30. (a)

31. (a) 32. (b) 33. (a) 34. (b) 35. (b) 36. (b) 37. (a) 38. (a) 39. (b) 40. (b)

41. (b) 42. (d) 43. (c) 44. (c) 45. (c) 46. (d) 47. (b) 48. (c) 49. (c) 50. (d) 51. (b)
A. Fill in the Blanks
1. tert-butyl carbonium ion is more stable due to hyperconjugation and +1 effect of methyl groups.
2. propadiene; in it carbon-carbon is $sp^3$ hybridised.
3. cyclopropane, because it has maximum deviation, from the normal bond angle of $109^\circ 28'$ present in alkanes. In it bond angle is $60^\circ$.

$$d = \frac{1}{2}(109^\circ 28' - 60^\circ)$$

4. $sp^3$
5. vicinal, adjacent (or stable, different).
6. non-superimposable, enantiomers;
7. $sp$;
8. Hyperconjugation;
9. Butane-1, 4-dioic acid; Succinic acid has the formula.

\[
\begin{align*}
\text{CH}_2 - \text{COOH} \\
\text{CH}_2 - \text{COOH}
\end{align*}
\]

B. True/False
1. True : Iodide is bigger in size than bromide, hence its electrons are more dispersed than that of bromide, with the result it is weaker nucleophile than bromide.
2. True : An electron-donating group increases the electron density in $\sigma$- and $\pi$- positions due to $+M$, $+E$ and/or $+I$ effects and hence orients the new electrophile to $\sigma$- and $\pi$- positions.
3. True : There are only two asymmetric (marked with *) carbon atoms.

\[
\begin{align*}
\text{CH}_3 - \text{C}^* & \quad \text{C}^* - \text{CH}_3 \\
\text{Cl} & \quad \text{Cl}
\end{align*}
\]

4. True : In SN1 (unimolecular nucleophilic substitution reaction), the leaving group leaves, thus producing a carbocation followed by the addition of the incoming group.

C. MCQs with One Correct Answer
1. (c) NOTE:
The phenomenon of resonance gives identical bonding and hence identical bond lengths.

\[
\begin{align*}
\text{C - C bond order in benzene} &= 1.5
\end{align*}
\]
9. (c) \[ \text{Cl} = \text{C} = \text{C} \quad \mu > 0 \]
\[ \text{Cl} = \text{C} = \text{C} \quad \mu > 0 \]
\[ \text{Cl} = \text{C} = \text{C} \quad \mu = 0 \]

[Note: dipole moment is a vector quantity]

10. (e) Carbon bonded with a triple bond (i.e. C\(_2\)) is \(sp^3\) hybridised. Carbon bonded with a double bond (C\(_2\)) is \(sp^2\) hybridised.

\[ \text{CH}_3 \]

11. (b) \[ \text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2 \]

(3-Methyl-1-butene)

12. (b) **TIPS/Formulæ:**

For knowing the possible isomers of the compound follow the following points.
(i) First write down the possible number of isomeric parent alkane.
(ii) Introduce the given functional group at different positions so as to get different isomeric compound.

There are 5 isomers possible for \(\text{C}_6\text{H}_{14}\):

\[ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3, \quad \text{CH}_3\text{CH} = \text{CHCH}_2\text{CH}_3; \]
\[ \text{CH}_3 \quad \text{(i)} \]
\[ \text{(CH}_3)_2\text{CCH}_2\text{CH}_3; \quad \text{CH}_3 - \text{CH} - \text{C}_2\text{H}_5; \]
\[ \text{C}_2\text{H}_5 \quad \text{(ii)} \]
\[ \text{(CH}_3)_2\text{CH} - \text{CH(CH}_3)_2 \quad \text{(iii)} \]

13. (a) **TIPS/Formulæ:**

The bond angle in \(sp^3\), \(sp^2\) and \(sp\) hybridization is respectively 109.28\(^\circ\), 120\(^\circ\) and 180\(^\circ\).
Tetrahloroethene being an alkene has \(sp^2\) hybridised C-atoms and hence the Cl – C – Cl angle is 120\(^\circ\), whereas in tetrachloromethane, carbon is \(sp^3\) hybridised, so the angle is 109.28\(^\circ\).

\[
\begin{align*}
\text{Cl} = \text{C} = \text{C} = \text{Cl} \\
\text{Cl} \\
\text{Cl} \\
\end{align*}
\]

14. (d) **NOTE:** Heterolytic fission occurs when the two atoms differ considerably in their electronegativities.
O – H bond undergoes cleavage most readily because O and H differ markedly in their electronegativity and further oxygen being highly electronegative can accommodate the negative charge more effectively developed after the cleavage.

15. (d) Isopropyl group

\[
\begin{align*}
\text{CH}_3 \\
\text{CH}_3 - \text{CH} - \text{CH}_2\text{CH}_3 \\
\end{align*}
\]

2-Methylpentane

16. (c) \(\text{C}_2\text{H}_6\) is a saturated hydrocarbon and its carbon is \(sp^3\) hybridised. Hence it is least electronegative among alkanes, alkenes and akynes with the result C – H bond length will be maximum.

17. (b) \(\text{CH}_2 = \text{CH} - \text{C} = \text{CH}_2\)

No of \(\sigma\) bonds = 2 + 1 + 1 + 1 + 1 + 1 = 7;
No of \(\pi\) bonds = 1 + 2 = 3

18. (b) **NOTE:** The order of stability of carbonium ion is tertiary > secondary > primary > methyl

Tertiary carbonium ions (formed in b) are more stable because of electron repelling (+1 effect) nature of \(\text{CH}_3\) group due to which the +ve charge gets dispersed and also due to hyperconjugation.

\[
\text{sp}^2 \quad \text{sp}^3
\]

19. (c) \(\text{HC} = \text{C} - \text{CH} = \text{CH}_2\)

20. (b) \(\text{C}_2\text{H}_5\text{SH} + \frac{9}{2} \text{O}_2(g) \rightarrow 2\text{CO}_2(g) + 3\text{H}_2\text{O}(l) + \text{SO}_2(g)\)

At 298 K, \(\text{CO}_2\) and \(\text{SO}_2\) exist as gases while \(\text{H}_2\text{O}\) exists as liquid.

21. (a) Stereoisomers which are mirror image of each other are enantiomers and the one which are not mirror images are diastereomers. **Conformation** of the molecule is the spatial arrangement of the atoms of a given molecular structure that are obtained merely by rotation about a sigma bond in the molecule.

22. (b) **NOTE:**

A compound which consists of at least one asymmetric carbon atom is capable of showing the phenomenon of optical isomerism.
The structure cannot show geometrical isomerism as one of the carbons along the double bond has identical group (methyl). Tautomerism is not possible because of the absence of –CO group. It shows optical isomerism because it has chiral C atom with four different groups, H, \(\text{CH}_3\), COOH and \((\text{CH}_3)_2\text{C} = \text{CH}\).

23. (c) \(\text{CH}_2 = \text{CH} - \text{CH}_2 - \text{N} \stackrel{\text{+}}{\text{C}}\)

The above structure of allyl isocyaneide clearly shows 5 C – H (\(\sigma\)), 2 C – C (\(\text{sp}^2\)), 1 C – N (\(\sigma\)), 1 N – C (\(\sigma\)), 1 C – C (\(\pi\)), 2 N – C (\(\pi\)) bonds, i.e., 9\(\sigma\) and 3\(\pi\) bonds in all. There are 2 non-bonded electrons on the C-atom (co-ordinate bond between N and C, the electron pair of N is shifted towards C).

24. (c) \[
\begin{array}{ccc}
\text{CH}_3 & \text{Cl} & \text{N}^+\text{H}_3\text{Cl}^- \\
\text{IV} & \text{I} & \text{III} \\
\end{array}
\]

Activating group due to +I
Deactivating due to –I but activating due to +M
Deactivating due to –I
25. (d) **TIPS/Formulae:**
The stability of carbonium ion is influenced by both resonance and inductive effect.

- ![Diagram of carbonium ions](image)
  - $\text{NO}_2^-$ intensifies $^+\text{CH}_2$
  - $^+\text{CH}_2$ due to $-1$ and $-M$ effects

26. (d) **NOTE:** $-\text{NO}_2$ is an electron-attracting group where as $-\text{CH}_3$ is an electron-releasing group.

An electron-attracting substituent tends to disperse the negative charge of the phenoxide ion and thus, makes it more stable. This, in turn, increases the acid strength of phenol. The substituent in para position is more effective than in the meta position as the former involves a resonating structure bearing negative charge on the carbon attached to the electron-withdrawing substituent.

An electron-releasing substituent tends to intensify the negative charge of the phenoxide ion and thus makes it more unstable. This, in turn, decreases the acid strength of phenol. Hence, the order of acid strength is

- ![Diagram of phenol derivatives](image)
  - $\text{NO}_2 < \text{OH} < \text{OH} < \text{OH}$

27. (b) Dipole moment of $p$-dichlorobenzene is zero because of symmetrical structure. $\alpha$- and $m$-dichlorobenzene have higher dipole moments than toluene due to high electronegativity of chlorine than $-\text{CH}_3$ group. Further, the $\alpha$-dichlorobenzene has higher dipole moment due to lower bond angle than the $m$-isomer. Hence, the order of increasing dipole moment is:

- $p$-dichlorobenzene (IV) < toluene (I)
- $< m$-dichlorobenzene (II) < $\alpha$-dichlorobenzene (III)

28. (b) The stereoisomers of butane-2,3-diol are

- ![Diagrams of stereoisomers](image)

29. (d) $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_2-\text{C}=\text{CH}$

30. (c) **TIPS/Formulae:**
Glyceraldehyde is taken as arbitrary standard for D, L – nomenclature

31. (a) Ph$\text{CH}_2\text{CH}=$CH$\text{CH}_3$ will exhibit geometrical isomerism because in others one of the doubly bonded carbon atom has two similar groups.

32. (e) $^-$CH$_3$ is the best nucleophile because carbon is least electronegative among the given options. The order is

$$H_3C^- > \text{NH}_2^- > \text{OH}^- > F^-$$

33. (d) Rate of reaction will be $R - I > R - Br > R - Cl > R - F$, because $I^-$ is the best, while $F^-$ is the poorest leaving groups among halide ions.

34. (b) In $\text{CH}_3-C-\text{CH}_2-C-\text{CH}_2-C=\text{CH}_2$, $^-\text{CH}_2-$ group is flanked on both sides by electron-withdrawing groups and hence its hydrogens are most acidic. Once a carbanion is formed, it is stabilised due to resonance.

35. (d) Number of isomers (six) can be derived by keeping the position of any one halogen (say Br) fixed and changing the position of the other halogen one by one.

- ![Diagrams of isomers](image)
  - (Z and E) (Z and E) (Z and E)

36. (d) $S_n^2$ reactions proceed with inversion of configuration. Since the attacking nucleophile is not necessarily the same as that of leaving group, the product cannot be enantiomer of the substrate and thus necessarily will not have opposite optical rotation. Moreover since only one product is obtained, we can not obtain diastereomers.

37. (d) 2-Methylbutanoic acid contains one asymmetric centre
38. (c) TIPS/Formulae:
(i) The inductive effect decreases with increase in distance of halogen atom from the carboxylic group and hence the strength of acid proportionally decreases.
(ii) The acidity increases with the increase in electronegativity of the halogen present. Smallest dissociation constant means weakest acid, which is BrCH₂ CH₂COOH because here Br (less electronegative than F) is two carbon atoms away from -COOH.

39. (b) In carboxylic acids, molecules are more strongly associated followed by alcohols.

40. (c) 
\[
\begin{align*}
\text{CH}_3 & > \text{Cl} & \text{NO}_2 \\
(\text{Activated by } & -I, \text{ hyperconjugation}) & \text{Deactivated due to } -I \\
\text{Deactivated due to } & -I, -M, -E \\
\end{align*}
\]

41. (b) CH₃C ≡ CCH₃ is linear and symmetrical; thus it has lowest dipole moment.

42. (a) H₂C = CH – C ≡ N.

43. (a) NOTE: Dipole moment is a vector quantity. Methane molecule being symmetrical, has zero dipole moment. Replacement of one of the H-atoms by Cl atom increases the dipole moment. The increase in dipole moment is rather more than what can be expected because of the fact that the bond dipole moment of C – H bond and that of C – Cl bond reinforce one another. Replacement of another H atom by Cl increases the bond angle due to lone pair – lone pair repulsion between two Cl-atoms thereby reducing the dipole moment of the molecule. Increase in angle is again caused by the the introduction of the third Cl-atom. When the fourth Cl-atom is introduced, the molecule (CCl₄) again becomes symmetrical and dipole moment reduces to zero. So, CH₃Cl will have the maximum dipole moment.

44. (c) TIPS/Formulae:
Any conformation between two extreme positions i.e. eclipsed and staggered is known as Gauche or Skew form.

45. (c) Structures (a) and (b) are quite stable because here every atom has complete octet; in structures (c) and (d), every atom does not have complete octet; hence these are less stable than (a) and (b). However, structure (d) is stabilised by resonance, which is not possible in (c). Hence (c) is least stable.

\[
\begin{align*}
\text{CH}_2 = & \text{CH} - \text{CH} = \text{CH} - \text{OCH}_3 \\
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3 - & \text{CH} - \text{CH} = \text{CH} - \text{OCH}_3 \\
\end{align*}
\]

\[
\begin{align*}
\text{CH}_2 = & \text{CH} - \text{CH} = \text{CH} - \text{OCH}_3 \\
\end{align*}
\]

\[
\begin{align*}
\text{CH}_2 = & \text{CH} - \text{CH} - \text{CH} - \text{OCH}_3 \\
\end{align*}
\]

46. (a) NOTE: This is an example of S_N1 reaction involving carboxylation as intermediate.

\[
\begin{align*}
\text{CH}_3O - & \text{O} \quad \text{O} - \text{NO}_2 \\
\text{H} & \text{Cl} \text{CH}_3 \\
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3O - & \text{O} \quad \text{O} - \text{NO}_2 \\
\text{H} & \text{Cl} \text{CH}_3 \\
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3O - & \text{O} \quad \text{O} - \text{NO}_2 \\
\text{H} & \text{Cl} \text{CH}_3 \\
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3O - & \text{O} \quad \text{O} - \text{NO}_2 \\
\text{H} & \text{Cl} \text{CH}_3 \\
\end{align*}
\]

(A) 2° Carbocation

(B) 3° Carbocation; more stable; (positive charge is dispersed due to +M effect of -OCH₃)
This carbocation is especially stabilised through resonance in which $\cdots$O–CH$_3$ group acts as a good electron donor.

\[
\text{(A) aq acetone (H}_2\text{O}) \rightarrow \begin{array}{c}
\text{CH}_3\text{O}\\
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{H}
\end{array} + \text{CH}_3\text{H}
\]

\[
\text{(B) aq acetone (H}_2\text{O}) \rightarrow \begin{array}{c}
\text{CH}_3\text{O}\\
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{H}
\end{array} + \text{CH}_3\text{H}
\]

47. (b) Carboxylic acids are named as oyl chlorides.

48. (b) The ring to which $\cdots$NH group is attached is activated due to the lone pairs on N (+M and +E effects), while the ring to which $\cdots$C = O is attached is deactivated. Hence, the electrophile would go to the para-position of the activated ring.

49. (a) Due to similar charges on adjacent atoms, the structure (a) is least stable.

50. (a) Anti addition of Br$_2$ on trans alkene provides meso compound.

51. (b) Alkyl groups with at least one hydrogen atom on the $\alpha$-carbon atom, attached to an unsaturated carbon atom, are able to release electrons in the following way.

\[
\text{H}_3\text{C} \begin{array}{c}
\text{C}\\
\text{H}\\
\text{H}\\
\end{array} \text{H} + \text{H}_2\text{Br} \rightarrow \begin{array}{c}
\text{H} \\
\text{Br} \\
\text{H} \\
\text{Br}
\end{array}
\]

52. (d) The correct stability order is $\text{I} > \text{III} > \text{II} > \text{IV}$

53. (b) –CN has highest priority. Further the sum of locants is 7 in (b) and 9 in (d).

54. (d) NOTE: Migrating tendency of hydride is greater than that of alkyl group. Further migration of hydride from C–2 gives more stable carbocation (stabilized by +R effect of OH group and +I and hyperconjugative effects of methyl group).

55. (c) o-Hydroxybenzoic acid is strongest acid and the decreasing order of acidity is

56. (b) Compounds

\[
\begin{array}{cccc}
\text{S} & \text{P} & \text{R} & \text{Q} \\
\text{Cl} : & \text{Cl} : & \text{Cl} : & \text{Cl} :
\end{array}
\]

Relative reactivities towards $S_n$ reaction

\[
1,00,000 \quad : \quad 200 \quad : \quad 79 \quad : \quad 0.02
\]
D. MCQs with One or More Than One Correct

1. (a,b,c) Resonating structures differ in bonding pattern.

2. (a, c) Higher the stability of the corresponding anion, more will be the acidic character of the parent compound.

\[
\begin{align*}
\text{O}^- & > \text{CH}_3-\text{C}^-\text{O}^- > \text{C}_6\text{H}_5\text{O}^- \\
\text{O}^- & > \text{CH}_3-\text{C}^-\text{O}^- > \text{C}_2\text{H}_5\text{O}^- 
\end{align*}
\]

Higher stability of acetate ions than phenoxide ion is due to equivalent resonating structures in the former.

3. (b, d) 1, 4-Dichlorobenzene (p-dichlorobenzene) and trans-1, 2-dichlooroethylene have zero dipole moment because of their symmetrical structures.

4. (a, d) In n-butane, Cl can add at either the first or second carbon giving two isomers.

Option (b) : \( \text{CH}_3 - \text{CH} - \text{CH}_2 - \text{CH} - \text{CH}_3 \)

will give three isomers with Cl group at either of the CH groups, second C-atom and 3rd C-atom.

Benzene forms only one single derivative.

Option (d) : \( \text{CH}_3 - \text{CH} - \text{CH}_3 \) will again give two isomers with Cl at either of the CH groups or on the central C-atom.

5. (c, d) An asymmetric carbon atom is one which is attached with 4 different groups. Hence (c) & (d) are correct.

6. (a) TIPS/Formulae:

Conjugate base of strong acid is weak while conjugate base of a weak acid is stronger.

Acidic strength of acids,

\( \text{HOH} > \text{CH} = \text{CH} > \text{NH}_2 > \text{CH}_3 \text{CH}_3 \)

Hence the order of strength of bases,

\( \text{CH}_3\text{CH}_2^- > \text{NH}_2^- > \text{CH} = \text{C}^- > \text{OH}^- \)

7. (a, c)

\[
\begin{align*}
\text{H}_2\text{C} = \text{C} & \quad \text{H} \\ \\
\text{H} & \quad \text{H} \\
\text{2-butene (a)} & \quad \text{propene (b)}
\end{align*}
\]

Only 2-butene and 1-phenylpropene can show geometrical isomerism (cis-and trans-isomers).

8. (d) Order of acidic strength

\( \text{CH}_3\text{OH} > \text{CH} = \text{CH} > \text{C}_6\text{H}_5 > \text{C}_2\text{H}_6 \); \( \text{CH}_3\text{OH} \) is most acidic because O is more electronegative than C and capable of accommodating negative charge in \( \text{CH}_3\text{O}^- \).

Although alcohols are neutral towards the litmus paper.

9. (a,c,d) TIPS/Formulae:

For a carbonyl compound to show tautomerism, it must have at least one H at the \( \alpha \) – carbon atom.

(a), (c) and (d) show tautomerism.

\[
\begin{align*}
\text{CH} = \text{CH} - \text{OH} & \leftrightarrow \text{CH} - \text{CH} = \text{CHO} \\
\text{enol form} & \leftrightarrow \text{keto form}
\end{align*}
\]

Tautomerism is not possible

10. (b,c,d) Note : An aromatic species will have:

- \((4n + 2)\) electrons (by Hückel’s Rule)
- planar structure (due to resonance)
- cyclic structure (due to presence of \( sp^2 \) - hybrid carbon atoms).

11. (b,c,d) E and F, and also E and G differ in position of atom (H), so these are tautomers (not resonating structures. Geometrical isomers are also diastereomers).

12. (a, d) The given molecule although possesses neither centre of symmetry nor a plane of symmetry (hence optically active) but it has an axis of symmetry (\( C_3 \)).

Note : A \( C_3 \) axis of symmetry is an axis about which the molecule can be rotated by 360°/n to produce a molecule indistinguishable from the original molecule.

13. (a,d) \( \text{CH}_3 - \text{C} - \text{CH} = \text{CH} - \text{C} - \text{CH}_3 \)

<table>
<thead>
<tr>
<th>Stereoisomer</th>
<th>Configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>( d ) cis ( d )</td>
</tr>
<tr>
<td>II</td>
<td>( l ) cis ( l )</td>
</tr>
<tr>
<td>III</td>
<td>( d ) cis ( l )</td>
</tr>
<tr>
<td>IV</td>
<td>( d ) trans ( d )</td>
</tr>
<tr>
<td>V</td>
<td>( l ) trans ( l )</td>
</tr>
<tr>
<td>VI</td>
<td>( d ) trans ( l )</td>
</tr>
</tbody>
</table>

Enantiomers : I and II; IV and V

Diastereomers : I (or II), III (or IV), V and VI

Meso : III and IV
14. (b, d)
Structural formula of 2, 2-dimethylbutane is

(I) Newman projection using \( C_1-C_2 \) bond

(II) Newman projection using \( C_3-C_2 \) bond

In 2-butene, hyperconjugation is between \( \sigma \rightarrow \pi^* \) bond.

E. Subjective Problems

1. (i) **TIPS/Formulæ:**
It is a case of nucleophilic addition reaction. More the electron deficiency of the carbonyl carbon, greater will be its reactivity towards nucleophilic addition.

\[
\text{C}_2\text{H}_5\text{COCH}_3 < \text{CH}_3\text{COCH}_3 < \text{CH}_3\text{CHO} < \text{HCHO}
\]

(ii) Isobutane \(<\) n-Butane \(<\) n-Butyl chloride \(<\) n-Butanol
van der Wall's forces dipole-dipole H-bonding attraction

Straight chain alkane isomer has higher boiling point than the isomeric branched chain isomer because the former isomer has larger surface area which leads to large vander Waals attractive forces.

(iii) **NOTE:** –OCH\(_3\) and –CH\(_3\) groups are activating group while –Cl is a deactivating group for electrophilic substitution.

(iv) Presence of electron withdrawing group increases the acidic character of the –COOH due to –I effect, while presence of electron-donating group (alkyl groups) decreases the acidic character due to +I effect. Thus

\[
\text{IV} < \text{II} < \text{V} < \text{III} < \text{I}
\]

(v) **NOTE:** A weaker base is a better leaving group.
Rate of reaction will be \( R-I > R-Br > R-Cl > R-F. \) because \( I^- \) is the best, while \( F^- \) is the poorest leaving groups among halide ions.

2. (i) \( ^{\text{5}}\text{CH}_3\text{CH}_2\text{CH} = \text{C}^{\text{3}}\text{H}_1\text{COOH} \)

Pent-2-en-1-oic acid Or 2-Pentenoic acid

(ii) \( ^{\text{5,6}}\text{diethyl-3-methyl-4-decene} \)

(iii) IUPAC name is

\( ^{\text{3-(N,N-dimethylamino)-3-methylpentane}} \)

3. (i) \( ^{\text{CH}_3-N\overset{\text{O}}{\text{O}}\text{O}^-} \leftrightarrow ^{\text{CH}_3-N\overset{\text{O}}{\text{O}}^+} \)

In tert butyl cation, carbon bearing positive charge has one vacant \( p \)-orbital hence it is \( \sigma-p \) (empty) conjugation or hyperconjugation.
In fornic acid, resonance is not possible with the result there are two types of C–O bonds. In sodium formate, resonance is possible, so both of the C–O bonds have same bond length.

Formic acid

Sodium formate (Resonating hybrid)

In biphosphine, one of the phenyl groups acts as an electron donor and the other electron acceptor due to mesomeric effect. This makes it more reactive than benzene.

The low reactivity of halogen atom in aryl and vinyl halides towards nucleophiles is due to resonance.

Resonating structures of chlorobenzene

NOTE: Due to resonance, carbon-chlorine bond acquires partial double bond character, hence it becomes shorter and stronger and thus cannot be easily replaced by nucleophiles.

$\text{CH} = \text{C}^+ \text{C}^-\text{sp hybridised and more electronegative then the } \text{CH of CH}_2 = \text{CH which is } \text{sp}^2\text{ hybridised. Thus the former can better accommodate electron pair hence less basic.}$

Benzene gives electrophilic substitution reaction rather than electrophilic addition reactions because it will have a stable benzene ring in the product, whereas electrophilic addition on benzene destroys the benzene ring.

$5\text{CH}_3^-4\text{CH}^-3\text{CH} = 2\text{CH}^-1\text{CH}_3$

$\text{cis}-2\text{-butene}$

$\text{cis}-2\text{-butene}$

$\text{cis}-\text{alkene}$

$\text{cis}-\text{alkene}$

$\text{cis}-\text{alkene}$

$\text{cis}-\text{alkene}$

$\text{cis}-\text{alkene}$

9. In order to convert a molecule with two stereogenic centres to its enantiomer, the configuration at both centres must be reversed. Reversing the configuration at only one stereogenic centre converts it to a destereomeric structure. Thus structures I and III are enantiomers; while structures I and II as well as II and III are diastereomers.

10. TIPS/Formulæ:

Diethyl ether acts as a Lewis base and anhydrous AlCl₃ as a Lewis acid.

Anhydrous AlCl₃ is more soluble in diethyl ether because the oxygen atom of ether donates its pair of electrons to the vacant orbital of electron deficient aluminium of AlCl₃ through the formation of coordinate bond. In case of hydrated AlCl₃ aluminium is not electron deficient as oxygen atom of water molecule has already donated its pair of electrons to meet the electron deficiency of aluminium.

11. NOTE: Higher the $K_a$ value, more stronger is the acid.

Correct order of acidic strength of the given acids is

$\text{(b) > (c) > (a) > (e) > (d)}$
Hence the \( K_a \) values of the five acids will be in the order:

<table>
<thead>
<tr>
<th>(b)</th>
<th>(c)</th>
<th>(a)</th>
<th>(e)</th>
<th>(d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 3.06 \times 10^{-5} )</td>
<td>( 10.2 \times 10^{-5} )</td>
<td>( 6.4 \times 10^{-5} )</td>
<td>( 4.2 \times 10^{-5} )</td>
<td>( 3.3 \times 10^{-5} )</td>
</tr>
</tbody>
</table>

12. \[
\begin{align*}
\text{H}_2\text{C} & \quad \text{CH} \quad \text{CH}_2 \\
\text{H}_3\text{C} & \quad \text{CH} \quad \text{CH}_2 \\
\end{align*}
\]

13. Presence of an electron-attracting group increases acidity of the compound. Thus

\[
\text{H}_2\text{N}^+ \quad \text{F} > \quad \text{H}_3\text{N}^+ 
\]

14. (i)

Anti conformer

Gaucho conformer

Given, mole fraction of anti conformer = 0.82
\[
\therefore \quad \text{mole fraction of gauche conformer} = 0.18
\]

\[
\mu_{\text{ob}} = \mu_{\text{anti}} \times x_{\text{anti}} + \mu_{\text{gauche}} \times x_{\text{gauche}}
\]

\[
1 = \mu_{\text{anti}} \times 0.82 + \mu_{\text{gauche}} \times 0.18
\]

\[
1 = 0.82 \times \mu_{\text{anti}} + 0.18 \times \mu_{\text{gauche}}
\]

\[
\therefore \quad \mu_{\text{anti}} = 0
\]

\[
\mu_{\text{gauche}} = \frac{1}{0.18} = 5.55 \quad \text{D}
\]

(ii)

F. Match the Following

1. (A) - q; (B) - p, s; (C) - r, s; (D) - q

E1 mechanisms are encountered only with tertiary or secondary substrates and in presence of either a weak base or a base in low concentration. So primary substrates will follow E2 mechanism, i.e. (A) \( \rightarrow \) E2 and (D) \( \rightarrow \) E2.

Further E1 mechanism (similar to S_N1) proceeds by first order kinetics and is determined by the slower (first) step of the formation of carboxation. Hence (B) \( \rightarrow \) E1 and first order reaction.

NOTE THIS STEP: Reaction of \( \text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{Br} \) on treatment with \( \text{C}_2\text{H}_5\text{O}^+ \) in presence of \( \text{C}_2\text{H}_5\text{OD} \) gives \( \text{C}_6\text{H}_5\text{CD} = \text{CH}_2 \).

This reaction follows E1CB (Elimination unimolecular conjugate base) mechanism. This 2 step mechanism follows the following path:

\[
\begin{align*}
\text{C}_6\text{H}_5^- \quad \text{CH} \quad \text{CH}_2 & \quad \text{C}_2\text{H}_5\text{O}^- \quad \text{fast} \\
\text{C}_6\text{H}_5^- \quad \text{CH} \quad \text{CH}_2 & \quad \text{Br} \quad \text{fast}
\end{align*}
\]

\[
\begin{align*}
\text{C}_6\text{H}_5^- \quad \text{CH} \quad \text{CH}_2 & \quad \text{Br} \quad \text{slow} \\
\text{C}_6\text{H}_5^- \quad \text{CD} = \text{CH}_2 & \quad \text{Br}^- \\
\end{align*}
\]

(formation of carbanion and elimination of \( \text{Br} \) from carbanion)

Although this mechanism involves 2 steps the overall rate of the reaction is limited to the slower second step and hence the rate of reaction depends only on the concentration of the carbanion, i.e. first order reaction. Hence, (C) \( \rightarrow \) (r), (s).

2. (A) - p, q, s; (B) - q; (C) - q, r, s; (D) - q, r

(A) \( \text{C}_6\text{H}_5\text{CHO} \) forms ppt. of 2, 4-dibromophenylhydrazone (p), forms silver mirror with ammonical silver nitrate – Tollens' reagent (q), forms cyanohydrin with \( \text{CN}^- \).

(B) \( \text{CH}_3\text{C} = \text{CH} \) gives ppt. with \( \text{AgNO}_3 \)

(C) \( \text{CN}^- \) reacts with \( \text{AgNO}_3 \) to form ppt. of \( \text{AgCN} \) (q), it is a nucleophile (r) and forms cyanohydrin (s)

(D) \( \text{I}^- \) gives ppt. of \( \text{AgI} \) with \( \text{AgNO}_3 \) (q), and it is a nucleophile (r)

3. (A) - p, q, t; (B) - p, s, t; (C) - r, s; (D) - p
4. A → r, s, t; B → p, s; C → r, s; D → q, r
H. Assertion & Reason Type Questions

1. (d) Statement -1 is false because aryl halides do not undergo nucleophilic substitution under ordinary conditions. This is due to resonance, because of which the carbon–chlorine bond acquires partial double bond character, hence it becomes shorter and stronger and thus cannot be replaced by nucleophiles.

2. (a) Due to +M effect of $-\overset{1}{O}H$, its intermediate carbocation is more stable than the one in benzene.

3. (e) Statement -1 is correct. Statement-2 is incorrect because compound can be chiral even in the absence of chiral atoms.

I. Integer Value Correct Type

1. The seven possible cyclic structural and stereoisomers are

   ![Cycloalkanes and stereoisomers](image)

2. The number of cyclic isomers for a hydrocarbon with molecular formula C₄H₆ is 5. The structures are

   ![Cycloalkanes](image)

3. 8

   ![Enantiomeric pair](image)

   Enantiomeric pair = 2

4. 6

   ![Stereocenters](image)

   $a = 3$ Hyperconjugative H's
   $b = 2$ Hyperconjugative H's
   $c = 1$ Hyperconjugative H

5. (3)

   ![Conformers](image)

   Following three conformers (with $\mu \neq 0$) are possible

6. (2) The molecule cannot show geometrical isomerism, so only its mirror image will be the other stereoisomer.

   ![Mirror images](image)
1. (b) \(-\text{CH}_3\) group has +I effect, as number of \(-\text{CH}_3\) group increases, the inductive effect increases. Therefore the correct order is:
\[
\text{CH}_3\text{H}_2\text{C} < (\text{CH}_3)_2\text{C} < (\text{CH}_3)_3\text{C} < \text{CH}_3\text{H}_2\text{C}
\]

2. (c) Stereosomatism involves those isomers which contain same ligands in their co-ordination spheres but differ in the arrangement of these ligands in space. Stereosomatism is of two type geometrical isomerism and optical isomerism. In geometrical isomerism ligands occupy different positions around the central metal atom or ion.

NOTE: In optical isomerism isomers have same formula but differ in their ability to rotate directions of the plane of polarised light.

3. (c) \(\text{ClC}=\text{CH}-\text{CH}_2-\text{CH}_2\text{CH}_3\) does not show geometrical isomerism due to presence of two similar Cl atoms on the same C-atom. Geometrical isomerism is shown by compounds in which the groups/atoms attached to C = C are different.

4. (d) Amino acids contain – NH_{2} and – COOH groups e.g. 
Glycine
\[
\text{H}_2\text{C}<\text{NH}_{2}\text{COOH}
\]

5. (c) The correct name is 3-methylbut-2-ol

6. (e) \(\text{CH}_3\text{C}==\text{CH}\text{CH}_3\);

3-methyl-2-butane

7. (b) In molecules (a), (c) and (d), the carbon atom has a multiple bond, only (b) has sp^{3} hybridization.

8. (d) A mixture of equal amount of two enantiomers is called a racemic mixture. A racemic mixture does not rotate plane-polarized light. They are optically inactive because for every molecule in a racemic mixture that rotate plane of polarized light in one direction, there is a mirror image molecule that rotates the plane in opposite direction.

9. (d) TIPS/Formulae:
Stereoisomerism is of two types i.e., geometrical isomerism and optical isomerism.
Both the structures shows stereoisomerism. Structure I shows geometrical isomerism as it contains two different atoms (H) and groups (CH_{3}) attached to each carbon containing double bond.

\[
\text{H}_2\text{C}==\text{C}<\text{CH}_3 \quad \text{H}_2\text{C}==\text{C}<\text{CH}_3
\]

Cis butene \hspace{1cm} Trans butene

Structure II shows optical isomerism as it contains a chiral carbon (attached to four different group) atom.

\[
\begin{array}{c}
\text{CH}_3 \quad \text{H}_3\text{C} \\
\text{H} \quad \text{C} == \text{OH} \quad \text{OH} \quad \text{C} == \text{H} \\
\text{CH}_2\text{CH}_3 \quad \text{H}_3\text{CH}_2\text{C} \\
\text{butyl alcohol} \quad \text{(Two enantiomers)}
\end{array}
\]

10. (b) The hydrolysis of t-butyl bromide is an example of S_{N}1 reaction. The reaction consists of two steps.

(i) \(\text{CH}_3\text{C}==\text{Br} \xrightarrow{\text{Slow step}} \text{CH}_3\text{C}==\text{Br} \quad \text{CH}_3\quad \text{Br} \)

(ii) \(\text{CH}_3\text{C}==\text{OH} \xrightarrow{\text{Fast step}} \text{CH}_3\text{C}==\text{OH} \quad \text{CH}_3\quad \text{OH} \)

11. (d) \(\text{HCOO}^{-}\) exists in following resonating structures

\[
\begin{array}{c}
\text{O} \\
\text{H} \quad \text{C} == \text{O}^{-} \leftrightarrow \text{H} \quad \text{C} == \text{O}
\end{array}
\]

Hence in it both the carbon oxygen bonds are found equal.

12. (a) \(\text{C}_n\text{H}_{2n}\text{O}_2\) is general formula for carboxylic acid

13. (a)

\[
\begin{array}{c}
\text{CH}_3 \quad \text{O} \\
\text{H}_2\text{C}==\text{C}==\text{C}==\text{CH}_3 \quad \text{H}_3\text{C}==\text{C}==\text{CH}_3 \\
\text{Chiral Carbon} \quad \text{Chiral Carbon}
\end{array}
\]

(i) \(\text{C}_n\text{H}_{2n+1}\text{C}==\text{C}==\text{C}==\text{CH}_3 \quad \text{H}_3\text{C}==\text{C}==\text{CH}_3 \\
\text{H} \quad \text{H}
\]

(ii) \(\text{C}_n\text{H}_{2n+1}\text{C}==\text{C}==\text{C}==\text{CH}_3 \quad \text{H}_3\text{C}==\text{C}==\text{CH}_3 \\
\text{H} \quad \text{H}
\]

14. (d) NOTE: Among isomeric alkanes, the straight chain isomer has higher boiling point than the branched chain isomer. The greater the branching of the chain, the lower is the boiling point. Further due to the presence of \(\pi\) electrons, these molecules are slightly polar and hence have higher boiling points than the corresponding alkanes.

Thus B.pt. follows the order: alkynes > alkene > alkanes (straight chain) > branched chain alkanes.
15. (a) \[
\text{IUPAC name – 3, 3-Dimethyl -1 cyclohexanol}
\]

16. (a) \[
\begin{align*}
\text{Acetone} & : \quad \text{CH}_3 - C - \text{CH}_3; \\
\text{Acetic acid} & : \quad \text{CH}_3 - C - \text{OH}; \\
\text{Acetonitrile} & : \quad \text{CH}_3 - C \equiv N; \\
\text{Acetamide} & : \quad \text{CH}_3 - C - \text{NH}_2.
\end{align*}
\]

17. (b) **NOTE**: The compounds containing two similar asymmetric C-atoms have plane of symmetry and exist in Meso form.

18. (c) 1-chloropentane is not chiral while others are chiral in nature.

19. (a) Only 2-cyclopropyl butane has a chiral centre.

20. (d) In aromatic acids presence of electron withdrawing substituent e.g. –NO₂ disperses the negative charge of the anion and stabilises it and hence increases the acidity of the parent benzoic acid. Further o-isomer will have higher acidity than corresponding m and p isomers. Since nitro group at p-position have more pronounced electron withdrawing than –NO₂ group at m-position hence the correct order is the one given above.

21. (d) Lone pair of electrons present on the nitrogen of benzyl amine is not involved in resonance.

22. (c) 1-chloropentane is not chiral while others are chiral in nature.

23. (d) Free radicals are electrically neutral, unstable and very reactive on account of the presence of odd electrons.

24. (a) In moving down a group, the basicity and nucleophilicity are inversely related, i.e. nucleophilicity increases while basicity decreases. In going from left to right across a period, the basicity and nucleophilicity are directly related. Both of the characteristics decrease as electronegativity of the atom bearing lone pair of electrons increases. If the nucleophilic centre of two or more species is same, nucleophilicity parallels basicity, i.e. more basic the species, stronger is its nucleophilicity. Hence based on the above facts, the correct order of nucleophilicity will be.

25. (d) R – C – X; when X is Cl the C–X bond is more polar and ionic which leaves the compound more reactive for nucleophilic substitution reaction.

26. (a) 3-bromo-1-chlorocyclohexene

27. (b) The order of stability of free radicals

\[
(C_6H_5)_3\dot{C} > (C_6H_5)_2\dot{CH} > (CH_3)_3\dot{C} > (CH_3)_2\dot{CH}
\]

The stabilisation of first two is due to resonance and last two is due to inductive effect.

28. (c) **TIPS/Formulae**:

The stronger the acid, the weaker the conjugate base formed.

The acid character follows the order:

\[
\text{CH}_3\text{COOH} > C_6\text{H}_5\text{OH} > \text{H}_2\text{O} > \text{CH}_3\text{OH}
\]

The basic character will follow the order:

\[
\text{CH}_3\text{COO}^- < C_6\text{H}_5\text{O}^- < \text{O}^+\text{H}^- < \text{CH}_3\text{O}^-.
\]
29. (b) **Hofmann's rule**: When theoretically more than one type of alkenes are possible in eliminations reaction, the alkene containing least alkylated double bond is formed as major product. Hence

```
\[ \text{Me} \quad \text{Et} \quad \Delta \quad \text{Me} \]
```

**NOTE**: It is less stearically β-hydrogen is removed

30. (a)

Due to hydrogen bonding between H & F gauche conformation is most stable hence the correct order is

Eclipse, Anti, Gauche

31. (a) 7 6 5 4 3 2 1

\[ \text{CH}_3 \quad \text{CH}_2 \quad \text{CH} \quad \text{CH}_2 \quad \text{CH}_2 \quad \text{CH}_3 \]

\[ \text{CH}_3 \quad \text{CH}_2 \quad \text{CH}_3 \]

3-ethyl-4,4-dimethylheptane

32. (b) **NOTE**: The organic compounds which have chiral carbon atom (a carbon atom attached to four different group or atoms and do not have plane of symmetry rotate plane polarised light.

\[ \text{CHO} \quad \text{HO} \quad \text{CH}_3 \quad \text{OH} \]

(* is asymmetric carbon)

33. (a) Nitro group is electron withdrawing group, so it deactivates the ring towards electrophilic substitution.

34. (b) Chiral conformation will not have plane of symmetry. Since twist boat does not have plane of symmetry it is chiral.

35. (b) The absolute configuration is (R, R) (using priority rules to get the absolute configuration)

So the correct answer is (b)

36. (b) In option (b) the complex formed is with benzene where as in other cases it is formed with nitrobenzene with -NO₂ group in different position (α, β, γ). The complex formed with nitrobenzene in any position of -NO₂ group is less stable than the complex formed with benzene so the correct answer is (b)

**NOTE**: The most stable complex has lowest energy.

37. (a) The correct order of priority for the given functional group is

\[ \text{O} \quad \text{O} \quad \text{COOH} > -\text{SO}_2\text{H} > -\text{C} \quad \text{NH}_2 > -\text{C} \quad \text{H} \]

38. (a)

\[ \text{CH}_3 \]

\[ \text{H}_3\text{C} \quad \text{C} \quad -\text{CH}_3 \]

\[ \text{CH}_3 \]

Neopentane

or 2,2- Dimethylpropane

39. (b)

\[ \text{C} \quad \text{Cl} \quad \text{Cl} \]

\[ \text{Cl} \quad \text{C}_2\text{H}_2\text{CH}_2 \quad (\text{CH}_3)_2\text{CH}^- \quad (\text{CH}_3)_3\text{C}^+ \]

-ve charge highly dispersed due to -1 effect

-M effect delocalises -ve charge

+1 effect of CH₃ group intensifies the -ve charge

40. (b)

41. (b) CH₃ - CH = CH₂ - *CH₃

exhibits both geometrical as well as optical isomerism.

\[ \text{cis} - \text{R} \quad \text{trans} - \text{R} \quad \text{cis} - \text{S} \quad \text{trans} - \text{S} \]

42. (d) The correct order of basicity is

\[ \text{RCOO}^- < \text{CH} = \text{C}^- < \text{NH}_2^- < \text{R}^- \]

43. (c) For a compound to show optical isomerism, presence of chiral carbon atom is a necessary condition.

\[ \text{H}_2\text{C} = \text{HC} \quad \text{C}^* \quad \text{CH}_2 - \text{CH}_3 \]

\[ \text{CH}_3 \]

3-methyl-1-pentene
44. (c) \[
\text{O} \quad \text{H} \\
\text{\(\text{H}_3\text{C} = \text{C} - \text{CH}_2 - \text{CH}_2 - \text{CH}_3\)} \quad \text{\(\implies\) Tautomerism} \quad \text{\(\text{O} - \text{H}\)} \\
\text{\(\text{H}_3\text{C} - \text{C} = \text{CH} - \text{CH}_2 - \text{CH}_3\)}
\]

45. (c) \[
\text{\(\text{Cl} - \text{CH} - \text{CH}_3\)}_{\text{Toluene}} \xrightarrow{\text{SbCl}_5} \text{\(\text{Ph} - \text{CH} - \text{CH}_3 + \text{SbCl}_5^-\)} \quad \text{(carbocation)} \\
\text{\(\text{Ph} - \text{CH} - \text{CH}_3 + \text{SbCl}_5^-\)} \quad \text{Cl} \\
\text{\(\text{(d+\ell)}\) mixture}
\]

46. (d) Higher stability of allyl and aryl substituted methyl carbocation is due to dispersal of positive charge due to resonance

\[
\text{\(\text{CH}_2 = \text{CH} - \text{CH}_2 \leftrightarrow \text{CH}_2 - \text{CH} = \text{CH}_2\)}
\]

Resonating structures of allyl carbocation

\[
\text{Resonating structures of benzyl carbocation}
\]

whereas in alkyl carbocations dispersal of positive charge on different hydrogen atoms is due to hyper conjugation hence the correct order of stability will be

\[
\text{\(\text{Benzyl}\)} \quad > \text{\(\text{CH}_2 = \text{CH} - \text{CH}_2\)} \quad > \text{\(\text{CH}_3 - \text{CH}_2 - \text{CH}_2\)} \quad \text{\(\text{Propyl}\)}
\]

47. (b) \[
\% \text{ of } N = \frac{1.4 \times \text{meq. of acid}}{\text{mass of organic compound}}
\]

\[
\text{meq. of } \text{H}_2\text{SO}_4 = 60 \times \frac{\text{M}}{10} \times 2 = 12
\]

\[
\text{meq. of } \text{NaOH} = 20 \times \frac{\text{M}}{10} \times 2
\]

\[
\therefore \text{meq. of acid consumed} = 12 - 2 = 10
\]

\[
\therefore \% \text{ of } N = \frac{1.4 \times 10}{1.4} = 10\%
\]

48. (c) \[
\text{\(\text{H}_3\text{C} = \text{C} = \text{CH} - \text{CH}_2\)} \\
\text{Ph}
\]

1.- Phenyl-2-butene the two groups around each of the doubly bonded carbon Because, all are different. This compound can show cis-and trans-isomerism.

49. (c) Mass of substance = 250 mg = 0.250 g

\[
\text{Mass of } \text{AgBr} = 141 \text{ mg} = 0.141 \text{ g}
\]

1 mole of AgBr = 1 g atom of Br

\[
188 \text{ g of AgBr} = 80 \text{ g of Br}
\]

\[
\therefore \text{188 g of AgBr contain bromine} = 80 \text{ g}
\]

\[
0.141 \text{ g of AgBr contain bromine} = \frac{80}{188} \times 0.141
\]

This much amount of bromine present in 0.250 g of organic compound

\[
\therefore \% \text{ of bromine} = \frac{80}{188} \times 0.141 \times 100 = 24\%
\]

50. (d)

\[
\text{At (1),}
\]

\[
\text{At (2),}
\]

It is 'S' configured

It is 'R' configured.

51. (b) Spent-lye and glycerol are separated by distillation under reduced pressure.

Under the reduced pressure the liquid boil at low temperature and the temperature of decomposition will not reach. e.g. glycerol boils at 290°C with decomposition but at reduced pressure it boils at 180°C without decomposition.
Hydrocarbons

Section-A: JEE Advanced/ IIT-JEE

1. ethyne
2. 2-butyne
3. $C_2H_2$
4. ethylene
5. $H_2SO_4, HgSO_4$
6. less
7. 3, 4-dibromo-1-butene-1 (at low temperature) or 1, 4-dibromo-2-butene (at high temperature)

Section-B: JEE Main/ AIEEE

1. (a)
2. (c)
3. (c)
4. (c)
5. (c)
6. (c)
7. (c)
8. (a)
9. (c)
10. (b)
11. (a)
12. (d)
13. (a)
14. (d)
15. (a)
16. (c)
17. (b)
18. (b)
19. (a)
20. (b)
21. (d)
22. (a)
23. (d)
24. (b)
25. (b)
26. (a)
27. (d)
28. (c)
29. (b)
30. (a)
31. (b)

A
1. F
2. F

B
1. (b)
2. (b)
3. (a)
4. (c)
5. (c)
6. (c)
7. (a)
8. (a)
9. (c)
10. (b)
11. (a)
12. (d)
13. (a)
14. (d)
15. (a)
16. (c)
17. (b)
18. (b)
19. (a)
20. (b)
21. (d)
22. (a)
23. (d)
24. (b)
25. (b)
26. (a)
27. (d)
28. (c)
29. (b)
30. (a)
31. (b)

D
1. (b)
2. (a, c)
3. (a)
4. (a, b, c, d)
5. (d)
6. (b, d)
7. (b, c, d)

E
8. $C_6H_{12}$
10. $55.55\degree$
11. Butene-2
12. 3-methylpentene-1

14. $H_3C-C-H-C-H_2-C=CH_3; CH_3-C-H-C=CH_2-C=CH_3; CH_3-C=CH-C=CH_3; CH_3-C=CH-C=CH_3$

$[X]$
$[Y]$
$[Z]$

15. $CH_3-C=CH=CH_2$

17. [A] C\equiv C

[B] COOH;

[C] Br

19. $CH_3CH_2CH=CHCH_2CH_3$

21. [A] $\xrightarrow{CHBr-CH_2Br}$, [B] $\xrightarrow{C=CH_3}$

22. $A: C_6H_5(CH_3)C=CH(CH_3)C_6H_5 B: C_6H_5COCH_3$, C: $C_6H_5C_2H_5$

23. $R_3Al + TiCl$

G
1. (d)
2. (b)
3. (a)
4. (c)

H
1. (a)
2. (c)
3. (b)
A. Fill in the Blanks

1. Ethyne, because of the high s character of the −C = H bond in ethyne (sp hybridisation).

2. 2-butyne

\[ \text{CH}_2 = \text{CH} + \text{Na} \xrightarrow{\text{NaLid_NH}_3} \text{CH} = \text{CNa} \xrightarrow{\text{NaNH}_2} \text{NaC} = \text{CNa} \]

NaC = CNa + 2CH\textsubscript{3}I \rightarrow CH\textsubscript{2}C = C CH\textsubscript{3}

2-Butyne

3. C\textsubscript{2}H\textsubscript{2}

CH = CH + HCl \rightarrow CH\textsubscript{2} = CHCl \rightarrow PVC

4. ethylene

\[ \text{CH}_2\text{COOK} \xrightarrow{\text{Ag}_2\text{CO}_3} \text{CH}_3\text{COO}^- + 2\text{K}^+ \]

\[ \text{CH}_2\text{COOK} \xrightarrow{\text{Ag}_2\text{CO}_3} \text{CH}_3\text{COO}^- \]

\[ \text{CH}_2 = \text{CH}_2 + 2\text{CO}_2 \]

5. H\textsubscript{2}SO\textsubscript{4}, H\textsubscript{2}SO\textsubscript{4} less;

**NOTE:**

Stability of free radical \( \propto \frac{1}{\text{Bond dissociation energy}} \)

Benzyl (C\textsubscript{6}H\textsubscript{5}CH\textsubscript{2}) free radical is more stable than methyl.

(CH\textsubscript{3}) free radical because of hyperconjugation (no bond resonance).

6. 3,4-dibromo-1-butene (at low temperature) or 1,4-dibromo-2-butene (at high temperature)

B. True/False

1. False : Ethylene reacts with sulphuric acid to form ethyl hydrogen sulphate. It can be dried by passing it through phosphorus pentoxide.

2. False : Bromine is less reactive, hence it is more selective and thus 3° hydrogen will be removed more easily than the 1° hydrogen leading to 2-bromo-2-methylpropane as the main product.

\[ \text{CH}_3 \]

\[ \text{CH}_3 - \text{CH} - \text{CH}_3 \]

3. MCQs with One Correct Answer

2. (b) Unsaturated hydrocarbons decolourise alk. KMnO\textsubscript{4} solution; C\textsubscript{2}H\textsubscript{4} (H\textsubscript{2}C = CH\textsubscript{2}) is an alkene.

3. (a) In a homologous series, higher the number of C-atoms, higher is the b.p.

4. (c) Four isomers

(i) CH\textsubscript{3}CH\textsubscript{2}CH = CH\textsubscript{2} (1-butene) 

(ii) CH\textsubscript{3}CHCH\textsubscript{3} (cis-2-Butene) 

(iii) CH\textsubscript{3}CHCH\textsubscript{2}CH\textsubscript{3} (trans-2-Butene) 

(iv) CH\textsubscript{3}CH\textsubscript{3}C = CH\textsubscript{2} (2-Methylpropane)

5. (c) CH\textsubscript{2}C = CH + H\textsubscript{2}O \xrightarrow{\text{H}_2\text{SO}_4} \text{H}_2\text{SO}_4 \rightarrow 

\[ \text{[CH}_3\text{CH(}\text{OH}\text{) = CH}_2\text{]} \rightarrow \text{CH}_3\text{COCH}_3 \text{acetone} \]

6. (c) CH\textsubscript{2} = CH\textsubscript{2} + H\textsubscript{2}SO\textsubscript{4} \rightarrow CH\textsubscript{3}CH\textsubscript{2}OSO\textsubscript{3}H 

C\textsubscript{6}H\textsubscript{6} + H\textsubscript{2}SO\textsubscript{4} \rightarrow C\textsubscript{6}H\textsubscript{5}SO\textsubscript{3}H + H\textsubscript{2}O

C\textsubscript{6}H\textsubscript{4} + H\textsubscript{2}SO\textsubscript{4} \rightarrow \text{No reaction}

C\textsubscript{6}H\textsubscript{5}NH\textsubscript{2} + H\textsubscript{2}SO\textsubscript{4} \rightarrow C\textsubscript{6}H\textsubscript{5}NH\textsubscript{3}HSO\textsubscript{4}

Only hexane does not dissolve in conc. H\textsubscript{2}SO\textsubscript{4} even on warming.

8. (a) Acidic hydrogen is present in alkynes, attached to the triply bonded C-atoms. They can be easily removed by means of a strong base.

9. (c) TIPS/Formulae :

Anti-Markovnikoff’s addition of HBr is observed only with unsymmetrical alkenes, a, b, and d.

CH\textsubscript{3}CH = CH\textsubscript{2} CH\textsubscript{2} = CHCH\textsubscript{2}CH\textsubscript{3} (a) (b)

CH\textsubscript{3}CH = CH\textsubscript{3} CH\textsubscript{3}CH = CHCH\textsubscript{2}CH\textsubscript{3} (c) (d)

10. (b) For isomeric alkanes, th one having longest straight chain has highest b.p. because of larger surface area.

11. (a) Ethylene has restricted rotation [due to C = C], acetylene no rotation [due to C = C], hexachloroethane has more rotation than ethylene but less than ethane because of greater size of the substituent (chlorine) than in ethane (substituent is hydrogen).

13. (a) TIPS/Formulae :

Hydration of alkynes via mercuration takes place in accordance with Markovnikov’s manner rule

\[ \text{CH}_3\text{CH}_2\text{C} = \text{CH} \xrightarrow{\text{+2H}_2\text{O}} \text{H}_2\text{SO}_4/\text{H}_2\text{SO}_4 \]

\[ \text{CH}_3\text{CH}_2\text{CH} = \text{C} - \text{CH}_3 \xrightarrow{\text{H}_2\text{O}} \text{CH}_3\text{CH}_2 - \text{C} - \text{CH}_3 \]
14. (d) In propyne (CH₃C=CH), the terminal hydrogen is acidic and reacts with ammonical AgNO₃.

15. (a) **TIPS/Formulæ**:
The relative rates of hydrogenation decreases with increase of steric hindrance.

RₓC = CH₂ > RCH = CHR > RₓC = CHR > RₓC = CRₓ

Among the four olefins, (a) and (b) are less stable (Saytzeff's rule). Further in (a), the bulky alkyl groups are on same side (cis-isomer), hence it is less stable.

16. (c) **TIPS/Formulæ**:
Peroxide effect is effective only in case of HBr and not in case of HCl and HI.

Step I: (a) R - O - O - R → 2RO⁻;
Step II: RO⁻ + H - X → RO⁻ + H⁻ X⁻

Step II: R'CH = CH₂ + X⁻ →

R⁻ X⁻ → R⁻ CH₂X + R⁻ CH⁻ CH₂⁻

For HCl, Step I (b) is endothermic while step II is exothermic but for HI, Step I(b) is exothermic while Step II is endothermic.

17. (b) **TIPS/Formulæ**:
Addition on triple bond takes place by the syn-addition of hydrogen.

Since the configuration of the double bond already present is cis, the compound formed will have a plane of symmetry and hence optically inactive.

18. (b) **TIPS/Formulæ**:
Alkenes undergo electrophilic addition reactions.

HOCl undergoes self-ionization

(HOCl + HOCl → H₂O + Cl⁻ + Cl⁻)

to give H₂O⁺ + Cl⁻ + Cl⁻.

So, it is the Cl⁻ that attacks in the first step.

19. (a) **TIPS/Formulæ**:
The π bond is formed by the sideways overlapping of two p-orbitals of the two carbon atoms.
The molecular plane does not have any π electron density as the p-orbitals are perpendicular to the plane containing the ethene molecule. The nodal plane in the π-bond of ethene is located in the molecular plane.

20. (b) Br⁺ is less reactive and more selective and so the most stable free radical (3°) will be the major product.

21. (d) **TIPS/Formulæ**:
In 1-butyn terminal hydrogen is acidic where as in 2-butyn there is no terminal hydrogen. Thus 2-butyn will not react with ammonical Cu₂Cl₂. While 1-butyn, being terminal alkyne, will give red ppt. with ammonical cuprous chloride

22. (a)

(Benzylic carbocation highly stable)

23. (d) H₂/Pd/BaSO₄ reduces an alkyne to cis-alkene, H₂/Pt reduces it to alkane, NaBH₄ does not reduce an alkyne. Reduction of an alkyne by active metal in liq. NH₃ gives trans-alkene.

24. (b) Cl₃CH₂CH₂CH₃ + Cl₂ → CH₃CH₂CH₂CH₂Cl

(i) Chlorination at C-2 and C-4 produces no chiral compounds

(ii) Chlorination at C-3 produces a chiral carbon marked with star (d and l form).

(iii) Chlorination at C-1 also produces a chiral carbon marked with star (d and l form).

25. (b) Nitrosylation with NOCl adds on olefins according to Markovnikor's rule, where NO⁺ constitutes the positive part of the addendum.

CH₃CH = CH₂ + NOCl → CH₃CHCH₂Cl

Cl" NO
31. (b) Greater the extent of branching, lesser is the boiling point of the hydrocarbon, so order of b.p is III > II > I.

D. MCQs with One or More Than One Correct

1. (b) TIPS/Formulae:

Heat of hydrogenation is related to stability of molecules; higher the stability, lower is the heat of hydrogenation.

Butadiene, \( \text{CH}_2=\text{CHCH}=\text{CH}_2 \) has two double bonds so its heat of hydrogenation will be more than the other three.

Alkenes follow the following order of stability

\[ \text{R}_2\text{C} = \text{CR}_2 \quad > \quad \text{R}_2\text{C} = \text{CHR} > \text{RCH} = \text{CHR} \]

tetrasubstituted (most stable due to hyper conjugative structures)

\[ > \text{RCH} = \text{CH}_2 \quad > \quad \text{CH}_2 = \text{CH}_2 \]

Unsubstituted (least stable due to no hyper conjugation)

Thus here stability order of the given monoalkenes is

\[ \text{CH}_3\text{CH} = \text{CHCH}_3 \quad > \quad \text{CH}_3\text{CH}_2\text{CH} = \text{CH}_2 \]

Butene-2

(cis- and trans-)

Butene-1

NOTE: The trans-2-butene is more stable than the cis-because in the cis-isomer the two bulky groups are crowded together with the result it has more van der Waal’s strain than the trans-isomer.

2. (a, c) Hyperconjugation in toluene activates the benzene ring for electrophilic substitution.

3. (a)

So, the value of \( N \) will be \( 1 + 2 + 2 + 1 = 6 \).

Since enantiomers have nearly same physical properties, II and III as well as IV and V can’t be separated, hence the number of isomers (M) will be

\[ 1 + 1 + 1 + 1 = 4 \]
4. (a, b, c, d)

\[
\text{Cl} \quad \xrightarrow{\text{AlCl}_3} \quad \text{Aromatic (P)} \quad \xrightarrow{\text{AlCl}_4;} \quad \text{Aromatic (Q)} \quad \xrightarrow{\text{NaH}} \quad \text{Na} + \text{H}_2 \uparrow \\
\]

\[
\text{NH}_3 \quad \text{from (NH}_4\text{)}_2\text{CO}_3 \quad \xrightarrow{\Delta} \quad 2\text{NH}_3 + \text{CO}_2 + \text{H}_2\text{O} \\
\]

Note: P has 2 \( \pi \) electrons, while Q, R & S have 6 \( \pi \) electrons each. Hence all the 4 are aromatic.

5. (d)

\[
\text{CH}_3 \quad \text{H}_2\text{C} \quad \xrightarrow{1 \text{ equiv. HBr}} \quad \text{Br} \quad \xrightarrow{\text{H}} \quad \text{Br} \\
\]

6. (b, d)

\[
(A) \quad \text{Optically active} \\
(B) \quad \text{Optically inactive} \\
(C) \quad \text{Optically active} \\
(D) \quad \text{Optically inactive} \\
\]

5. (d)

\[
\text{CH}_3 \quad \xrightarrow{\text{Br}} \quad \text{NaOE} \quad \overset{+}{\text{Br}} \\
\]

7. (b, c, d)

E. Subjective Problems

1. Bromine water test: \( \text{C}_2\text{H}_2 \) decolourises bromine water while \( \text{CH}_4 \) does not decolourises bromine water.

2. (i) \( \text{CH} = \text{CH} \xrightarrow{\text{hydration}} \text{CH}_3\text{CHO} \xrightarrow{\text{OH}^+} \text{aldol cond.} \)

\[
\text{OH} \quad \text{CH}_3\text{CHCH}_2\text{CHO} \quad \xrightarrow{\text{H}_2\text{O}^{-}} \quad \text{CH}_3 = \text{CHCHO} \\
\]

3-hydroxybutanal
(ii) Ethylene oxide

\[
\text{CH}_2 = \text{CH}_2 \xrightarrow{\text{O}} \text{C(CH}_3)_3
\]

NOTE: that the 1° carbocation, (CH\(_3\))\(_2\)CH\(_+\)H\(_2\) formed during reaction rearranges to the more stable, 3° carbocation, (CH\(_3\))\(_3\)C\(^+\) and hence the above product is formed] (see also ix part)

(iv) \(\text{C}_6\text{H}_6 + (\text{CH}_3)_2\text{CHCH}_2\text{OH} \xrightarrow{\text{H}_2\text{SO}_4} \text{C}_6\text{H}_5(\text{CH}_3)_3\) tert-Butylbenzene

Explanation:

\[
(\text{CH}_3)_2\text{CHCH}_2\text{OH} \xrightarrow{\text{H}^+} (\text{CH}_3)_2\text{CH}^+\text{H}_2
\]

1° carbocation

\[
\xrightarrow{\text{rearranges to}} (\text{CH}_3)_2\text{C}^+\text{H}_6 \xrightarrow{} \text{C}_6\text{H}_5\text{C}(\text{CH}_3)_3
\]

3° carbocation

(v) \(\text{C}_6\text{H}_5\text{C}_2\text{H}_5 \xrightarrow{\text{Br}_2, \Delta, \text{light}} \text{C}_6\text{H}_5 - \text{CH} - \text{CH}_3 \xrightarrow{} \text{Br}
\]

\[
\text{NaCN} \xrightarrow{} \text{C}_6\text{H}_5 - \text{C} - \text{CH}_3 \xrightarrow{} \text{CN}
\]

2-phenylpropanenitrile

(vi) \(\text{H}_3\text{C} - \text{CH} - \text{CH}_2\text{Br} \xrightarrow{\text{Anhydrous AlCl}_3} \text{H}_3\text{C} - \text{C} - \text{CH}_2\text{Br} - \text{C}(\text{CH}_3)_3
\]

(vii) \(\text{CH}_2 = \text{CH}_2 + \text{CHBr}_3 + \text{t-BuOK} \rightarrow \)

(viii) (Partial reduction of triple bond in syn-manner)

3. \(\text{CH}_2 = \text{CH}_2 \xrightarrow{\text{Br}_2, \text{Br}} \text{CH}_2\text{CH}_2 \xrightarrow{2\text{KOH, alcoholic}} \text{CH} = \text{CH}
\]

OH OH

4. \(\text{CH}_3 - \text{CH} = \text{CH}_2 + \text{H}_2\text{O} + [\text{O}] \rightarrow \text{CH}_3 - \text{CH} = \text{CH}_2 \rightarrow \text{CH} = \text{CH}_2
\]

Propene [NOTE: Colour of KMnO\(_4\) is discharged]

5. (i) TIPS/Formulae:

Chlorination of methane is a free radical substitution reaction.

In dark, chlorine is unable to be converted into free radicals, hence the reaction does not occur.

(ii) TIPS/Formulae:

Addition of unsymmetrical addendum (HBr in present case) to unsymmetrical olefin (CH\(_2\)CH = CH\(_2\), in present case) takes place according to Markownikoff rule.

\(\text{CH}_3\text{CH} = \text{CH}_2 + \text{HBr} \rightarrow \text{CH}_3\text{CHBrCH}_3\)

Propene iso-Propyl bromide

(iii) Unlike olefins, \(\pi\)-electrons of benzene are delocalised (resonance) and hence these are unreactive towards addition reactions. Moreover, addition reaction leads to destruction of the benzenoid ring.

(iv) In presence of light, toluene undergoes side chain bromination through a free radical mechanism.

In presence of FeBr\(_3\), toluene undergoes electrophilic substitution in the benzene ring.

[v] TIPS/Formulae:

1, 3 - Butadiene is a conjugated diene and is a resonance hybrid:

\[
\begin{bmatrix}
1 & 2 & 3 & 4 \\
-C = C = C = C-
\end{bmatrix} \leftrightarrow
\begin{bmatrix}
-C = C = C = C-
\end{bmatrix} \leftrightarrow
\begin{bmatrix}
-C = C = C = C-
\end{bmatrix} \leftrightarrow
\begin{bmatrix}
-C = C = C = C-
\end{bmatrix}
\]

Thus resonance induces some double bond character in the central C-C bond leading to the shortening of this bond. Alternatively, all the four C atoms of 1, 3-butadiene are \(sp^2\) hybridised and thus their C-C bond length will be lower than that of n-butane in which all the four C atoms are \(sp^3\) hybridised.

(vi) tert-Butylbenzene does not give benzoic acid on treatment with acidic KMnO\(_4\) because it does not contain any hydrogen atom on the key carbon atom.

(vii) Reduction of central ring to form A involves reduction of all the three cyclobutadiene rings (which are
6. (i) NOTE: Under normal conditions, tert-butyl bromide is formed, isobutyl bromide is formed in presence of peroxide.

\[
\begin{align*}
\text{CH}_3 & \quad \text{BrH}_2C=CH-\text{CH}_3 \\
\text{peroxide} & \quad \text{H}_2\text{C}=\text{C}-\text{CH}_3 \\
\text{HBr} & \quad \text{2-Methylpropene}
\end{align*}
\]

(ii) Ethyne (HC = CH) and only those derivatives which have at least one acetylenic hydrogen atom (H = C - H) i.e. terminal alkynes will give white precipitate with ammonical silver nitrate solution.

7. \[\text{[C}_2\text{H}_5\text{OH} + \text{PCl}_5 \longrightarrow \text{C}_2\text{H}_5\text{Cl}]\]

\[\text{C}_6\text{H}_5 + \text{C}_2\text{H}_5\text{Cl} \xrightarrow{\text{anhy. AlCl}_3} \text{C}_6\text{H}_5\text{CH}_3 + \text{HCl}\]

Benzene Ethylbenzene

8. Calculation of molecular formula of A.

<table>
<thead>
<tr>
<th>Element</th>
<th>Percentage</th>
<th>Relative No. of atoms</th>
<th>Simplest whole ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>85.7%</td>
<td>85.7/12 = 7.14</td>
<td>7.14/7.14 = 1</td>
</tr>
<tr>
<td>H</td>
<td>14.3%</td>
<td>14.3/1 = 14.3</td>
<td>14.3/7.14 = 2</td>
</tr>
</tbody>
</table>

\[\therefore \text{Empirical formula of A} = \text{CH}_2\]

Determination of molecular weight of A
1 g of A consumes = 38.05 g of 5% Br_2 (in CCl_4)

\[\frac{38.05 \times 5}{100} = 1.90 \text{ g of 100% Br}_2\]

Now since 1.90 g of Br_2 is consumed by 1 g of compound A
\[\therefore 160 \text{ g (1 mole) of Br}_2 \text{ will be consumed by} \]

\[\frac{1}{1.90} \times 160 = 84.2 \text{ g of A} \text{ (app.) g of A} \]

\[\therefore \text{Molecular weight of A} = 84\]

Hence, \( n = \frac{84}{12 + 2} = 6 \)

\[\therefore \text{Molecular formula of A} = (\text{CH}_2)_6 = \text{C}_6\text{H}_{12}\]

Since the hydrocarbon A consumes 1 molar equivalent of hydrogen, it must contain one double bond. Oxidation of compound A with KMnO_4 to form compound C (C_4H_8O) and acetic acid indicates = CH.CH_3 fragment in A, i.e.

\[\text{C}_4\text{H}_8 = \text{CHCH}_3 \xrightarrow{\text{KMnO}_4} \text{C}_4\text{H}_8\text{O} + \text{CH}_3\text{COOH}\]

Acetic acid

Now the fragment C_4H_8 of A on oxidation forms the compound 'C' (C_4H_8O) which may be easily obtained from butyne-2 and acidic aq. HgSO_4, the compound 'C' must be ethylmethyl ketone.

\[\text{CH}_3\text{C} \equiv \text{C.CH}_3 \xrightarrow{\text{H}^+ / \text{H}_2\text{SO}_4} \text{CH}_3.\text{CH}_2.\text{CH}_3 \text{ (Ethylmethyl ketone)}\]

Butyne-2

The formation of ketone 'C' from C_4H_8 fragment of 'A' can be explained by the following structure of A.

\[\text{CH}_3\text{CH}_2.\text{C} = \text{CH.CH}_3 \xrightarrow{\text{KMnO}_4} \]

\[\text{CH}_3\text{CH}_2.\text{COOH} + \text{CH}_3\text{CH}_2.\text{CH}_3 \text{ (Ethylmethyl ketone)}\]

Acetic acid

Hence formation of 'B' can be represented as below.

\[\text{CH}_3\text{CH}_2.\text{C} = \text{CH.CH}_3 + \text{H}_2 \xrightarrow{\text{CH}_3\text{CH}_2.\text{CH}_2.\text{CH}_3} \text{ (C_6H}_{12}\]

9. (i) By amm. AgNO_3 or by acidic-H tests: Terminal alkynes give white precipitate with amm. AgNO_3 or red ppt. with amm. Cu_2Cl_2 (H atom attached on sp hybridized carbon is acidic).

\[2\text{CH}_3\text{CH}_2.\text{C} = \text{CH} + \text{Ag}_2\text{O} \rightarrow 2\text{CH}_3\text{CH}_2.\text{C} = \text{CAg} + \text{H}_2\text{O}\]

CH_3 - C = C - CH_3 + Ag_2O \rightarrow No reaction

NOTE: Only terminal alkynes respond to these reactions.

(ii) Cyclohexene gives positive response to bromine water test and Baeyer's test while cyclohexane does not respond to these reagents.

10. \[\text{C}_2\text{H}_6 \xrightarrow{\text{monobromination}} 2\text{C}_2\text{H}_5\text{Br} \text{ (yield 90%) (given)}\]

\[2\text{C}_2\text{H}_5\text{Br} \xrightarrow{\text{Wurtz reaction}} \text{C}_4\text{H}_{10} + 2\text{HBr} \text{ (yield 85%) (given)}\]

Moles of n-butane to be produced

\[\frac{55 \text{ g}}{58 \text{ g mol}^{-1}} = 0.948 \text{ mol (∵ molecular mass of C}_4\text{H}_{10} = 58)\]

Amount of C_2H_5Br required to obtain 0.948 mol. of C_4H_{10} = 2 \times 0.948 \text{ mol.}
11. TIPS/Formulæ:
A symmetric alkene does not follow Markovnikoff and anti-
Markovnikoff’s rule (Peroxide effect).
B has to be a symmetric alkene (butene-2)
CH₃CH = CHCH₃ as it will give the same product
CH₃CH(Br) = CH₂CH₃ in presence/absence of peroxide.

12. An optically active hydrocarbon will have an asymmetric
C-atom. This means D(C₆H₁₂)₂ should have an asymmetric
C-atom & C₆H₁₄ will have no asymmetric C-atom, hence D
would be 3-methylpentene-1,

CH₃ — CH₂ — CH — CH = CH₂
  \(\text{CH}_3\)
(D) Optically active(C₆H₁₂)

H₂ → CH₃CH₂ — CH — CH₂CH₃
  \(\text{CH}_3\)
Optically inactive(C₆H₁₄)

13. (i) S₉₂ reaction leads to inversion in configuration.

\[
\begin{align*}
\text{Br} & \quad \text{H} \quad \text{NaOH} \quad \text{S₉₂} \quad \text{OH} \\
\text{CH₃} & \quad \text{CH₃}
\end{align*}
\]

(ii) \(\text{R} — \text{C} \equiv \text{C} — \text{R}\) \(\text{H}_2\) Lindlar catalyst \(\text{R} \equiv \text{C} — \text{C} \equiv \text{R}\) (cis-alkene)

NOTE:
(i) Lindlar’s catalyst is Pd supported over CaCO₃ which
is partially poisoned by \((\text{CH₃COO})₂\text{Pb}\). It can restrict
the hydrogenation of alkyne to alkene stage. It yields a
cis-alkene.
(ii) Reduction of alkynes to alkene stage can also be carried
out with sodium or lithium in liquid NH₃. Here trans-
alkene is major product.

14. TIPS/Formulæ:
(i) 1, 4-Pentadiene reacts with \(\text{HCl}\) in presence of benzoyl
peroxide in Markovnikoff’s way.
NOTE: Peroxide effect applies to HBr only.

(ii) Grignard reagent reacts with ethyl acetate to form ketones, or \textit{ter}-alcohol if Grignard reagent is taken in
excess.

Thus the given reactions can be written as below.

\[
\begin{align*}
\text{H₂C} = \text{CH} — \text{CH₂} — \text{CH} = \text{CH₂} & \quad \text{excess HCl} \\
\overset{(\text{C₆H₄CO})₂\text{O}}{} & \quad \text{H₃C} — \text{CH} — \text{CH₂} — \text{CH} — \text{CH₃} \\
\overset{(\text{Mg in dry ether})}{\text{Cl}} & \quad \overset{(\text{MgCl})}{\text{Cl}} \\
\overset{(\text{MgCl})}{\text{Cl}} & \quad \overset{(\text{MgCl})}{\text{Cl}}
\end{align*}
\]

15. Summary of the given reactions

\[
\begin{align*}
\text{C₆H₁₂} & \overset{\text{H₂}}{\text{C₆H₁₂}} \overset{\text{ozonolysis}}{\text{HCHO + CH₃} — \text{C} — \text{CHO}} \\
\text{CH₃} & \overset{\text{CH₂}}{\text{CH₃}} \overset{\text{2-Ketopropanal}}{\text{CH₃} — \text{C} — \text{CHO}} + \text{CH₂O}
\end{align*}
\]

Since hydrogenation of (E) to (F) takes up two molecules of
hydrogen, it indicates the presence of two double bonds in
E which is further supported by its ozonolysis to form two
products having three carbonyl groups. Further structure of
ozonolysis product leads to following structure to compound (E).

\[
\begin{align*}
\text{CH₃} & \quad \text{CH₂} \\
\text{CH₃} — \text{C} — \text{CH₂} — \text{CH₃} & \quad \overset{\text{2H₂}}{\text{CH₃} — \text{C} — \text{CH = CH₂}} \\
\overset{\text{O₃}}{\text{O}} & \quad \text{2-Ketopropanal}
\end{align*}
\]

16. TIPS/Formulæ:
In \(\text{S₉₁}\) reaction racemization as well as inversion is observed.
Reaction of optically active 2-iodobutane with \text{NaI} in acetone
is an \(\text{S₉₁}\) reaction which involves formation of carbocation as
intermediate.

\[
\begin{align*}
\text{CH₃} — \text{C} — \text{CH₂} & \quad \overset{\text{Planar}}{\text{CH₃} — \text{CH₂H₅}} \\
\text{CH₃} — \text{CH₂H₅} & \quad \overset{\text{Planar (+)} + \text{(-)}}{\text{CH₃} — \text{CH₂H₅}}
\end{align*}
\]

Thus the product, being a racemic mixture will be optically
inactive.

17. Summary of the given facts

\[
\begin{align*}
\text{C₈H₁₀} & \overset{(\text{i})\text{O₂}}{\text{C₄H₆O₂}} \\
\text{(A)} & \quad \overset{(\text{ii})\text{hydrolysis}}{\text{C₄H₆O₂}} \\
\text{(B)} & \quad \overset{(\text{ii})\text{CO₂, (iii)H⁺}}{\text{C₃H₂Br}}
\end{align*}
\]

Since compound \text{B} is obtained from compound \text{C} \text{C₃H₂Br}
through reaction with \text{Mg} and \text{CO₂}, it seems that compound
Hydrocarbons

(B) is a carboxylic acid formed via the formation of Grignard reagent. Hence compound (C) should be an alkyl halide having three carbon atoms. The alkyl halide (C) is unsaturated (indicated by number of hydrogen atoms) which is present in the form of ring and thus (C) should be bromocyclopropane.

18. (a) CH₃CH₂ - C = CH - CH₃
CH₂CH₃

(unsymmetrical)

(b) CH₃CH₂ - C = CH - CH₃
CH₂CH₃

Br
HBr / Peroxide
(Peroxide effect)

CH₃CH₂ - C = CH - CH₃
CH₂CH₃

OH
Br

B₂O₃/H₂O
CH₃CH₂ - C = CH - CH₃
CH₂CH₃

(c) CH₃CH₂ - C = CH - CH₃
CH₂CH₃

Hg(OAc)₂/H₂O
NaBH₄

CH₃CH₂ - C = CH - CH₃
CH₂CH₃

19. TIPS/Formulœ:
(i) It should be an alkene as it adds one mole of H₂.
(ii) The C₆ alkene should be symmetrical because on oxidation it gives a single carboxylic acid having three carbon atoms.

CH₃(CH₂)₄CH₃ → H₂ → CH₃CH₂CH₂CH = CHCH₂CH₃

n-Hexane

CH₃CH₂CH₂CH = CHCH₂CH₃

(A)

(0) KMnO₄ → 2CH₃CH₂COOH

20. (i) CH₃CH₃ → KMnO₄ → COOH

Soda lime
(CaO + NaOH)

21. (i)

22. C₁₆H₁₆ (an alkene) → O₃ → only C₈H₈O → NaOH/Na₂

KOH/NH₂NH₂

C₆H₅COONa

(C)

(i) Conversion of (B) to (C) involves iodoxy reaction, hence (B) must contain – COCH₃ group leading to C₆H₅COCH₃ (C₆H₅O) as its molecular formula.

(ii) Since the given alkene gives only one product on ozonolysis, so the given alkene must be a symmetrical alkene containing a double bond in centre. Thus the alkene (A) must have following structure:

C₆H₅

C = C

CH₃

(O) → C₆H₅COCH₃

(A, C₁₀H₁₆)

CH₃

(O) → C₆H₅

(B, C₆H₆O)

CH₃
Note: Since catalytic hydrogenation of alkenes takes place in cis-(sym-) manner; hence recemic mixture will be formed by the trans-isomer.

23. Ziegler – Natta catalyst (R₃Al + TiCl₄)

24. (i) Formation of HCOONa and a primary alcohol due to Cannizzaro reaction of F and G indicate that either F or G should be HCHO. Thus the alkene A should have CH₂=CH₂ grouping. The remaining 5 C's of A should have grouping = HCC₄H₉.

(ii) Formation of only E by the ozonolysis of D (C₆H₁₂) indicates that D should have following structure

\[ \text{CH}_3 \quad \text{CH}_3 \]
\[ \text{CH} \quad \text{CH} \]
\[ \text{O} \quad \text{O} \]
\[ \text{CH}_3 \quad \text{CH}_3 \]
\[ \text{CH} \quad \text{CH} \quad \text{CH}_3 \]

(E) negative test with Fehling solution, but responds to iodoform reaction

Note: Fehling's test is given by aldehydes and not ketones.

(iii) Since A is isomer of D, former should have following structure.

\[ \text{CH}_3 \quad \text{CH}_3 \]
\[ \text{CH} \quad \text{CH} \]
\[ \text{CH} \quad \text{CH} \]

(A) (C₆H₁₂, alkene)

\[ \text{CH}_3 \quad \text{CH}_3 \]
\[ \text{CH}_3 \quad \text{CH}_3 \]

2° carbocation

3° carbocation

\[ \text{CH}_3 \quad \text{CH}_3 \]
\[ \text{CH}_3 \quad \text{CH}_3 \]
Hydrocarbons

\[ \text{CH}_3\text{CH}_2\text{CHBr} + \text{Br}^- \rightarrow \text{CH}_3\text{CH}_2\text{CH} = \text{CH}_2 \]

1° free radical (less stable)

[\[ \text{Br}^- \]

\[ \text{CH}_3\text{CH}_2\text{CH} = \text{CH}_2 \]

2° free radical (more stable)

Section-B

1. (a) Acetylene reacts with the other three as:

\[ \text{CH} = \text{C} = \text{Na} \xrightarrow{\text{lq. NH}_3} \text{CH} = \text{CH} + \text{HCl} \]

\[ \text{CH} = \text{CH} + \text{HCl} \rightarrow \text{CHOH} \]

\[ \text{CHCl} \]

2. (c) \[ \text{CH} = \text{CH} + \text{HOCI} \rightarrow \text{HCHO} \]

\[ \text{CHCl}_2 \]

3. (c) In neopentane all the H atoms are same (1°).

\[ \text{CH}_3 \]

\[ \text{CH}_3 \]

\[ \text{CH}_3 \]

4. (c) \[ \text{CH}_3 \]

\[ \text{CH}_3 \]

Ease of replacement of H-atom 3° > 2° > 1°.

5. (c) Alkenes combine with hydrogen under pressure and in presence of a catalyst (Ni, Pt or Pd) and form alkanes.

Butene - 1 \[ \xrightarrow{\text{H}_2/\text{Pd}} \text{Butane} \]

6. (c) \[ \text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2 + \text{HBr} \rightarrow \text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2 \]

At ~80°C the product is 1, 2-addition

\[ \text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2 \]

\[ \xrightarrow{\text{Br}} \]

At 40°C the product is 1, 4-addition

3. (b) TIPS/Formulae:

With trans-2-butene, the product of Br₂ addition is optically inactive.

Even though, both assertion and reason are correct, the correct reason for the formation of meso-2,3-dibromobutane from trans-2-butene is anti addition of Br₂.

Section-B

JEE Main/ AIEEE

7. (c) \[ \text{CH}_3 - \text{CH} - \text{CH} - \text{CH}_3 \]

Since it contains only two types of H-atoms hence it will give only two mono chlorinated compounds viz. \[ \text{ClCH}_2 - \text{CH} - \text{CH} - \text{CH}_3 \]

1-chloro-2,3-dimethyl butane

and \[ \text{CH}_3 - \text{C} - \text{CH} - \text{CH}_3 \]

2-chloro-2,3-dimethyl butane

8. (a) Water adds directly to the more reactive alkene in presence of a strongly acidic catalyst forming alcohols. Addition occurs according to Markownikov’s rule.

\[ \text{CH}_3 - \text{CH} = \text{CH} + \text{H}_2\text{O} \xrightarrow{\text{H}_2\text{SO}_4} \text{CH}_3 - \text{CH} - \text{CH}_3 \]

2° alcohol

\[ \text{CH}_3 \]

\[ \text{CH}_3 \]

\[ \text{CH}_3 \]

9. (c) \[ \text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2 \]

\[ \text{H}_2\text{SO}_4 \xrightarrow{\text{H}_2\text{SO}_4} \text{CH}_3 - \text{C} - \text{CH}_3 \]

\[ \text{OH} \]

3° alcohol

NOTE: Addition follows Markownikoff’s rule.

10. (d) When alkyl benzene are oxidised with alkaline K\text{MnO}_4 (strong oxidising agent) the entire alkyl group is oxidised to –COOH group regardless of length of side chain.

\[ \text{CH}_2\text{CH}_3 \]

\[ \xrightarrow{(O), \text{KmNO}_4/\text{OH}} \text{COOH} \]

Ethyl benzene

Benzoic acid
11. (b) The reaction follows Markownikoff rule which states that when unsymmetrical reagent adds across unsymmetrical double or triple bond the negative part adds to carbon atom having lesser number of hydrogen atoms.

\[ \text{CH}_3 - \text{C} = \text{CH} + \text{HBr} \rightarrow \text{CH}_3 - \text{C} = \text{CH}_2 \quad \text{HBr} \rightarrow \quad \text{CH}_3 - \text{C} - \text{CH}_2 \]

2, 2-dibromo-propane

12. (d) FeCl₃ is Lewis acid. In presence of FeCl₃ side chain hydrogen atoms of toluene are substituted.

\[
\begin{array}{c}
\text{Toluene} \\
\text{CH}_3 + \text{Cl}_2 \xrightarrow{\text{FeCl}_3} \quad \text{o-chloro toluene} \\
\text{p-chloro toluene}
\end{array}
\]

13. (a) **NOTE:** Toluene (\( \text{CH}_3 \)) contains \(-\text{CH}_3\) group which is \(\sigma-, \pi-\) directing group so on nitration of toluene the \(-\text{NO}_2\) group will occupy \(\sigma-, \pi-\) positions.

\[
\begin{array}{c}
\text{CH}_3 \\
\xrightarrow{\text{HNO}_3 + \text{H}_2\text{SO}_4} \quad \text{o-nitro toluene} \\
\text{p-nitro toluene}
\end{array}
\]

On reduction with \(\text{Sn/HCl}\) they will form corresponding anilines in which \(-\text{NO}_2\) group changes to \(-\text{NH}_2\). The mixture now contains \(\text{CH}_3\text{NH}_2\) and \(\text{CH}_3\text{NH}_2\). These anilines when diazotized and then treated with \(\text{CuBr}\) forms \(\sigma-, \pi-\) bromotoluenes.

14. (d) Completing the sequence of given reactions,

\[
\text{CH}_3 - \text{CH} = \text{CH} - \text{CH}_3 \xrightarrow{\text{O}_3} \]

\[
\text{CH}_3\text{CHO} + \text{H}_2\text{O} + \text{ZnO}
\]

Thus ‘B’ is \(\text{CH}_3\text{CHO}\)

Hence (d) is correct answer.

15. (b) Alkynes having terminal \(-\text{C} = \text{H}\) react with \(\text{Na}\) in liquid ammonia to yield \(\text{H}_2\) gas of the given compounds

\[
\text{CH}_3\text{CH}_2\text{C} = \text{CH} \quad \text{Na in} \quad \text{liquid NH}_3
\]

\[
\text{CH}_3\text{CH}_2\text{C} = \text{C}^-\text{Na}^+ + \frac{1}{2}\text{H}_2(g)
\]

16. (d) Writing the reaction we get

\[
\text{CH}_3\text{MgX} + \text{CH}_3 - \text{C} = \text{C} - \text{H} \rightarrow \quad \text{CH}_3 - \text{C} = \text{CMgX} + \text{CH}_4(g)
\]

So we find that \(\text{CH}_4\) is produced in this reaction.

17. (c) The given molecular formula suggests that the aldehyde formed will be acetaldehyde hence the alkene will be

\[
\text{CH}_3\text{CH} = \text{CHCH}_3 \xrightarrow{\text{O}_3} \quad \text{H}_2\text{O} \xrightarrow{\text{Zn/H}_2\text{O}} \quad 2\text{CH}_3\text{CHO} + \text{H}_2\text{O}_2
\]

18. (b) Compound must contain a vinyl group \((-\text{C} = \text{C} = \text{H}\)) in order to give formaldehyde as one of the product.

\[
\text{R} - \text{C} = \text{H} + \text{O}_3 \rightarrow \quad -\text{H}_2\text{O} \xrightarrow{\text{H}_2\text{O}} \quad \text{R} - \text{C} = \text{O} + \text{HCHO}
\]

19. (b) \(\text{H}_2\text{C} - \text{C} - \text{CH}_3 \xrightarrow{\text{Cl}_2/\text{h}_2\text{v}} \text{monohalogenation} \rightarrow \text{single product}

\[
\text{CH}_3\text{CH} = \text{CHCH}_3 \quad \text{neopentane}
\]

20. (b) Anti addition of hydrogen atoms to the triple bond occurs when alkynes are reduced with sodium (or lithium) metal in ammonia, ethylamine, or alcohol at low temperatures. This reaction called, a dissolving metal reduction, produces an \((\text{E})-\) or \((\text{trans})\)-alkene. Sodium in liq. \(\text{NH}_3\) is used as a source of electrons in the reduction of an alkyne to a \((\text{trans})\) alkene.

\[
\text{CH}_3 - \text{CH} \xrightarrow{\text{Li/\text{NH}_3}} \text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{C} = \text{C} - \text{CH}_3 \quad \text{2-Hexyne}
\]

\[
\text{Birch reduction} \quad \text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{C} = \text{C} - \text{CH}_3
\]

\[
\text{Trans-2-Hexene}
\]
21. (d) When 1, 3-dimethylcyclopentene is heated with ozone and then with zinc and acetic acid, oxidative cleavage leads to keto-aldehyde.

\[ \text{CH}_3 - \text{C} = \text{CH}_2 - \text{CH}_2 - \text{CH} = \text{C} - \text{H} \rightarrow \text{CH}_3 - \text{C} = \text{O} - \text{CH} - \text{H} \]

\[ \text{O} \quad \text{O} \]

\[ \text{CH}_3 \]

5-keto-2-methylhexanal

22. (d) Region 2 (blue flame) will be the hottest region of Bunsen flame shown in given figure

23. (d) \[ \text{C}_x\text{H}_y + \left(\frac{4x+y}{4}\right)\text{O}_2 \rightarrow x\text{CO}_2 + \frac{y}{2}\text{H}_2\text{O}(l) \]

Volume of \( \text{O}_2 \) used = \( 375 \times \frac{20}{100} = 75 \text{ ml} \)

24. (d) From the reaction of combustion

\[ 1 \text{ ml C}_x\text{H}_y \text{ requires} = \frac{4x+y}{4} \text{ ml O}_2 \]

\[ 15 \text{ ml} = 15 \left(\frac{4x+y}{4}\right) = 75 \]

So, \( 4x + y = 20 \)

\( x = 3 \)

\( y = 8 \)

\[ \text{C}_3\text{H}_8 \]

24. (d) More stable intermediate
Section-A : JEE Advanced/ IIT-JEE

1. (a) For bcc structure, atomic radius, \( r = \frac{\sqrt{3}}{4} \) a

\[
= \frac{\sqrt{3}}{4} \times 4.3 = 1.86
\]

Since, \( r = \) half the distance between two nearest neighbouring atoms.

\( \therefore \) Shortest interionic distance = \( 2 \times 1.86 = 3.72 \)

2. (a) In a hcp structure atoms are located at the corners and at centres of two hexagons placed parallel to each other; three more atoms are placed in a parallel plane midway between these two planes. Here each atom is surrounded by 12 others and is said to have co-ordination number of 12.

3. (d) Effective number of ‘A’ atoms = \( \left( 8 \times \frac{1}{8} \right) + \left( 4 \times \frac{1}{2} \right) = 3 \)

Effective number of ‘B’ atoms = \( \left( 12 \times \frac{1}{4} \right) + 1 = 4 \)

\( \therefore \) Formula of the solid = \( A_3B_4 \)

4. (a) Effective number of atoms at corners, \( A = 8 \times \frac{1}{8} = 1 \)

Effective number of atoms at centre, \( B = \frac{1}{2} \times 6 = 3 \)

Thus, the composition will be \( AB_3 \)

5. (a) Rate of physisorption increases with decrease of temperature

\[ \frac{x}{m} = \text{amt of gas adsorbed per unit mass of adsorbent} \]

\[ t = \text{temperature} \]
6. (b) When a gas is adsorbed on the surface, the freedom of movement of its molecules becomes restricted. This causes decrease in the entropy of the gas after adsorption, i.e. $\Delta S$ becomes negative.

7. (b) In ZnS structure, sulphide ions occupy all FCC lattice points while Zn$^{2+}$ ions are present in alternate tetrahedral voids.

8. (d) Lyophilic sols are self-stabilizing because these sols are reversible and are highly hydrated in the solution.

9. (b) We know that surface acting agents (i.e. surfactants) such as soaps and detergents belong to the class of micelles. A micellar system when dissolved in water, dissociates to give ions. The anion consists of two parts. The polar groups such as (COO$^-$ or SO$_4^{2-}$) ion is water loving (i.e. hydrophilic) in nature. It is called head of the species. The hydrocarbon chain which is quite big in size is water repelling (i.e. hydrophobic) in nature. It is called tail of the species. The hydrocarbon chain aggregates into the micelle above the critical concentration.

NOTE: It may also be noted that the critical concentration for micelle formation decreases with increase in the molecular weight of the hydrocarbon chain of surfactant. Here the two anions that are formed are in case of "B" (i.e. CH$_3$ (CH$_2$)$_{11}$ OSO$_3^-$) and "C" (i.e. CH$_3$ (CH$_2$)$_6$ COO$^-$).

The molecular weight of hydrocarbon chain is more in case of "B" so it has lower value of critical concentration for micelle formation in aqueous solution.

Hence the correct answer is option (b).

10. (c) As Sb$_2$S$_3$ is a negative sol, so Al$_2$(SO$_4$)$_3$ will be the most effective coagulant due to higher positive charge on Al (Al$^{3+}$) — Hardy-Schulze rule.

11. (d) Packing efficiency = \frac{\text{Area occupied by effective circles}}{\text{Area of square}}

= \frac{2\pi^2}{L^2} \times 100 = \frac{2\pi^2}{(2\sqrt{2}r)^2} \times 100 = \frac{\pi\times 100}{4} = 78.54\%

12. (b) No. of M atoms = $\frac{1}{4} \times 4 + 1 = 1 + 1 = 2$

No. of X atoms = $\frac{1}{2} \times 6 + \frac{1}{8} \times 8 = 3 + 1 = 4$

So, formula = M$_2$X$_4$ \rightarrow MX$_2$

13. (a) The arrangement given shows octahedral void arrangement-limiting radius ratio for octahedral void is $\frac{r_{A^+}}{r_{X^-}} = 0.414$

$\frac{r_{A^+}}{r_{X^-}} = 0.414 \times r_{X^-} = 0.414 \times 250 = 103.5 \approx 104$ pm.

14. (b) The adsorption of methylene blue on activated charcoal is an example of physisorption which is exothermic, multilayer and does not have energy barrier.

D. MCQs with One or More Than One Correct

1. (a, c, d) The crystals of CsCl has body-centred cubic unit cell. Hence, each ion in this structure has coordination number of eight.

NOTE: In case of crystals of NaCl two interpenetrating face-centred cubic lattices are present, one of these is composed entirely of Na$^+$ ions and the other of Cl$^-$ ions. Each Na$^+$ ion is located half way between two Cl$^-$ ions and vice versa. A unit cell of NaCl crystal has Cl$^-$ ions at the corners as well as at the face centres and Na$^+$ ions are located in octahedral voids. On each edge of cubic unit cell, there are two Cl$^-$ ions and one Na$^+$ ions. Hence $a = 2(\frac{r_{Na^+} + r_{Cl^-}}{2}) = 2(95\text{ pm} + 181\text{ pm}) = 552\text{ pm}$.

2. (b, c) Frenkel defect is a dislocation effect, observed when the size of the cation and anion differ largely. F-center is created when an anion is lost from the lattice and vacancy is filled by trapping of an electron. Schottky defect changes the density of a crystalline solid.

3. (a, b, d) (a) $\Delta H$ is negative for adsorption

(b) Fact based

(d) Chemical bonds are stronger than vander Waal’s forces, so chemical adsorption is more exothermic.

4. (a, d)

5. (a, e) Graph (I) and (III) represent physisorption because, in physisorption, the amount of adsorption decreases with the increase of temperature and increases with the increase of pressure.

Graph (II) represent chemisorption, because in chemisorption amount of adsorption increases with the increase of temperature. Graph (IV) is showing the formation of a chemical bond, hence chemisorption.

6. (a) In ccp, O$^{2-}$ ions are 4.

Hence total negative charge = -8

Let Al$^{3+}$ ions be x, and Mg$^{2+}$ ions be y.

Total positive charge = 3x + 2y

$\Rightarrow 3x + 2y = 8$

This relation is satisfied only by x = 2 and y = 1.

Hence number of Al$^{3+}$ = 2.

and number of Mg$^{2+}$ = 1.

$\Rightarrow n = \text{fraction of octahedral holes occupied by Al}^{3+}$

$= \frac{2}{4} = \frac{1}{2}$

and $m = \text{fraction of tetrahedral holes occupied by Mg}^{2+}$

$= \frac{1}{8}$

7. (b, c, d) Reaction on metal surface

$M \rightarrow M^+ + e^-$

$O_2 + e^- \rightarrow O_2^-$

This is an example of chemisorption.
E. Subjective Problems

1. Avogadro's number = $6.023 \times 10^{23}$
   At. wt. of mercury (Hg) = 200
   \[ \therefore \text{In 1 g of Hg, the total number of atom} \]
   \[= \frac{6.023 \times 10^{23}}{200} = \frac{6.023 \times 10^{23}}{2 \times 10^2} \]
   \[= 3.0115 \times 10^{21} = 3.012 \times 10^{21} \]
   Density of Mercury (Hg) = 13.6 g/cc
   \[\therefore \text{mass of } 3.012 \times 10^{21} \text{ atoms} = 1 \text{ g} \]
   \[\therefore \text{mass of } 3.012 \times 10^{21} \text{ atoms} = \frac{1}{3.012 \times 10^{21}} \text{ g} \]
   Now volume of 1 atom of mercury (Hg)
   \[= \frac{1}{3.012 \times 10^{21} \times 13.6} \text{ c.c.} = \frac{10^{3} \times 10}{3.012 \times 10^{21} \times 136} \text{ c.c.} \]
   \[= \frac{10^{-17}}{3012 \times 136} \text{ c.c.} = \frac{10^{-17}}{409632} \text{ c.c.} = \frac{1000000 \times 10^{-23}}{409632} \text{ c.c.} \]
   \[= 2.44 \times 10^{-23} \text{ c.c.} \]
   Since each mercury atom occupies a cube of edge length equal to its diameter, therefore,
   diameter of one Hg atom = $(2.44 \times 10^{-23})^{\frac{1}{3}} \text{ cm}$
   \[= (24.4 \times 10^{-24})^{\frac{1}{3}} \text{ cm.} \]
   \[= 2.905 \times 10^{-8} \text{ cm} \approx 2.91 \text{ Å} \]

2. TIPS/Formulae:
   For bcc lattice, (radius), $r = \frac{\sqrt{3}a}{4}$
   Solution
   \[\therefore r = \frac{\sqrt{3} \times 4.29 \text{Å}}{4} = \frac{1.73 \times 4.29 \text{Å}}{4} = 1.86 \text{ Å} \]

3. For a hcp unit cell, there are 6 atoms per unit cell. If $r$ is the radius of the metal atoms, volume occupied by the metallic atoms = $6 \times \frac{4}{3} \pi r^3 = 6 \times 1.33 \times \frac{22}{7} r^3 = 25.08 \times r^3$
   Geometrically it has been shown that the base area of hcp unit cell
   \[= 6 \times \frac{\sqrt{3}}{4} \times 4r^2 \text{ and the height } = 4r \times \sqrt{2/3} \]

4. For bcc lattice, $r = \frac{\sqrt{3}a}{4} = \frac{\sqrt{3}}{4} \times 287 = 124.27 \text{ pm}$
   Now Density = $\frac{n \times \text{at.wt.}}{V \times \text{Av. No.}}$
   \[n = 2 \text{ for bcc; } a = 287 \times 10^{-10} \text{ cm} \]
   \[\therefore \text{Density} = \frac{2 \times 51.99}{(287 \times 10^{-10})^3 \times 6.023 \times 10^{23}} = 7.30 \text{ g/ml} \]

5. TIPS/Formulae: Density in fcc = $\frac{n_1 \times \text{at.wt.}}{V_1 \times \text{No.}}$
   Density in bcc = $\frac{n_2 \times \text{at.wt.}}{V_2 \times \text{Av.No.}}$
   fcc unit cell length = 3.5 Å; bcc unit cell length = 3.0 Å
   \[\therefore \text{Density in fcc} = \frac{n_1 \times \text{at.wt.}}{V_1 \times \text{Av.No.}} \]
   \[\text{Density in bcc} = \frac{n_2 \times \text{at.wt.}}{V_2 \times \text{Av.No.}} \]
   \[\frac{D_\text{fcc}}{D_\text{bcc}} = \frac{n_1}{n_2} \times \frac{V_2}{V_1} \]
   \[n_1 \text{ for fcc} = 4; \text{ Also } V_1 = a^3 = (3.5 \times 10^{-8})^3 \]
   \[n_2 \text{ for fcc} = 2; \text{ Also } V_2 = a^3 = (3.0 \times 10^{-8})^3 \]
   \[\frac{D_\text{fcc}}{D_\text{bcc}} = \frac{4 \times (3.5 \times 10^{-8})^3}{2 \times (3.5 \times 10^{-8})^3} = 1.259 \]

6. \[\text{The area of square} = 4 \times 4 = 16 \text{ cm}^2 \]
   Again to have the maximum number of spheres the packing must be hcp.
   Maximum number of spheres = $14 + 8 = 14 + 4 = 18$. 
   Area = 16 cm$^2$
   \[\therefore \text{Number of spheres per cm}^2 = \frac{18}{16} = 1.126 \]
8. Number of moles of acetic acid in 100 ml before adding charcoal = 0.05
   Number of moles of acetic acid in 100 ml after adding charcoal = 0.049
   Number of moles of acetic acid adsorbed on the surface of charcoal = 0.001
   Number of molecules of acetic acid adsorbed on the surface of charcoal = 0.001 \times 6.02 \times 10^{23} = 6.02 \times 10^{20}
   Surface area of charcoal = 3.01 \times 10^{-2} m^2 (given)
   Area occupied by single acetic acid molecule on the surface of charcoal = \frac{3.01 \times 10^2}{6.02 \times 10^{20}} = 5 \times 10^{-19} m^2
   \therefore \text{No. of sites occupied by each N}_2 \text{ molecule} = \frac{12.04 \times 10^{16}}{6.016 \times 10^{16}} = 2

9. (a) **TIPS/Formulae**: Density of \( AB = \frac{Z \times M}{N_0 \times a^3} \)
   Here, \( Z = 4 \) (for fcc), \( M = 6.023 \ Y \),
   \( a = 2 \frac{\sqrt[3]{13}}{4} \ \text{nm} = 2 \frac{\sqrt[3]{13}}{4} \times 10^{-9} \text{m} \)
   Thus,
   Density = \frac{4 \times 6.023 Y}{6.023 \times 10^{23} \times (2 \frac{\sqrt[3]{13}}{4} \times 10^{-9})^3} = 5.0 \text{ kg m}^{-3}

   (b) Since the observed density (20 kg m\(^{-3}\)) of AB is higher than the calculated (5 kg m\(^{-3}\)), the compound must have **metal excess defect**, non-stoichiometric defect.

10. **TIPS/Formulae**: For an octahedral void \( a = 2 (r + R) \)
    In fcc lattice the largest void present is octahedral void. If the radius of void sphere is \( R \) and of lattice sphere is \( r \). Then,
    \( r = \frac{\sqrt{2} \times 400}{4} = 141.12 \text{ pm} \) \ (a = 400 pm)
    Applying condition for octahedral void, \( 2 (r + R) = a \)
    \( \therefore 2R = a - 2r = 400 - 2 \times 141.12 \)
    \( \therefore \text{Diameter of greatest sphere} = 117.16 \text{ pm} \)

11. \( P_{N_2} = 0.001 \text{ atm}, T = 300 \text{ K}, V = 2.46 \text{ cm}^2 \)

    \( \therefore \text{Number of N}_2 \text{ molecules} = \frac{PV}{RT} \times N_{Av} = \frac{0.001 \times 2.46 \times 10^{-3}}{0.0821 \times 300} \times 6.023 \times 10^{23} = 6.016 \times 10^{16} \)

    Now total number of surface sites = Density \times \text{Total surface area}

    = 6.023 \times 10^{14} \times 1000 = 6.023 \times 10^{17}

    Sites occupied by \( N_2 \text{ molecules} = \frac{20}{100} \times 6.023 \times 10^{17}

    = 12.04 \times 10^{16}

12. **TIPS/Formulae**: For bcc; \( r = \frac{3}{2} a \),
    \( d = \frac{n \times M}{N_{Av} \times a^3} \) or \( n = \frac{d \times N_{Av} \times a^3}{M} \)
    \( \Rightarrow n = \frac{2 \times 6 \times 10^{23} \ (5 \times 10^{-8})^3}{75} = 2 \)
    Therefore Metal crystallizes in BCC structure and for a BCC lattice \( \sqrt{3}a = 4r \)
    \( \therefore r = \frac{\sqrt{3} \times a}{4} = \frac{\sqrt{3} \times 5}{4} = 2.165 \times 10^5 \text{ pm} \)
    So the required answer is 217 pm.

**F. Match the Following**

1. A-p.s; B-p,q; C-q; D-q.r.
   A→ p, s. Parameters of a cubic system are \( a = b = c \) and \( \alpha = \beta = \gamma = 90^\circ \)
   There are three types of lattices in cubic system
   These are simple, Face centred and body centred
   B→ p, q; The parameters of a Rhombohedral system are \( a = b = c, \alpha = \beta = \gamma = 90^\circ \)
   Cubic and Rhombohedral are two crystal systems. There are seven crystal systems in all
   C→ q; These are two crystal systems.
   D→ q, r. Hexagonal and monoclinic are two crystal systems.
   The parameters of these are
   Hexagonal; \( a = b \neq c \) and \( \alpha = \beta = 90^\circ, r = 120^\circ \)
   Monoclinic; \( a \neq b \neq c \) and \( \alpha = \gamma = 90^\circ, \beta \neq 90^\circ \)

**G. Comprehension Based Questions**

1. (b) In 1 unit cell of hcp, the number of atoms can be calculated as follows
   Number of atoms in a unit cell of hcp

   = 12 \times \frac{1}{6} + 2 \times \frac{1}{2} + 3 = 6

   i.e. the correct answer is option (b)
   [NOTE: in a hexagonal close packing (hcp) the spheres in the first and third layers are vertically aligned. (See figure below)]
2. (a) The volume of hcp unit cell is given by the formula:-

\[
\text{Volume of hexagon} = \frac{\sqrt{3}}{4} (2r)^2 \times \frac{2}{\sqrt{3}}
\]

\[
= 2\sqrt{2} r^3
\]

i.e. the correct answer is option (a)

3. (d) In a hcp unit cell the space occupied is 74%, as calculated below

\[
\text{Packing fraction} = \frac{\text{Volume of the atoms in a unit cell}}{\text{Volume of a unit cell}}
\]

\[
= \frac{6 \times \frac{4}{3} \pi r^3}{24\sqrt{2} r^3} = \frac{\pi}{3\sqrt{2}} = \frac{22}{7} \times \frac{1}{3\sqrt{2}}
\]

\[
= 0.74 \text{ or } 74 \%
\]

\[
\therefore \text{Empty space is HCP unit cell = (100-74)% = 26%}
\]

H. Assertion & Reason Type Questions

1. (a) Schottky defect is defined as a vacancy developed for anion and cation site, so cation and anion vacancy will be same in number. Therefore an ionic solid MX with Schottky defects will still have the same number of anions and cations.

2. (b) Statement-1 is correct because the surfactant molecules aggregate to form micelles only at or above the critical micellar concentration (CMC). Although statement-2 is also correct, i.e., the conductivity of the solution having surfactant molecules decreases sharply at CMC. However, statement-2 is not the explanation for statement-1. The explanation is that "each micelle contains at least 100 molecules" and thus, with the formation of micelles, the number of ions in solution decreases and mobility of the bulkier micelle particles decreases. This finally leads to decrease in conductivity of the solution.

Section-B

1. (b) It is zero order reaction

[NOTE: Adsorption of gas on metal surface is of zero order]

2. (d) In bcc - points are at corners and one in the centre of the unit cell.

Number of atoms per unit cell = \(8 \times \frac{1}{8} + 1 = 2\).

In fcc - points are at the corners and also centre of the six faces of each cell.

Number of atoms per unit cell = \(8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4\).

3. (d) Since in NaCl type of structure 4 formula units form a cell. Number of formulas in cube shaped crystals

\[
\frac{1.0}{58.5} \times 6.02 \times 10^{23}
\]

No. of unit cells present in a cubic crystal = \(P \times a^3 \times N_A \)

\[
M \times Z
\]

\[
P = \frac{1.0 \times 6.02 \times 10^{23}}{58.5 \times 4} = 2.57 \times 10^{23} \text{ unit cells.}
\]

4. (a) As adsorption is an exothermic process.

\[
\therefore \text{Rise in temperature will decrease adsorption (according to Le-chatelier principle).}
\]

5. (b) When equal number of cations and anions are missing from their regular lattice positions, we have schottky defect. This type of defects are more common in ionic compounds with high co-ordination number and where the size of positive and negative ions are almost equal e.g. NaCl KCl etc.

6. (d) Enzymes are very specific biological catalysts possessing well - defined active sites

7. (b) Number of A ions in the unit cell = \(\frac{1}{8} \times 8 = 1\)

Number of B ions in the unit cell = \(\frac{1}{2} \times 6 = 3\)

Hence empirical formula of the compound = \(AB_4\)

8. (a) Particle size of colloidal particle = 1μm to 100 μm

(suppose 10 μm)

\[
V_c = \frac{4}{3} \pi r^3 = \frac{4}{3} \pi (10)^3
\]

Particle size of true solution particle = 1μm

\[
V_s = \frac{4}{3} \pi l^3 \quad \text{hence now} \quad \frac{V_c}{V_s} = 10^3
\]
9. (b) When oppositely charged sols are mixed their charges are neutralised. Both sols may be partially or completely precipitated.

10. (b) The face centered cubic unit cell contains 4 atom

\[ \text{Total volume of atoms} = 4 \times \frac{4}{3} \pi r^3 = \frac{16}{3} \pi r^3 \]

11. (a) According to Langmuir's Model of adsorption of a gas on a solid surface the mass of gas adsorbed \( x \) per gram of the adsorbent \( m \) is directly proportional to the pressure of the gas \( p \) at constant temperature i.e.

\[ \frac{x}{m} \propto p \]

12. (a) From the given data, we have

Number of Y atoms in a unit cell = 4

Number of X atoms in a unit cell = \( 8 \times \frac{2}{3} = \frac{16}{3} \)

From the above we get the formula of the compound as \( X_{16/3}Y_4 \) or \( X_4Y_3 \)

13. (c) For a protective colloid lesser the value of gold number better is the protective power.

Thus the correct order of protective power of A, B, C and D is

\[ (A) < (C) < (B) < (D) \]

Gold number 0.50 0.10 0.01 0.005

Hence (c) is the correct answer

14. (c) Adsorption is an exothermic process, hence \( \Delta H \) will always be negative

15. (a) For fcc unit cell, \( 4r = \sqrt{2} \ a \); \( r = \frac{\sqrt{2} \times 361}{4} = 127 \) pm

16. (d) For an Fcc crystal

\[ r_{\text{cation}} + r_{\text{anion}} = \frac{\text{edge length}}{2} \]

\[ 110 + r_{\text{anion}} = \frac{508}{2} \]

\[ r_{\text{anion}} = 254 - 110 = 144 \text{ pm} \]

17. (b) Packing fraction is defined as the ratio of the volume of the unit cell that is occupied by the spheres to the volume of the unit cell.

P.F. for ccpp and bcc are 0.74 and 0.68 respectively. So, the free space in ccpp and bcc are 26% & 32% respectively.

18. (d) No. of atoms in the corners (A) = \( 8 \times \frac{1}{8} = 1 \)

No. of atoms at face centres (B) = \( 5 \times \frac{1}{2} = 2.5 \)

\[ \therefore \text{Formula is } AB_{2.5} \text{ or } A_2B_5 \]

19. (d) For BCC structure \( \sqrt{3} a = 4r \)

\[ r = \frac{3}{4} \ a = \frac{3}{4} \times 351 = 152 \text{ pm} \]

20. (d) The Freundlich adsorption isotherm is mathematically represented as

\[ \frac{x}{m} = kP^{1/n} \]

at high pressure \( 1/n = 0 \). Hence, \( x/m \propto P^0 \)

at low pressure \( 1/n = 1 \). Hence, \( x/m \propto P^1 \)

21. (b) Among the given crystals only silicon is as a covalent solid.

22. (b) According to Hardly Schulze rule, greater the charge on cation, greater is its coagulating power for negatively charged solution. Hence the correct order of coagulating power: \( \text{Na}^+ < \text{Ba}^{2+} < \text{Al}^{3+} \)

23. (c) Relation between radius of cation, anion and edge length of the cube

\[ 2r_{\text{Cs}^+} + 2r_{\text{Cl}^-} = \sqrt{3}a \]

\[ r_{\text{Cs}^+} + r_{\text{Cl}^-} = \frac{\sqrt{3}a}{2} \]

24. (c) In bcc the atoms touch along body diagonal

\[ 2r + 2r = \sqrt{3}a \]

\[ r = \frac{\sqrt{3}a}{4} = \frac{\sqrt{3} \times 4.29}{4} = 1.857 \text{Å} \]

25. (c) Let the weight of acetic acid initially be \( w_1 \) in 50 ml of 0.060 N solution.

Let the N = \( \frac{w_1 \times 1000}{M \text{ wt.} \times 50} \) (Normality = 0.06 N)

\[ 0.06 = \frac{w_1 \times 1000}{60 \times 50} \]

\[ \Rightarrow w_1 = \frac{0.06 \times 60 \times 50}{1000} = 0.18 \text{ g} = 180 \text{ mg} \]

After an hour, the strength of acetic acid is 0.042 N so, let the weight of acetic acid be \( w_2 \)

\[ \frac{N = \frac{w_2 \times 1000}{60 \times 50} ; 0.042 = \frac{w_2 \times 1000}{3000} \]

\[ \Rightarrow w_2 = 0.126 \text{ g} = 126 \text{ mg} \]

So amount of acetic acid adsorbed per 3g = 180 - 126 mg = 54 mg

Amount of acetic acid adsorbed per g

\[ = \frac{54}{3} = 18 \text{ mg} \]

26. (a) According to Freundlich adsorption isotherm

\[ \log \frac{x}{m} = \log K + \frac{1}{n} \log P \]

Thus if a graph is plotted between \( \log (x/m) \) and \( \log P \), a straight line will be obtained.

The slope of the line is equal to \( 1/n \) and the intercept on \( \log x/m \) axis will correspond to \( \log K \).
### Section-A : JEE Advanced/ IIT-JEE

<table>
<thead>
<tr>
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<th>A. Fill in the Blanks</th>
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<tbody>
<tr>
<td>1.</td>
<td>$K_f$; Depression in freezing point, $\Delta T_f = K_f \cdot m$, where $K_f$ is the molar depression constant or cryoscopic constant and $m$ is the molality of the solution given by moles of solute per 1000 g of the solvent.</td>
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<th>C. MCQs with One Correct Answer</th>
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<tbody>
<tr>
<td>1.</td>
<td>(c) Lower the B. pt., higher will be the V.P. The V.P. of the mixture is greater than either of the two liquids. [NOTE : : In case of positive deviation from Roul't's law the partial vapour pressure of each liquid and total vapour pressure of solution will be greater as compared to initial solution]</td>
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<td>2.</td>
<td>$\frac{p^0 - p}{p^0} = \frac{w}{m + \frac{W}{M}} = \text{mole fraction of solute} = x_B$ [Mathematical statement of Raoul't's law]</td>
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<td>3.</td>
<td>(a) Added HgI$_2$ forms a complex with KI in the solution as follows $2\text{KI} + \text{HgI}_2 \rightarrow \text{K}_2[\text{HgI}_4]$ As a result, number of particles decreases and so $\Delta T_f$ increases. [NOTE : : Depression in freezing point is a colligative property]</td>
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<td>4.</td>
<td>(a) NOTE : The salt producing highest number of ions will have lowest freezing point. $\text{K}_2\text{SO}_4 \rightarrow 2\text{K}^+ + 2\text{SO}_4^{2-}$; $\text{K}_2\text{SO}_4$ gives highest number of particles $(2 + 1 = 3)$. Glucose, being non-electrolyte gives minimum no. of particles and hence minimum $\Delta T_f$ or maximum F. pt</td>
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<td>5.</td>
<td>(d) TIPS/Formule : The salt that ionises to least extent will have highest freezing point. [i.e., minimum $\Delta T_f$] Glucose, being non-electrolyte, gives minimum no. of particles and hence minimum $\Delta T_f$ or maximum F. pt</td>
</tr>
</tbody>
</table>
6. (a) Depression in freezing point, \( \Delta T_f = i \times K_f \times m \)

Van't Hoff factor, \( i = \frac{1 - \alpha + n\alpha}{1} \), where \( n \) = no. of ions produced by complete dissociation of 1 mole of HX.

\[ \text{HX} \rightleftharpoons \text{H}^+ + \text{X}^- \Rightarrow n = 2 \]

\[ i = \frac{1 - 0.2 + 2 \times 0.2}{1} = 1.2 \]

[For 20% ionisation, \( \alpha = \frac{20}{100} = 0.2 \)]

\[ \therefore \Delta T_f = 1.2 \times 1.86 \times 0.2 = 0.45 \] \[ \therefore m = 0.2 \]

Hence freezing point of solution is \( 0 - 0.45 = -0.45 \) F.P. of water = 0.0 C

7. (b) Benzoic acid exists as dimer in benzene.

\[
\begin{array}{c}
\text{C} \quad \text{O} \quad \text{H} \quad \text{O} \\
\text{O} \quad \text{H} \quad \text{O}
\end{array}
\]

[Normal molecular mass = 122 amu
 observed molecular mass = 244 amu, in case of complete association]

\[ \alpha = \frac{20}{100} = 0.2 \]

\[ \alpha = \frac{20}{100} = 0.2 \]

\[ \alpha = \frac{20}{100} = 0.2 \]

8. (a) NOTE: At the freezing point liquid and solid remain in equilibrium. If a solution of a non-volatile solute is cooled to a temperature below the freezing point of solution, some of liquid solvent will separate as a solid solvent and thus the concentration of solution will increase.

9. (a) TIPS/Formulae:

(i) \( i = \frac{\text{No. of particles after ionisation}}{\text{No. of particles before ionisation}} \)

(ii) \( \Delta T_b = i \times K_b \times m \)

CuCl\(_2\) \( \rightleftharpoons \) Cu\(^{2+}\) + 2Cl\(^-\)

\[ i = \frac{1 + 2\alpha}{1} \]

\[ i = 1 + 2\alpha \]

Assuming 100% ionization \( \therefore \alpha = 0.2 \)

\[ \Delta T_b = 3 \times 0.52 \times 0.1 = 0.156 \approx 0.16 \]

[\( m = \frac{13.44}{134.4} = 0.1 \)]

10. (a) Molecular weight of naphthoic acid

\( \text{C}_{11}\text{H}_{10}\text{O}_2 = 172 \text{g mol}^{-1} \)

The theoretical value of depression in freezing point

\[ \gamma = K_f \times \text{molality} = 1.72 \times \frac{20 \times 1000}{172 \times 50} = 4K \]

Van't Hoff factor,

\[ i = \frac{\text{Observed value of colligative property}}{\text{Theoretical value of colligative property}} \]

\[ i = \frac{2}{4} = 0.5 \]

11. (a) \( \text{P}_N_2 = \kappa H X N_2 \); \( 0.8 \times 5 = 1 \times 10^5 \times X N_2 \)

\[ \therefore \chi N_2 = 4 \times 10^{-5} \]; Solubility in 10 moles = \( 4 \times 10^{-4} \)

12. (c) Number of moles of urea = \( \frac{120}{60} = 2 \)

Total mass of solution = 1000 + 120 = 1120 g

Total volume of solution (in L) = \( \frac{\text{Mass}}{\text{Density}} \)

\[ = \frac{1120}{1.15 \times 10^3} = \frac{115}{112} \text{L} \]

Molarity of the solution = \( \frac{\text{Number of moles}}{\text{Volume in L}} \)

\[ = \frac{2 \times 115}{112} = 2.05 \text{ mol L}^{-1} \]

13. (a) \( \Delta T_f = i \times K_f \times m \)

Where \( m = \text{Molarity of the solution} \)

\( \text{(i.e. number of moles of solute per 1000 g of the solvent)} \)

Here \( m = \frac{0.1}{329} \times 100 \)

\[ \text{Thus} \Delta T_f = 4 \times 1.86 \times \frac{0.1 \times 100}{329} = 2.3 \times 10^{-2} \]

Thus \( T_f = 0 - 2.3 \times 10^{-2} = -2.3 \times 10^{-2} \text{°C} \)

14. (a) From Raoult's law relation,

\[ \frac{p^p - p}{p^p} = \frac{\text{No. of moles of solute}}{\text{No. of moles of solvent} + \text{No. of moles of solute}} \]

When the concentration of solute is much lower than the concentration of solvent,

\[ \frac{p^p - p}{p^p} = \frac{\text{No. of moles of solute}}{\text{No. of moles of solvent}} \]

\[ \frac{760 - p}{760} = \frac{2.5/m}{100/18} \]

\[ m = \frac{2}{0.76} \]

...(i)

From elevation in boiling point, \( \Delta T_b = K_b \times m \)

\[ 2 = 0.76 \times m \]

\[ m = \frac{2}{0.76} \]

...(ii)

From (i) and (ii), \( p = 724 \text{ mm} \)

D. MCQs with One or More Than One Correct

1. (a, d) The freezing point of a solvent depresses as a non-volatile solute is added to a solvent. According to Raoult's law, when a non-volatile solute is added to a solvent the vapour pressure of the solvent decreases. At the freezing point it will be only the solvent molecules which will solidify.

2. (b, c, d) For ideal solution, \( \Delta S_{\text{system}} > 0 \)

\( \Delta S_{\text{surrounding}} = 0; \quad \Delta H_{\text{mixing}} = 0 \)
3. \( (a, b) \)
   (A) H-bonding of methanol breaks when \( \text{CCl}_4 \) is added so bonds become weaker, resulting positive deviation.
   (B) Mixing of polar and non-polar liquids will produce a solution of weaker interaction, resulting positive deviation.
   (C) Ideal solution
   (D) \(-ve\) deviation because stronger H-bond is formed.

**E. Subjective Problems**

1. **TIPS/Formulae**
   (i) \( \text{Molarity} = \frac{\text{Moles of solute}}{\text{Volume of solution in L}} \)
   (ii) \( N_1 V_1 = N_2 V_2 \)
   A 13% solution (by weight) contains 13g of solute (i.e. \( \text{H}_2\text{SO}_4 \)) per 100 gm of solution
   \[
   \text{Moles of solute} = \frac{\text{Mass of } \text{H}_2\text{SO}_4}{\text{M. wt. of } \text{H}_2\text{SO}_4} = \frac{13}{98} = 0.1326
   \]
   Volume of solution in L
   \[
   = \frac{\text{Mass of solution}}{\text{density of solution} \times 1000} = \frac{100}{1.02 \times 1000} = 0.0980 \text{ Litr}
   \]
   \( \therefore \) Molarity of solution = \( \frac{0.1326}{0.0980} = 1.35 \text{ M} \)

   Again, \( \text{Molality} = \frac{\text{Moles of solute}}{\text{Mass of solvent in kg}} \)
   Mass of solute in 100 ml of solution = 13 g [13% solution]
   Mass of solvent = Mass of solution – Mass of solvent
   = 100 – 13 = 87 g
   \( \therefore \) Molality = \( \frac{13/98}{87/1000} = 1.57 \text{ m} \)

   Normality = Molarity \times \frac{\text{Eq. wt. of solute}}{\text{Mol. wt. of solute}} \quad \text{or} \quad 1.35 \times \frac{98}{49} = 2.70 \text{ N}

2. \( M \) = \( \frac{86/98}{100/1.787} \times 1000 = \frac{0.8775}{55.5} \times 1000 = 15.81 \text{ M} \)
   \( M_1 V_1 = M_2 V_2 \)
   \( M_1 = 15.81, V_1 = ? \)
   \( M_2 = 0.2, V_2 = 1 \text{ L} = 1000 \text{ ml} \)
   \( 15.81 \times V_1 = 0.2 \times 1000 \)
   \( \therefore V_1 = \frac{0.2 \times 1000}{15.81} = 12.65 \text{ ml} \)
   \( \therefore \) Amount of acid to be used to make 1 L of 0.2 M \( \text{H}_2\text{SO}_4 \)
   = 12.65.

3. \( N_1 = 1, V_1 = ?, N_2 = 26.7, V_2 = 0.4 \)
   \( N_1 V_1 = N_2 V_2 \)
   \( 1 \times V_1 = 26.7 \times 0.4 \)
   \( V_1 = \frac{26.7 \times 0.4}{1} = 10.68 \)

4. **TIPS/Formulae**
   \( \frac{P^0 - P}{P^0} = \frac{n}{N} \) [Roult’s Equation]
   Let the molality of the solution = \( m \)
   Now the solution contains ‘\( m \)’ moles of solute per 1000 gm of benzene
   Vapour pressure of benzene, \( P^0 = 639.7 \text{ mm} \)
   Vapour pressure of solution, \( P = 631.9 \text{ mm} \)
   \( \text{Moles of benzene (Mol. wt. 78), } N = \frac{1000}{78} \)
   \( \text{Moles of solute, } n = ? \)
   Substitute these values in the Raoult’s equation
   \( \frac{P^0 - P}{P^0} = \frac{n}{N} \quad \text{or} \quad \frac{639.7 - 631.9}{639.7} = \frac{n}{1000} \)
   \( \therefore n = \frac{639.7}{78} \times 78 = 0.156 \)

5. The chemical equation for the combustion of organic compound \( \text{C}_2\text{H}_2\text{O}_5 \) can be represented as:
   \( \text{C}_2\text{H}_2\text{O}_5 + 2x\text{O}_2 = x\text{ CO}_2 + y\text{ H}_2\text{O} + x\text{ O}_2 \)
   The gases obtained after cooling = \( x + x = 2x \)

   \( \therefore 2x = 2.24 \text{ litres} \) \( \therefore \text{H}_2\text{O} \text{ is in liquid state} \)
   \( \therefore \frac{2.24}{2} = 1.12 \text{ litres} \)

   Number of moles of \( \text{CO}_2 = \frac{1.12 \text{ litres}}{22.4 \text{ litres mole}} \)

   \( = \frac{1}{20} \text{ mole = 0.05 mole} \)
The empirical formula of the organic compound is C(H$_2$O)$_n$ ...(I)

The mole fraction of the solute (A) = relative decrease in vapour pressure of the solvent (B)

\[ \frac{p^o - p}{p^o} = \frac{\frac{W_A}{M_A}}{\frac{W_A}{M_A} + \frac{W_B}{M_B}} \]

or

\[ \frac{0.104}{17.5} = \frac{\frac{50}{M_A}}{\frac{50}{M_A} + \frac{100}{18}} \]

[M$_A$ = mol wt. g A]

or

\[ \frac{0.104}{17.5} \approx \frac{50}{M_A \left( \frac{50 \times 18 + 1000M_A}{18M_A} \right)} \]

or

\[ \frac{104}{17500} = \frac{50 \times 18}{900 + 1000M_A} \quad \text{or} \quad M_A = 150.6 \]

Molecular wt. of the organic compound (CH$_2$O)$_n$ = 150

Molecular wt. of CH$_2$O = 32 + 2 + 16 = 30

\[ \therefore 30 \times n = 150 \quad \text{[} \therefore (\text{CH}_2\text{O})_n = \text{mol. formula]} \]

or

\[ n = \frac{150}{30} = 5 \]

\[ \therefore \text{Molecular formula of the given organic compound is (CH}_2\text{O)}_5 \text{ or C}_5\text{H}_{10}\text{O}_5 \]

6. If they form an ideal solution which obeys Raoults’ Law and for which
\[ \Delta H_{\text{mixing}} = 0 \quad \text{and} \quad \Delta V_{\text{mixing}} = 0 \]

Thus we can separate two volatile and miscible liquids by fractional distillation if, they should not form azeotropic solutions.

7. TIPS/Formulae:
\[ P_{\text{total}} = p_1 + p_2 \]

Molecular weight of CH$_3$OH = 12 + 3 + 16 + 1 = 32

Molecular weight of C$_2$H$_5$OH = 24 + 5 + 16 + 1 = 46

According to Raoult’s law

\[ p_{\text{total}} = p_1 + p_2 \]

where \( p_{\text{total}} \) = Total vapour pressure of the solution

\( p_1 = \) Partial vapour pressure of one component

\( p_2 = \) Partial vapour pressure of other component

Again, \( p_1 = \) Vapour pressure (\( p_1^o \)) \times mole fraction

Similarly, \( p_2 = \) Vapour pressure (\( p_2^o \)) \times mole fraction

Mole fraction of CH$_3$OH = \[ \frac{\frac{40}{60}}{\frac{40}{60} + \frac{46}{60}} = 0.49 \]

Mole fraction of ethanol = \[ \frac{\frac{46}{60}}{\frac{46}{60} + \frac{40}{32}} = 0.51 \]

\[ \text{NOTE THIS STEP: } \text{Thus now let us first calculate the partial vapour pressures, i.e.,} \ p_1 \ \text{and} \ p_2 \ \text{of the two component.} \]

Partial vapour pressure of CH$_3$OH (\( p_1^o \)) = 88.7 \times 0.49 = 43.48 mm

Partial vapour pressure of C$_2$H$_5$OH (\( p_2^o \)) = 44.5 \times 0.51 = 22.69 mm

\[ \therefore \text{Total vapour pressure of the solution} \]

\[ = 43.48 + 22.69 \text{ mm} = 66.17 \text{ mm} \]

Mole fraction of CH$_3$OH in vapour = \[ \frac{43.48}{66.17} = 0.65 \]

8. TIPS/Formulae:

\[ \text{Molarity, M} = \frac{\text{moles of solute}}{\text{kg of solvent}} \]

Mole fraction, \( x_A = \frac{n_A}{n_A + n_B} \), \( x_B = \frac{n_B}{n_A + n_B} \)

\( p_1 = x_1 p_1^o \)

\( \therefore x_1 = \frac{p_1}{p_1^o} = \frac{750}{760} = 0.9868 \)

\( x_2 \text{ (solute)} = 1 - 0.9868 = 0.0132 \)

Molarity, \( m = \frac{n_B}{x_1M_1} \times 1000 \)

\[ = \frac{0.0132 \times 1000}{0.9868 \times 18} \]

\[ = 0.7503 \text{ mol kg}^{-1} \]

9. TIPS/Formulae:

According to Raoult’s law,

\[ \frac{p^o - p}{p^o} = \frac{w/m}{w/m + W/M} \]

Here, \( p^o = 640 \text{ mm} \)

\( w = 2.175 \text{ g} \)

\( W = 39.0 \)

\( M = \) ?

\( M = 78 \)

Substituting the various values in the above equation for Raoult’s law:

\[ \frac{640 - 600}{640} = \frac{2.175}{m + 39/78} \]

\[ \frac{1}{16} = \frac{2.175}{2.175 + 0.5m} \]

\[ \Rightarrow m = 65.25 \]

10. TIPS/Formulae:

First find moles of Ca(NO$_3$)$_2$ and water.

Then use the expression \[ \frac{p^o - p}{p^o} = \frac{n}{n + N} \]

to find vapour pressure of solution.

Let initially 1 mole of Ca(NO$_3$)$_2$ is taken

Degree of dissociation of Ca(NO$_3$)$_2$ = \[ \frac{70}{100} = 0.7 \]

Ionisation of Ca(NO$_3$)$_2$ can be represented as

\[ \text{Ca(NO}_3\text{)}_2 \rightleftharpoons \text{Ca}^{2+} + 2\text{NO}_3^- \]

At start \[ \begin{array}{c|c|c}
1 & 0 & 0 \\
\hline
0 & 0.7 & 2 \times 0.7 \\
\end{array} \]

\[ \therefore \text{Total number of moles in the solution at equilibrium} \]

\[ = (1 - 0.7) + 0.7 + 2 \times 0.7 = 2.4 \]
No. of moles when the solution contains 1 gm of calcium nitrate instead of 1 mole of the salt

\[ \text{No. of moles} = \frac{2.4}{164} \]  
(164 is the mol. wt. of Cal. nitrate)

\[ \therefore \text{No. of moles of the solute in the solution containing 7 g of salt} = \frac{2.4}{164} \times 7 = 0.102 \]

No. of moles of water \( (N) = \frac{\text{Wt. of water}}{\text{Mol. wt. of water}} = \frac{100}{18} = 5.55 \)

Applying Raoul’s law,

\[ \frac{p^0 - p}{p^0} = \frac{n}{n + N} \]

\[ \frac{760 - p}{760} = 0.102 \quad \Rightarrow \quad \frac{760 - p}{760} = 0.0180 \]

\[ \Rightarrow p = 760 - (760 \times 0.0180) = 746.3 \text{ mm Hg} \]

11. **TIPS/Formulae**:

Given Wt. of benzene (solvent),

\[ W = \text{Volume} \times \text{density} = 50 \times 0.879 = 43.95 \text{ g} \]

Wt. of compound (solute), \( w = 0.643 \text{ g} \)

Mol. wt. of benzene, \( M = 78 \); Mol. wt. of solute, \( m = ? \)

Depression in freezing point, \( \Delta T_f = 5.51 - 5.03 = 0.48 \)

Molal freezing constant, \( K_f = 5.12 \)

Now we know that,

\[ m = \frac{1000 \times K_f \times w}{W \times \Delta T_f} = \frac{1000 \times 5.12 \times 0.643}{43.95 \times 0.48} = 156.056 \]

12. **TIPS/Formulae**:

\[ \frac{p^0 - p}{p^0} = \frac{w}{m + W} \]

Here, \( w \) and \( m \) are wt. and molecular wt. of solute, \( W \) and \( M \) are wt. and molecular weight of solvent

\[ p = \text{Pressure of solution}; \quad p^0 = \text{Normal vapour pressure} \]

Let the initial (normal) pressure \( (p^0) = p \)

\[ \therefore \text{Pressure of solution} = \frac{75}{100} \times p = \frac{3}{4} p \]

\[ m = 60, \quad M = 18, \quad W = 100 \text{ gm} \]

\[ \frac{p - \frac{3}{4}p}{p} = \frac{w/60}{100} \quad \Rightarrow \quad \frac{1}{4} = \frac{w}{60} \quad \Rightarrow \quad \frac{w}{60} + 5.55 \]

\[ 4w/60 = 5.55 \quad \Rightarrow \quad \frac{3w}{60} = \frac{w}{20} = 5.55 \text{ or } w = 111 \text{ g} \]

Molality \( = \frac{\text{No. of moles of solute}}{\text{Wt. of solvent}} \times 1000 \)

\[ = \frac{111 \times 1000}{60 \times 100} = 18.52 \text{ m} \]

13. **TIPS/Formulae**:

(i) \( \text{Volume} = \frac{\text{No. of moles} \times \text{molar mass}}{\text{density}} \)

(ii) \( PV = nRT \quad \therefore \quad P = \frac{nRT}{V} \)

Volume of 1 mole of liq. benzene = \( \frac{78}{0.877} \)

Volume of 1 mole of toluene = \( \frac{92}{0.867} \)

In vapour phase, At \( 20^\circ \text{C}, \) for 1 mole of benzene,

\[ \text{Volume} = \frac{1 \times 78 \times 2750}{0.877} = 244583.80 \text{ mL} = 244.58 \text{ L} \]

Similarly for 1 mole of toluene,

\[ \text{volume} = \frac{1 \times 92}{0.867} \times 7720 = 819192.61 \text{ mL} = 819.19 \text{ L} \]

As we know that, \( PV = nRT \)

For benzene, \( P_B = \frac{nRT}{V} = \frac{1 \times 0.0821 \times 293}{244.58} \text{ atm} = 0.098 \text{ atm} \)

For toluene, \( P_T = \frac{nRT}{V} = \frac{1 \times 0.0825 \times 293}{819.19} \text{ atm} = 0.029 \text{ atm} \)

\[ P = P_B X_B + P_T (1 - X_B) \]

\[ \therefore \quad X_B + X_T = 1 \quad \therefore \quad X_T = 1 - X_B \]

\[ P = P_B X_B + P_T (1 - X_B) \]

Total vapour-pressure = 46 torr = \( \frac{46}{760} \)

Thus, \( 0.060 = 0.098 X_B + 0.029 (1 - X_B) \)

\[ \Rightarrow \quad 0.060 = 0.098 X_B + 0.029 - 0.029 X_B \Rightarrow 0.031 = 0.069 X_B \]

\[ \therefore \quad X_B = \frac{0.031}{0.069} = 0.45 \text{ (in liquid phase)} \]

\[ X_B + X_T = 1 \]

\[ X_T = 1 - 0.45 = 0.55 \text{ (in liquid phase)} \]

Also, \( P_B = P_B X_B + P_T X_T = P_X_B \)

So, \( 0.098 \times 0.045 = 0.060 \times X_B \)

\[ X_B = \frac{0.098 \times 0.45}{0.060} = 0.735 \text{ (in gas phase)} \]

14. **TIPS/Formulae**:

\[ \Delta T_f = K_f m \]

\[ \frac{p^0 - p}{p^0} = \frac{\text{moles of solute}}{\text{moles of solvent}} \]

Depression in freezing point, \( \Delta T_f = 0 - (-0.30) = 0.30 \)

Now we know that \( \Delta T_f = K_f m \)

\[ \therefore \quad m = \frac{\Delta T_f}{K_f} = \frac{0.30}{1.86} = 0.161 \]
According to Raoult's law

\[
\frac{p^0 - p}{p^0} = \frac{\text{No. of moles of solute}}{\text{No. of moles of solvent}}
\]

\[
\frac{23.51 - p}{23.51} = \frac{0.161}{1000/18} = 0.161 \times 18
\]

\[
\therefore \text{No. of moles of } H_2O = \frac{1000}{18}
\]

On usual calculations,

\[
\frac{23.51 - P}{23.51} = 0.0020898
\]

\[
p = 23.51 - 23.51 \times 0.0020898 = 23.51 - 0.068
\]

\[
p = 23.44 \text{ mm Hg}
\]

15. **TIPS/Formulæ**: \( \Delta T_b = k_b \times m \)

<table>
<thead>
<tr>
<th>Element</th>
<th>%</th>
<th>Relative no. of atoms</th>
<th>Simplest ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>42.86</td>
<td>\frac{42.86}{12} = 3.57</td>
<td>\frac{3.57}{1.19} = 3</td>
</tr>
<tr>
<td>H</td>
<td>2.40</td>
<td>\frac{2.40}{1} = 2.40</td>
<td>\frac{2.40}{1.19} = 2</td>
</tr>
<tr>
<td>N</td>
<td>16.67</td>
<td>\frac{16.67}{14} = 1.19</td>
<td>\frac{1.19}{1.19} = 1</td>
</tr>
<tr>
<td>O</td>
<td>38.07</td>
<td>\frac{38.07}{16} = 2.38</td>
<td>\frac{2.38}{1.19} = 2</td>
</tr>
</tbody>
</table>

\[ \because \text{Empirical formula of the minor product is } C_3H_2NO_2 \]

Molar empirical formula mass of the minor product
\[ = 3 \times 12 + 2 \times 1 + 1 \times 14 + 2 \times 16 = 84 \text{ g mol}^{-2} \]

Let \( M \) be the molar mass of the minor product. For 5.5 g of the minor product dissolved in 45 g benzene, the molality \( (m) \) of the solution
\[ = \frac{5.5 \text{ g solute}}{0.045 \text{ kg solvent}} \]

Substituting this in the expression of elevation of boiling point,

\[ \Delta T_b = K_b \times m \Rightarrow 1.84 K = (2.53 K \text{ kg mol}^{-1}) \left( \frac{5.5 \text{ g solute}}{0.045 \text{ kg solvent}} \right) \]

or \( M = 168 \text{ g mol}^{-1} \)

No. of unit of empirical formula in molecular formula
\[ = \frac{168 \text{ g mol}^{-1}}{84 \text{ g F}} = 2 \]

Hence the molecular formula of the minor product is \( 2 \text{ (C}_3\text{H}_2\text{NO}_2) \), i.e., \( \text{C}_6\text{H}_4(\text{NO}_2)_2 \).

The product is **m - dinitrobenzene**.

16. **TIPS/Formulæ**:
\[ \Delta T_f = i \times K_f \times m \]

\[ \text{Weight of water} = 500 \times 0.997 = 498.5 \text{ g} \]

\( \text{No. of moles of acetic acid} \)
\[ \text{Wt. of CH}_3\text{COOH in g} \]
\[ = \frac{3 \times 10^{-3} \times 10^3}{60} = 0.05 \text{ g} \]

Since 498.5 g of water has 0.05 moles of CH₃COOH

\[ 1000 \text{ g of water has} = \frac{0.05 \times 1000}{498.5} = 0.1 \]

Therefore molality of the solution = 0.1

\[ \text{Determination of van't Hoff factor; } i \]

\[ \text{CH}_3\text{COOH} \rightarrow \text{CH}_3\text{COO}^- + \text{H}^+ \]

\[ \begin{array}{ccc}
\text{No. of moles at start} & 1 & 0 & 0 \\
\text{No. of moles at equib.} & 1 - 0.23 & 0.23 & 0.23 \\
\end{array} \]

Therefore vant Hoff factor

\[ = \frac{1 - 0.23 + 0.23 + 0.23}{1} = 1.23 \]

Now we know that
\[ \Delta T_f = i \times K_f \times m = 1.23 \times 1.86 \times 0.1 = 0.228 K \]

17. (i) **TIPS/Formulæ**:
\[ \Delta T_b = K_b \times M \]
In first case,
\[ \Delta T_b = K_b \times m = K_b \times \frac{\text{Wt. of solute}}{\text{Mol. wt. of solute}} \]

or \( 0.17 = 1.7 \times \frac{122}{M \times 100 \times 10^{-3}} \) or \( M = 122 \)

Thus the benzoic acid exists as a monomer in acetone

(ii) In second case,
\[ \Delta T_b = K_b \times \frac{\text{Wt. of solute}}{\text{Mol. wt. of solute}} \]

or \( 0.13 = 2.6 \times \frac{122}{M' \times 100 \times 10^{-3}} \) \( \Rightarrow M' = 224 \)

**NOTE**: Double the expected molecular weight of benzoic acid (244) in acetone solution indicates that benzoic acid exists as a dimer in acetone.

18. **TIPS/Formulæ**:
\[ 2\text{C}_6\text{H}_5\text{OH} \rightleftharpoons (\text{C}_6\text{H}_5\text{OH})_2 \]
Initial no. of moles
\[ \begin{array}{ccc}
1 & 0 & 0 \\
\text{No. of moles at equilibrium} & 1 - \alpha & \alpha/2 \\
\end{array} \]

Total number of moles at equilibrium
\[ = 1 - \alpha + \frac{\alpha}{2} = 1 - \frac{\alpha}{2} \]

\[ \Delta T_f = iK_f \times (\text{molality}) \]

\[ \Rightarrow 7 = 14 \times \frac{75.2}{94} \times \left( 1 - \frac{\alpha}{2} \right) \left[ \text{weight of phenol} = 75.2 \text{ g} \right] \]

\[ \therefore \alpha = 0.75 \]

So the percentage of phenol that dimerises = 75%.
G. Comprehension Based Questions

1. (d) The solution M is a mixture of ethanol and water. In it the mole fraction of ethanol is 0.9 and mole fraction of water is 0.1 (1.0 - 0.9 = 0.1). Also given are:
   - Standard freezing point of ethanol = 155.7 K.
   - Freezing point depression constant (K_f) for ethanol = 2.0 kg mol⁻¹
   - Molecular weight of ethanol (C₂H₅ OH) = 46
   - Now molality (m) of solution = \( \frac{0.1 \times 1000}{0.9 \times 46} \)

   **Using the formula**: 
   Depression in freezing point \( (\Delta T_f) = K_f \times m \),
   Substituting various values, we get
   \[ \Delta T_f = \frac{2 \times 0.1 \times 1000}{0.9 \times 46} = \frac{2000}{414} = 4.83 \text{ K.} \]
   \[ \therefore \text{Freezing point of solution } 'M' = (155.7 - 4.83) \text{ K} = 150.9 \text{ K} \]
   i.e. (d) is the correct answer.

2. (b) Given: Vapour pressure of pure ethanol (\( P_A^0 \)) = 40 mmHg
   Mole fraction (\( X_A \)) of ethanol in solution = 0.9

   **Using the formula**: Total pressure (P) = \( P_A^0 \times X_A \)
   Substituting the given values, we get
   P = 40 \times 0.9 = 36.0 \text{ mm Hg}
   i.e. (b) is the correct answer.

3. (b) Given: Standard boiling point of water = 373 K
   Boiling point elevation constant of water (\( K_b \)) = 0.52 Kg mol⁻¹
   Molecular weight of water (H₂O) = 18
   Mole fraction of water in solution = 0.1 (1.0 - 0.9 = 0.1)
   molality (m) = \( \frac{0.1 \times 1000}{0.9 \times 18} \)
   Using the relation \( \Delta T_b = K_b \times m \)
   Substituting the given values, we get
   \[ \Delta T_b = 0.52 \times \frac{0.1 \times 1000}{0.9 \times 18} = \frac{520}{9 \times 18} = 3.20 \text{ K} \]
   \[ \therefore \text{Boiling point of solution } = (373 + 3.20) \text{ K} = 376.2 \text{ K} \]
   i.e. option (b) is correct answer.

4. (1) Given \( \Delta T_f = 0.058^\circ \text{C} \)
   as we know, \( \Delta T_f = i \times K_f \times m \)
   \[ i = \frac{0.058}{1.86 \times 0.01} \]
   \[ [i = 3] \]
   Therefore the complex will be [Co(NH₃)₂Cl]Cl₂
   Hence number of chloride in co-ordination sphere is 1.

5. (9) 1 mole solution has 0.1 mole solute and 0.9 mole solvent.
   Let \( M_1 = \text{Molar mass solute} \)
   \( M_2 = \text{Molar mass solvent} \)
   
   **Molarity of stock solution of HCl**
   \[ m = \frac{0.1}{0.9 M_2} \times 1000 \]
   
   **Molarity**
   \[ M = \frac{0.1 M_1 + 0.9 M_2}{0.1 M_1 + 0.9 M_2} \times 2 \times 1000 \]
   \[ \therefore m = M \]
   \[ 0.1 \times 1000 = \frac{200}{0.1 M_1 + 0.9 M_2} \]
   \[ \Rightarrow \frac{M_1}{M_2} = 9 \]
1. \( \Delta T_b = K_b \frac{W_B}{M_B \times W_A} \times 1000 \)
\[ \Delta T_f = K_f \frac{W_B}{M_B \times W_A} \times 1000 \]
\[ \frac{\Delta T_b}{\Delta T_f} = \frac{K_b}{K_f} = \frac{0.512}{-0.186} = \frac{0.512}{0.186} = 0.0512^\circ C. \]

2. (d) In solution containing A and B component showing negative deviation A–A and B–B interactions are weaker than that of A–B interactions. For such solutions, \( \Delta H = -\text{ve} \) and \( \Delta V = -\text{ve} \)

3. (d) When A and B form an ideal solution, \( \Delta H_{\text{mix}} = 0 \)

4. (d) \( \Delta T_f = K_f \times m \times i \)
\[ \Delta T_f = 1.85 \times 0.2 \times 1.3 = 0.48^\circ C \]
\[ \therefore T_f = 0 - 0.48^\circ C = -0.48^\circ C \]
\( (HX \rightleftharpoons H^+ + X^- , i = 1.3) \)

5. (a) **NOTE:** On increasing pressure, the temperature is also greater. Thus in pressure cooker due to increase in pressure the b.p. of water increases.

6. (e) \( \therefore \Delta T_b = T_b - T_b^o \)

Where \( T_b = \text{b.p. of solution} \) \( T_b^o = \text{b.p. of solvent} \)

\( \Delta T_b = \text{b.p. of solvent} - \text{b.p. of solution} \)

**NOTE:** Elevation in boiling point is a colligative property, which depends upon the no. of particles. Thus the greater the number of particles, greater is its elevation and hence greater will be its boiling point.

\[ \begin{align*}
\text{Na}_2\text{SO}_4 & = 2\text{Na} + \text{SO}_4^{2-} \\
\text{Since Na}_2\text{SO}_4 \text{ has maximum number of particles (3) hence has maximum boiling point.}
\end{align*} \]

7. (d) Gaseous densities of ethanol and dimethyl ether would be same at same temperature and pressure. The heat of vapourisation, V.P. and b.p.s will differ due to H-bonding in ethanol.

8. (b) **NOTE:** Positive deviations are shown by such solutions in which solvent-solvent and solute-solute interactions are stronger than the solvent interactions. In such solution, the interactions among molecules becomes weaker. Therefore their escaping tendency increases which results in increase in their partial vapour pressures.

In a solutions of benzene and methanol there exists inter molecular H-bonding.
\[ \cdots \cdot \overset{\text{O}}{\cdot} \cdots \overset{\text{O}}{\cdot} \cdots \overset{\text{O}}{\cdot} \cdots \overset{\text{O}}{\cdot} \cdots \]
\[ \left| \begin{array}{c}
\text{C}_2\text{H}_5 \\
\text{C}_2\text{H}_5 \\
\text{C}_2\text{H}_5
\end{array} \right| \]

In this solution benzene molecules come between ethanol molecules which weaken intermolecular forces. This results in increase in vapour pressure.

9. (d) \( \Delta T_f = K_f \times m \times i \). Since \( K_f \) has different values for different solvents, hence even if the m is the same \( \Delta T_f \) will be different

10. (d) Given, Vapour pressure of benzene = 75 torr
Vapour pressure of benzene = 22 torr
mass of benzene in = 78 g

\[ \text{hence moles of benzene} = \frac{78}{78} = 1 \text{mole} \]

(mol wt of benzene = 78)

\[ \text{mass of toluene in solution} = 46 \text{g} \]

\[ \text{hence moles of toluene} = \frac{46}{92} = 0.5 \text{mole} \]

now partial pressure of benzene
\[ = P_b \times x_b = 75 \times \frac{1}{1 + 0.5} = 50 \text{ torr} \]

\[ = 75 \times \frac{1.5}{3} = 50 \]

11. (d) Equimolar solutions of normal solutes in the same solvent will have the same b.pts and same f. pts.

12. (d) Acetonitrile \((\text{CH}_3 - \overset{\delta}{\text{C}} \overset{\delta^-}{\text{CN}})\) and acetone
\[ \overset{\delta^+}{(\text{CH}_3)} \overset{\delta^-}{\text{C}} = \overset{\delta^+}{(\text{CH}_3)} \overset{\delta^-}{\text{O}} \]
both are polar molecules, hence dipole-dipole interaction exist between them. Between KCl and water ion-dipole interaction is found and in Benzene ethanol and Benzene–Carbon tetra chloride dispersion force is present

13. (b) Moles of glucose = \( \frac{18}{180} = 0.1 \)

Moles of water = \( \frac{178.2}{18} = 9.9 \)

Total moles = 0.1 + 9.9 = 10

\( \text{PH}_2\text{O} = \text{Mole fraction} \times \text{Total pressure} = \frac{9.9}{10} \times 760 = 752.4 \text{ Torr} \)

14. (b) \( p_A^\circ = ?, \text{Given } p_B^\circ = 200 \text{mm} , x_A = 0.6, \)
\[ x_B = 1 - 0.6 = 0.4, \text{ P} = 290 \]
\[ p = P_A + P_B = p_A^\circ x_A + p_B^\circ x_B \]
\[ \Rightarrow 290 = p_A^\circ \times 0.6 + 200 \times 0.4 \quad \therefore \quad p_A^\circ = 350 \text{ mm} \)

15. (d) Let the mass of methane and oxygen = m gm.
Mole fraction of \( \text{O}_2 \)
\[ = \frac{\text{Moles of } \text{O}_2}{\text{Moles of } \text{O}_2 + \text{Moles of } \text{CH}_4} \]
\[ = \frac{m/32}{m/32 + m/16} = \frac{3m/32}{1} = \frac{1}{3} \]
Partial pressure of \( \text{O}_2 \) = \( \text{Total pressure} \times \text{mole fraction} \)
of \( \text{O}_2 \)
\[ p_{\text{O}_2} = P \times \frac{1}{3} = \frac{1}{3} \text{ P} \]
16. (a) **TIPS/FORMULAE:**

Osmotic pressure \( (\pi) \) of isotonic solutions are equal.

For solution of unknown substance (\( \pi = CRT \))

\[
C_1 = \frac{5.25}{V}
\]

For solution of urea, \( C_2 \) (concentration) = \( \frac{1.5}{60} \)

Given, \( \pi_1 = \pi_2 \)

\( \therefore \pi = CRT \)

\( \therefore C_1RT = C_2RT \) or \( C_1 = C_2 \) or \( \frac{5.25}{V} = \frac{1.8}{60} \)

\( \therefore M = 210 \) g/mol

17. (d) At 1 atmospheric pressure the boiling point of mixture is 80°C.

At boiling point the vapour pressure of mixture, \( P_T = 1 \)

atmosphere = 760 mm Hg.

Using the relation,

\[
P_T = P_A^0x_A + P_B^0x_B,
\]

we get

\[
P_T = 520x_A + 1000(1-x_A)
\]

\( \therefore P_A^0 = 520 \text{ mm Hg} \),

\( \therefore P_B^0 = 1000 \text{ mm Hg}, x_A + x_B = 1 \}

or 760 = 520x_A + 1000 - 1000x_A or 480x_A = 240

or \( x_A = \frac{240}{480} = \frac{1}{2} \) or 50 mol. percent

i.e., The correct answer is (d).

18. (a) **NOTE:** On addition of glucose to water, vapour pressure of water will decrease. The vapour pressure of a solution of glucose in water can be calculated using the relation

\[
\frac{P_A^0 - P_s}{P_s} = \frac{\text{Moles of glucose in solution}}{\text{moles of water in solution}}
\]

or \( \frac{17.5 - P_s}{P_s} = \frac{18/180}{178.2/18} \) \( \therefore P^0 = 17.5 \)

or \( 17.5 - P_s = 0.1\times \frac{P_s}{9.9} \) or \( P_s = 17.325 \) mm Hg.

Hence (a) is correct answer.

19. (b) For this solution intermolecular interactions between \( n \)-heptane and ethanol aare weaker than \( n \)-heptane - \( n \)-heptane & ethanol-ethanol interactions hence the solution of \( n \)-heptane and ethanol is non-ideal and shows positive deviation from Raoult's law.

20. (b) \( P_{\text{total}} = P_A^0x_A + P_B^0x_B \); \( 550 = P_A^0 \times \frac{1}{4} + P_B^0 \times \frac{3}{4} \)

\( P_A^0 + 3P_B^0 = 550 \times 4 \) ... (i)

In second case

\( P_{\text{total}} = P_A^0 \times \frac{1}{5} + P_B^0 \times \frac{4}{5} \)

\( P_A^0 + 4P_B^0 = 560 \times 5 \) ...(ii)

Subtract (i) from (ii)

\( \therefore P_B^0 = 560 \times 5 - 550 \times 4 = 600 \quad \therefore P_A^0 = 400 \)

21. (b) Sodium sulphate dissociates as

\[
\text{Na}_2\text{SO}_4(s) \longrightarrow 2\text{Na}^+ + \text{SO}_4^{2-}
\]

hence van't hoff factor \( i = 3 \)

Now \( \Delta T_f = ik_f m = 3 \times 1.86 \times 0.01 = 0.0558 \) K

22. (a) \( P_{\text{total}} = P_A^0x_A + P_B^0x_B \)

\[
= P_{\text{Heptane}}^0x_{\text{Heptane}} + P_{\text{Octane}}^0x_{\text{Octane}}
\]

\[
= \frac{105\times \frac{25}{100}}{25} + \frac{45\times \frac{35}{114}}{25} = \frac{26.25 + 13.5}{72} = 72 \text{ kPa}
\]

23. (c) 5.2 molal solution means 5.2 moles of methyl alcohol in 1000 gm water or in \( \frac{1000}{18} \) mole of water.

\( \therefore \) mole fraction of methyl alcohol

\[
= \frac{\text{moles of methyl alcohol}}{\text{moles of methyl alcohol + moles of water}}
\]

\( = \frac{5.2}{5.2 + \frac{1000}{18}} = 0.086 \)

24. (a) Given \( K_f = 1.86 \text{ K kg mol}^{-1} \)

\( \Delta T_f = 0 - (-6) = 6^\circ \text{C} \)

As we know that

\( \Delta T_f = K_f \times \text{molarity} \)

\( = \frac{K_f \times 1000 \times \text{mass of solute}}{\text{molar mass of solute} \times \text{mass of solvent}} \)

Substituting given values in formula

\[
6 = \frac{1.86 \times 1000 \times w}{62 \times 4}; \quad w = 0.8 \text{ kg} = 800 \text{ gm}
\]

25. (a) \( A_xB_y \rightarrow xA^{y+} + yB^{x-} \)

\( t = 0 \quad 1 \quad 0 \quad 0 \)

\( t_{eq} = 1 - \alpha \quad x\alpha \quad y\alpha \)

Total no. of moles \( i = 1 - \alpha + x\alpha + y\alpha \)

\( i = 1 + x\alpha + y\alpha - \alpha = x + y - 1 \)

\( \therefore \alpha = \frac{x + y - 1}{(x + y - 1)} \)

26. (d) Molarity \( = \frac{\text{moles of solute}}{\text{volume of solution} \times \text{time}} \)

Mass of solution = 1000 + 120 = 1120

\[
d = \frac{M}{V}; \quad V = \frac{M}{d} = \frac{120}{1.15} \text{ mL} = \frac{120 \times 1.15 \times 1000}{60 \times 1120} = 2.05 \text{ M}
\]
27. (b) \( \Delta T_f = i \times K_f \times m \)

Given \( \Delta T_f = 2.8 \), \( K_f = 1.86 \) K kg mol\(^{-1} \)

wt. of solvent = 1 kg; Let of wt of solute = \( x \)

Mol. wt of ethylene glycol = 62

\[ 2.8 = 1 \times 1.86 \times \frac{x}{62 \times 1} \] or \( x = \frac{2.8 \times 62}{1.86} = 93 \) gm

28. (a) From Molarity equation:

\[ M_1 V_1 + M_2 V_2 = M \times V \]

\[ M = \frac{M_1 V_1 + M_2 V_2}{V} \text{ where } V = \text{total volume} \]

\[ = \frac{750 \times 0.5 + 250 \times 2}{1000} = 0.875 \text{ M} \]

29. (a) \( \pi = i C R T \)

\[ \pi_{C_2H_5OH} = 1 \times 0.500 \times R \times T = 0.5 \text{ RT} \]

\[ \pi_{Mg_3(PO_4)_2} = 5 \times 0.100 \times R \times T = 0.5 \text{ RT} \]

\[ \pi_{KBr} = 2 \times 0.250 \times R \times T = 0.5 \text{ RT} \]

\[ \pi_{Na_3PO_4} = 4 \times 0.125 \times R \times T = 0.5 \text{ RT} \]

Since the osmotic pressure of all the given solutions is equal. Hence all are isotonic solution.

30. (d) Using relation,

\[ \frac{P^o - P_s}{P_s} = \frac{w_1 M_1}{w_1 M_2} \]

where \( w_1, M_1 = \text{mass in g and mol. mass of solvent} \)

\( w_2, M_2 = \text{mass in g and mol. mass of solute} \)

Let \( M_1 = x \)

\[ P^o = 185 \text{ torr} \; ; \; P_s = 183 \text{ torr} \]

\[ \frac{185 - 183}{183} = \frac{1.2 \times 58}{100 x} \]

(Mol. mass of acetone = 58)

\[ x = 64 \]

\( \therefore \) Molar mass of substance = 64

31. (a) According to Raoul's Law

\[ \frac{P^o - P_s}{P_s} = \frac{W_B \times M_A}{M_B \times W_A} \]

Here \( P^o = \text{Vapour pressure of pure solvent} \)

\( P_s = \text{Vapour pressure of solution} \)

\( W_B = \text{Mass of solute} \)

\( W_A = \text{Mass of solvent} \)

\( M_B = \text{Molar mass of solute} \)

\( M_A = \text{Molar Mass of solvent} \)

Vapour pressure of pure water at 100\(^o\) C (by assumption = 760 torr)

By substituting values in equation (i) we get,

\[ \frac{760 - P_s}{P_s} = \frac{18 \times 18}{180 \times 178.2} \]

On solving (ii) we get

\[ P_s = 752.4 \text{ torr} \]
Electrochemistry

A. Fill in the Blanks

1. \( \Gamma \) (\( \because I_1 \) is weakest oxidising agent)

2. negative, greater; Among the various metals, since sodium has the minimum reduction potential, it is known as the strongest reducing agent. In general, the more the reduction potential, lesser is its reducing action.

3. increased;

B. True/False

1. False: When the temperature is 273, the value of the factor will come out as 0.0541 instead of 0.0591. The value 0.0591 comes out at 298 K and not at 273 K.

C. MCQs with One Correct Answer

1. (a) More negative is the value of reduction potential, higher will be the reducing property, i.e., the power to give up electrons.

2. (c) \[ \frac{W_1}{W_2} = \frac{E_1}{E_2} = \frac{Z_1 \text{ if } Z_2}{Z_2 \text{ if } Z_1} \]

Here \( E_1 \) & \( E_2 \) are equivalent weights of the ions.

3. (c) The reduction potentials (as given) of the ions are in the order:

\( \text{Ag}^+ > \text{Hg}_2^{2+} > \text{Cu}^{2+} > \text{Mg}^{2+} \)

\( \text{Mg}^{2+} (aq.) \) will not be reduced as its reduction potential is much lower than that of water (-0.83 V).

Hence the sequence of deposition of the metals will be Ag, Hg, Cu.
4. (d) Charge of one mole of electrons = 96500 C. : 1 mole gram equivalent of substance will be deposited by one mole of electrons.

5. (c) **NOTE**: Oxidation is loss of electron and in a galvanic cell it occurs at anode. Reduction is gain of electron and in a galvanic cell it occurs at cathode.

**Cell representation**:
Anode / Anodic electrolyte | Cathodic electrolyte / Cathode
---|---
Reaction at Anode: $\text{H}_2\text{O} \rightarrow 2\text{H}^+ + 2\text{e}^-$
Reaction at Cathode: $\text{AgCl} + \text{e}^- \rightarrow \text{Ag} + \text{Cl}^-$

6. (a) Water is reduced at the cathode and oxidized at the anode instead of $\text{Na}^+$ and $\text{SO}_4^{2-}$.

**Cathode**: $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$

**Anode**: $\text{H}_2\text{O} \rightarrow 2\text{H}^+ + \frac{1}{2}\text{O}_2 + 2\text{e}^-.$

7. (b) **TIPS/FORMULA:**

   (i) In a galvanic cell oxidation occurs at anode and reduction occurs at cathode.

   (ii) Oxidation occurs at electrode having higher oxidation potential and it behaves as anode and other electrode acts as cathode.

   (iii) $E_{\text{cell}} = E_{\text{C}} - E_{\text{A}}$

   (substitute reduction potential at both places).

   $\text{Fe}^{2+} + \text{Zn} \rightarrow \text{Zn}^{2+} + \text{Fe}$

   $\therefore \text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$ and $\text{Fe}^{2+} + 2\text{e}^- \rightarrow \text{Fe}$

   $\therefore \text{Zn}$ is anode and Fe is cathode.

   $E_{\text{cell}} = E_{\text{C}} - E_{\text{A}} = 0.41 - (-0.76) = 0.35 V.$

8. (a) $\text{H}_2\text{O}$ is more readily reduced at cathode than $\text{Na}^+$. It is also more readily oxidized at anode than $\text{SO}_4^{2-}$. Hence, the electrode reactions are

   $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 \uparrow + 2\text{OH}^- \ [\text{at cathode}]

   $\text{H}_2\text{O} \rightarrow \frac{1}{2}\text{O}_2 \uparrow + 2\text{H}^+ + 2\text{e}^- \ [\text{at anode}].$

9. (c) We have

<table>
<thead>
<tr>
<th>Half-cell</th>
<th>Half-cell reaction</th>
<th>$\Delta G^\circ = -nFE^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Cu}^{2+} \mid \text{Cu}$</td>
<td>$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$</td>
<td>$\Delta G^\circ = -2FE^\circ_{\text{Cu}^{2+} \mid \text{Cu}}$</td>
</tr>
<tr>
<td>$\text{Cu}^{2+} \mid \text{Cu}^+$</td>
<td>$\text{Cu}^{2+} + \text{e}^- \rightarrow \text{Cu}^+$</td>
<td>$\Delta G^\circ = -FE^\circ_{\text{Cu}^{2+} \mid \text{Cu}^+}$</td>
</tr>
<tr>
<td>$\text{Cu}^+ \mid \text{Cu}$</td>
<td>$\text{Cu}^+ + \text{e}^- \rightarrow \text{Cu}$</td>
<td>$\Delta G^\circ = -FE^\circ_{\text{Cu}^+ \mid \text{Cu}}$</td>
</tr>
</tbody>
</table>

From the half-cell reactions, it follows that

$\Delta G^\circ = \Delta G^\circ_1 - \Delta G^\circ_2$

*i.e.*, $-FE^\circ_{\text{Cu}^+ \mid \text{Cu}} = -2FE^\circ_{\text{Cu}^{2+} \mid \text{Cu}} - \left(-FE^\circ_{\text{Cu}^{2+} \mid \text{Cu}^+}\right)$

or $E^\circ_{\text{Cu}^+ \mid \text{Cu}} = 2E^\circ_{\text{Cu}^{2+} \mid \text{Cu}} - E^\circ_{\text{Cu}^{2+} \mid \text{Cu}^+}$

$= 2(0.337 V) - 0.153 V = 0.521 V$

10. (a) The given order of reduction potentials is $Z > Y > X$. A spontaneous reaction will have the following characteristics

   Z reduced and Y oxidised

   Z reduced and X oxidised

   Y reduced and X oxidised

   Hence, Y will oxidise X and not Z.

11. (b) For $\text{M}^+ + \text{X}^- \rightarrow \text{M} + \text{X}^-$, $E_{\text{cell}} = 0.44 - 0.33 = 0.11 V$ is positive, hence reaction is spontaneous.

12. (c) The salt used to make ‘salt-bridge’ must be such that the ionic mobility of cation and anion are of comparable order so that they can keep the anode and cathode half cells neutral at all times. $\text{KNO}_3$ is used because velocities of $\text{K}^+$ and $\text{NO}_3^-$ ions are nearly same

13. (b) As we go down the group 1 (i.e. from $\text{Li}^+$ to $\text{K}^+$), the ionic radius increases, degree of solvation decreases and hence effective size decreases resulting in increase in ionic mobility. Hence equivalent conductance at infinite dilution increases in the same order.

14. (a) $\text{MnO}_4^-$ will oxidise $\text{Cl}^-$ ion according to the following equation

   $2\text{MnO}_4^- + 16\text{H}^+ + 10\text{Cl}^- \rightarrow 2\text{Mn}^{2+} + 8\text{H}_2\text{O} + 5\text{Cl}_2 \uparrow$

   The cell corresponding to this reaction is as follows: $\text{Pt, Cl}_2 \ (1 \text{ atm}) \mid \text{Cl}^- \parallel \text{MnO}_4^-, \text{Mn}^{2+}, \text{H}^+ \parallel \text{Pt}$

   $E_{\text{cell}} = 1.51 - 1.40 = 0.11 \text{ V}$

   $E_{\text{cell}}$ being +ve, $\Delta G^\circ$ will be -ve and hence the above reaction is feasible. $\text{MnO}_4^-$ will not only oxidise $\text{Fe}^{2+}$ ion but also $\text{Cl}^-$ ion simultaneously. So the quantitative estimation of $\text{aq Fe(NO}_3)_2$ cannot be done by this.

15. (c) **NOTE**: In an electrolytic cell, electrons do not flow themselves. It is the migration of ions towards oppositely charged electrodes that indirectly constitutes the flow of electrons from cathode to anode through internal supply.

16. (b) **TIPS/FORMULA**:

   Use Nernst's equation,

   **Cell reaction**: $\text{Zn} + \text{Fe}^{2+} \rightarrow \text{Zn}^{2+} + \text{Fe}$

   Using Nernst equation

   $E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.0591}{n} \log \left(\frac{[\text{Zn}^{2+}]}{[\text{Fe}^{2+}]}\right)$

   $E = E^\circ - \frac{0.0591}{2} \log \frac{10^{-2}}{10^{-3}}$

   $E^\circ = 0.2905 + \frac{0.0591}{2} = 0.32$

   or $0.32 = \frac{0.0591}{2} \log K_{eq}$ or $K_{eq} = 10^{0.0295} \times 0.32$
17. (a) \[ \text{Fe(s)} \rightarrow \text{Fe}^{2+} + 2\text{e}^-; \quad E^o = 0.44 \, \text{V} \]

\[
2\text{H}^+ + 2\text{e}^- + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}(l); \quad E^o = +1.23 \, \text{V}
\]

\[
\text{Fe(s)} + 2\text{H}^+ + \frac{1}{2}\text{O}_2 \rightarrow \text{Fe}^{2+} + \text{H}_2\text{O};
\]

\[
E^o_{\text{cell}} = 0.44 + 1.23 = 1.67 \, \text{V}
\]

\[
\because \Delta G^o = -nF E^o_{\text{cell}} = -2 \times 96500 \times 1.67 = -322 \, \text{kJ}
\]

18. (b) 

Give: \( I = 10 \, \text{milliamps} \); \( \text{IF} = 96500 \, \text{C mol}^{-1} \)

\( t = ? \); \( \text{Moles of H}_2 \text{ produces} = 0.01 \, \text{mol} \)

From the law of electrolysis, we have

\[
\text{Equivalents of H}_2 \text{ produces} = \frac{1 \times t (\text{sec})}{96500}
\]

Substituting given values, we get

\[
0.01 \times 2 = \frac{10 \times 10^{-3} \, \text{amperes} \times t (\text{sec})}{96500}
\]

or \( t = \frac{0.01 \times 2 \times 96500}{10 \times 10^{-3}} \, \text{sec} = 19.3 \times 10^4 \, \text{sec} \)

i.e. (b) is the correct answer.

19. (d) \( \text{AgNO}_3(aq) + \text{KCl(aq)} \rightarrow \text{AgCl(s)} + \text{KNO}_3(aq) \)

Conductivity of the solution is almost compensated due to formation of \( \text{KNO}_3(aq) \). However, after at end point, conductivity increases more rapidly due to addition of excess \( \text{AgNO}_3 \) solution.

20. (d) Here \( n = 4 \), and \( [\text{H}^+] = 10^{-pH} = 10^{-3} \)

Applying Nernst equation

\[
E = E^o - \frac{0.059}{n} \log \left( \frac{[\text{Fe}^{2+}]^2}{[\text{H}^+]^4 \, P_{\text{O}_2}} \right)
\]

\[
= 1.67 - \frac{0.059}{4} \log \left( \frac{10^{-3}}{10^{-3}} \right)^4 \times 0.1
\]

\[
= 1.67 - \frac{0.03}{2} \log 10^7 = 1.67 - 0.105 = 1.565 \, \text{V}
\]

21. (d) At anode: \( \text{H}_2(g) \rightarrow 2\text{H}^+(aq) + 2\text{e}^- \)

At cathode: \( \text{M}^{4+} (aq) + 2\text{e}^- \rightarrow \text{M}^{2+} (aq) \)

Net cell reaction: \( \text{H}_2(g) + \text{M}^{4+} (aq) \rightarrow 2\text{H}^+(aq) + \text{M}^{2+} (aq) \)

Now, \( E^o_{\text{cell}} = \left( E^o_{\text{M}^{4+}/\text{M}^{2+}} - E^o_{\text{H}^+}/\text{H}_2 \right) - \frac{0.059}{n} \log \left( \frac{[\text{H}^+]^2 [\text{M}^{2+}]}{P_{\text{H}_2} \times [\text{M}^{4+}]} \right) \)

or, \( 0.092 = (0.151 - 0) - \frac{0.059}{2} \log \frac{[\text{M}^{2+}]}{[\text{M}^{4+}]} \)

\[
\because \frac{[\text{M}^{2+}]}{[\text{M}^{4+}]} = 10^2 \Rightarrow x = 2
\]

D. MCQs with One or More Than One Correct

1. (a) NOTE: More negative or lower is the reduction potential, more is the reducing property. Thus the reducing power of the corresponding metal will follow the reverse order, i.e. \( Y > Z > X \).

2. (a,b,d) The species having less reduction potential with respect to \( \text{NO}_3^- (E^o = +0.96 \, \text{V}) \) will be oxidised by \( \text{NO}_3^- \). These species are \( \text{V, Fe and Hg} \).

3. (a) Salt bridge is introduced to keep the solutions of two electrodes separate, so that the ions in electrodes do not mix freely with each other. Salt bridge maintains the diffusion of ions from one electrode to another.

E. Subjective Problems

1. Wt. of \( \text{Cu} \) deposited = \( Z \)

Electrochemical equivalent of \( \text{Cu} = \frac{63.5}{2} = 31.75 \)

Volume of surface = area \times thickness = \( 10 \times 10 \times 10^{-2} = 1 \, \text{cc} \)

Weight of \( \text{Cu} = \text{density} \times \text{volume} = 8.94 \times 1 = 8.94 \, \text{g} \)

According to Faraday’s laws of electrolysis

\[
31.75 \, \text{g of Cu is deposited by} = \frac{96500 \times 8.94}{31.75} = 27171.96 \, \text{coulombs}
\]

2. (a) \( 2\text{SnCl}_2 \rightarrow \text{Sn} + \text{SnCl}_4 \)

\[
2[119 \times (2 \times 35.5)] \quad 119 \quad 119 + (4 \times 35.5)
\]

\[
= 380 \quad = 261
\]

\[
\therefore \ 119 \, \text{g Sn deposits from} = 380 \, \text{g SnCl}_2
\]

\[
\therefore \ 0.119 \, \text{g Sn deposits from} = \frac{380 \times 0.119}{119} = 0.380 \, \text{g SnCl}_2
\]

\[
380 \, \text{g SnCl}_2 \, \text{gives} = 261 \, \text{g SnCl}_4
\]

\[
\therefore \ 0.380 \, \text{SnCl}_2 \, \text{gives} = \frac{261 \times 0.380}{380} = 0.261 \, \text{g SnCl}_4
\]

\[
\therefore \ \text{Wt of SnCl}_2 \, \text{left after decomposition} = 19.00 - 0.380 = 18.620 \, \text{g}
\]

Ratio \( \text{SnCl}_2 : \text{SnCl}_4 \)

\[
= 18.620 : 0.261 \Rightarrow 71.34 : 1
\]

(b) \( \text{NaCl} \rightarrow \text{Na}^+ + \text{Cl}^- \)

At Cathode; \( \text{Na}^+ + e^- \rightarrow \text{Na} \)
2Na + H₂O → 2NaOH + H₂

At anode: Cl⁻ → Cl + e⁻

Cl + Cl → Cl₂

2OH⁻ + Cl₂ → Cl⁻ + OCl⁻ + H₂O

OCl⁻ + 2HOCI → ClO₃⁻ + 2Cl⁻ + 2H⁺

Na⁺ + ClO₃⁻ → NaClO₃

Sod. Chlorate

On prolonged electrolysis

ClO₃⁻ + Cl⁻ → Cl⁻ + ClO₄⁻

Na⁺ + ClO₄⁻ → NaClO₄

Sod. perchlorate

(c) Charge on N³⁻ = 3

No. of ions in 14 g of N³⁻ = 6.02 × 10²³

No. of ions in 1 g of N³⁻ = \( \frac{6.02 \times 10^{23}}{14} \)

No. of electronic charges on 1 g N³⁻ = \( \frac{6.02 \times 10^{23} \times 3}{14} \)

Charge on 1 gm of N³⁻ = \( 2.06 \times 10^4 \) Coulombs

(∵ Charge on one electron is 1.6 × 10⁻¹⁹ Coulombs)

3. (i) 2KNO₃ + 8FeSO₄ + 4H₂SO₄ (conc)

\[ \rightarrow 2(FeSO₄ NO) + K₂SO₄ + 3Fe₂(SO₄)₃ + 4H₂O \]

(ii) 3H₂S + 2K₂Cr₂O₇ + 5H₂SO₄

\[ \rightarrow 2K₂SO₄ + Cr₂(SO₄)₃ + 3S + 8H₂O \]

(iii) 2K₂Cr₂O₇ (conc) \( \xrightarrow{\Delta} \) I₂ + SO₄ + K₂SO₄ + 2H₂O

(iv) Mg₃(NO₂) + 6H₂O → 3Mg(OH)₂ + 2NH₃

(v) Al is covered by layer of Al₂O₃

4. (i) The two half cell reactions can be written as below:

**Oxidation half reaction:** Zn → Zn²⁺ + 2e⁻

**Reduction half reaction:** Cu²⁺ + 2e⁻ → Cu

**Thus the cell reaction will be:** Zn + Cu²⁺ → Zn²⁺ + Cu

(ii) EMF of cell, \( E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} \)

\( E^\circ_{cell} = 0.350 - (-0.763) \)

\( = 0.350 + 0.763 \) volts = 1.113 volts

(iii) Since emf of the cell is positive, the reaction as written is spontaneous.

5. Gold deposited in the first cell = 9.85 g

At. wt. of Gold = 197, Oxidation number of gold = +3

Eq. Wt. of Gold = \( \frac{197}{3} \)

W = Zit

(where W stands for the weight of ions deposited, i for current and t for time and Z for electro-chemical equivalent of the electrolyte.)

\[ \therefore \] Charge required to deposit 1 g eq. of gold = 1F = 96,500 C

\[ \therefore \] Charge required to deposit 9.85 g of gold or

\[ \frac{9.85}{197/3} \] g eq. of gold = \( \frac{96,500 \times 9.85 \times 3}{197} \)

= 965 × 5 × 3 C = 14475 C

According to Faraday’s second law,

\[ \frac{Wt. of Cu}{Eq. wt. of Cu} = \frac{Wt. of Gold}{Eq. wt. of Gold} \]

\[ \Rightarrow \frac{Wt. of Cu deposited}{193} = \frac{14475}{2} = 4.7625 \text{ g} \]

Current = \( \frac{Q}{t} = \frac{14475}{5 \times 3600} \)

\[ A = \frac{193}{240} = 0.8042 \text{ A} \]

6. Volume of the surface = area × thickness

\[ = 80 \text{ cm}^2 \times \frac{0.005}{10} \text{ cm} = \frac{1}{25} \text{ cm}^3 \]

Mass of Ag deposited = Volume × Density

\[ = \frac{1}{25} \times 10.5 \text{ g/cm}^3 = \frac{21}{50} \text{ g} \]

**Cell reaction:** Ag⁺ + e⁻ → Ag

We know that, \( \frac{W}{E} = \frac{Q}{F} = \frac{i \times t}{F} \)

E = Eq. wt. of Ag = 108

\[ \therefore \frac{21}{50} = \frac{i \times t}{96500} \]

\[ \therefore \frac{21}{50} \times 108 = \frac{3 \times t}{96500} \]

\[ : t = 125.09 \text{ sec} \]

7. Half cell reactions will be

Zn²⁺ + 2e⁻ ⇌ Zn  ......(i)

H⁺ + e⁻ ⇌ \( \frac{1}{2} \) H₂ or 2H⁺ + 2e⁻ ⇌ H₂  ......(ii)

We know that \( E^\circ_{Zn/Zn^{2+}} = \frac{E^\circ_{Zn/Zn^{2+}} - \frac{RT}{nF} \ln \left[ \frac{Zn^{2+}}{Zn} \right]}{nF} \)

Here R = 8.314 J mol⁻¹ deg⁻¹, T = 298 K, F = 96,500 coul/equi, n = 2, \( E^\circ_{Zn/Zn^{2+}} = 0.76 \) V.

Substituting the values in the above equation

\[ E^\circ_{Zn/Zn^{2+}} = 0.76 - \frac{8.314 \times 298}{2 \times 96500} \ln \frac{1}{1} = 0.79 \text{ V} \]
Similarly, \( E_{H^+/H_2} = E_{H^+/H_2}^o - \frac{RT}{nF} \ln \left( \frac{[H_2]}{[H^+]} \right)^2 \)

\[
= 0 - \frac{8.314 \times 298}{2 \times 96500} \ln \left( \frac{1}{[H^+]} \right)^2 \\
= 0.05915 \log_{10} [H^+] = -0.05915 \text{pH} \\
(\because \ \log_{10} [H^+] = \text{pH})
\]

Now since \( E = E_{Zn/Zn^{2+}} + E_{H^+/H_2} \)

\[
0.28 = 0.79 - 0.05915 \text{pH} \Rightarrow \text{pH} = \frac{0.51}{0.05915} = 8.62
\]

8. In lead storage battery the anodic and cathodic reactions during discharge (or operation or working) are as:

(i) Anodic reaction:

\[
Pb(s) + SO_4^{2-} \rightarrow PbSO_4(s) + 2e^-
\]

(ii) Cathodic reaction:

\[
PbO_2(s) + SO_4^{2-} + 4H^+ + 2e^- \rightarrow PbSO_4(s) + 2H_2O
\]

In both the half cell reactions \( H_2SO_4 \) is consumed and hence conc. of \( H_2SO_4 \) decreases during the working (discharging) of the battery. For the withdrawal of \( 2F = 2 \times 96500 \) C of electric charge, 2 mol of \( H_2SO_4 \) are consumed. Density of \( H_2SO_4 \) solution (used as electrolyte) falls during working of the cell.

Both reactions get reversed on charging the battery leading to regeneration of \( H_2SO_4 \) as:

Formerly anode but now cathode (recharging)

\[
PbSO_4 + 2e^- \rightarrow Pb(s) + SO_4^{2-}\text{(aq)}
\]

Formerly cathode but now anode:

\[
PbSO_4(s) + 2H_2O \rightarrow PbO_2(s) + SO_4^{2-}(\text{aq}) + 4H^+ + 2e^-
\]

[NOTE: In 1986 IIT-JEE paper there was a mistake in the question paper itself. Reaction (ii) was shown to take place during recharging of the battery which is incorrect the reaction occurring at cathodic half cell during operation (discharging) of the battery.]

9. TIPS/FORMULAE:

Watt = Volt \times Current \Rightarrow 100 = 110 \times Current

or \[ \text{Current} = \frac{100}{110} = \frac{10}{11} \text{ amp}. \]

Now we know that,

\[
Q = i \times t = \frac{10}{11} \times 10 \times 3600 \times \frac{1}{96500} = 0.339 \text{ F}
\]

Wt. of cadmium deposited = \[ \frac{0.339 \times 112.4}{2} = 19.06 \text{ g} \]

10. TIPS/FORMULAE:

For a concentration cell

\[
E_{cell} = \frac{0.059}{n} \log \frac{C_1}{C_2}
\]

NOTE: It is a concentration cell as both the electrodes are made of same element. Negative electrode acts as anode in a galvanic cell.

At anode: \( H_2 \rightarrow 2H^+ + 2e^- \quad [H^+] = 10^{-6} \text{ M} \)

At cathode: \( 2H^+ + 2e^- \rightarrow H_2 \)

\[
E_{cell} = \frac{0.059}{1} \log \left( \frac{C_{H^+}}{10^{-6}} \right) \text{ or } 0.118 = \frac{0.059}{1} \log \left( \frac{C_{H^+}}{10^{-6}} \right)
\]

\[
\log \left( \frac{C_{H^+}}{10^{-6}} \right) = \frac{0.118}{0.059} = 2 \Rightarrow C_{H^+} = 10^{-4} \text{ M}
\]

11. For the given reactions, it is obvious that 22.4 litres of \( H_2 \) gas require 2 Faraday electricity.

\[ 67.2 \text{ litres of } H_2 \text{ will produce } = 6 \text{ Faraday electricity} \]

\[
Q = C \times t; 6 \times 96500 = C \times 15 \times 60
\]

\[
C = \frac{6 \times 96500}{15 \times 60} = 643.3 \text{ ampere}
\]

Calculation of amount of \( Cu \) deposited by 6 \text{ F}

Since \( 1 \text{ F deposits } = \frac{63.5}{2} = 31.75 \text{ g of } Cu \)

6 \text{ F will deposit } = 31.75 \times 6 = 190.50 \text{ g}

12. The chemical reactions taking place at the two electrodes are

At cathode: \( Cu^{2+} + 2e^- \rightarrow Cu \)

\[
H_2O \rightarrow H^+ + OH^-
\]

NOTE: Only \( Cu^{2+} \) ions will be discharged so as these are present in solution and \( H^+ \) will be discharged only when all the \( Cu^{2+} \) ions have been deposited.

At anode: \( 2OH^- \rightarrow H_2O + O + 2e^- \)

Thus in first case, \( Cu^{2+} \) ion will be discharged at the cathode and \( O_2 \) gas at the anode. Let us calculate the volume of gas \( (O_2) \) discharged during electrolysis.

According to Faraday's second law

31.75 \text{ g Cu} = 8 \text{ g of oxygen} = 5.6 \text{ litres of } O_2 \text{ at NTP}

\[
0.4 \text{ g Cu} = \frac{5.6}{31.75} \times 0.4 \text{ litres of } O_2 \text{ at NTP}
\]

\[
= 0.07055 \text{ litres} = 70.55 \text{ ml}
\]

As explained earlier, when all the \( Cu^{2+} \) ion will be discharged at cathode, \( H^+ \) ions will start going to cathode liberating hydrogen \( (H_2) \) gas, \( i.e. \)

\[
H^+ + e^- \rightarrow H \quad H + H_2
\]

NOTE THIS STEP: However, the anode reaction remains same as previous. Thus in the second (latter) case, amount of \( H_2 \) collected at cathode should be calculated.

8 \text{ g of } O_2 = 1 \text{ g of } H_2

5.6 \text{ litres of } O_2 \text{ at NTP} = 11.2 \text{ litres of hydrogen}

Quantity of electricity passed after 1st electrolysis, \( i.e. Q = i \times t = 1.2 \times 7 \times 60 = 504 \text{ coulombs} \)

504 coulombs will liberate \[ \frac{5.6 \times 504}{96500} = 29.24 \text{ ml of } O_2 \]
Similarly, \( H_2 \) liberated by 504 coulombs
\[
= 11.2 \times \frac{504}{96500} = 58.48 \text{ ml}
\]
(Twice the volume of \( O_2 \) liberated in latter phase
\[
= 2 \times 29.24 = 58.48 \text{ ml}
\]
Total volume of \( O_2 \) liberated = 70.55 + 29.24 = 99.79 ml
Vol. of \( H_2 \) liberated = 58.48 ml

13. TIPS/FORMULAE:
\[
E_c^{0} = \frac{RT}{nF} \log K_c \quad \text{or} \quad E_c^{0} = \frac{RT}{nF} \log K_c
\]
Let us split the desired reaction into two half cell reactions:
**Oxidation half reaction:**
\[
H_2O + \frac{1}{2} H_2(g) \rightleftharpoons H_2O^+ + e^- \quad E^0 = 0.00 \text{ V}
\]
**Reduction half reaction:**
\[
H_2O + e^- \rightarrow \frac{1}{2} H_2 + OH^- \quad E^0 = -0.8277 \text{ V}
\]
Net reaction:
\[
2H_2O \rightleftharpoons H_2O^+ + OH^- \quad E^0_{cell} = -0.8277 \text{ V}
\]
So, the number of electrons involved in redox reaction, \( n = 1 \)
We know that
\[
E_c^{0} = \frac{RT}{nF} \log K_c
\]
\[
\log K_c = \frac{E_c^{0} \times n}{RT} = \frac{(-0.8277) \times 1}{0.0591} = -14.005
\]
\[
K_c = \text{Antilog}[15.995] = 9.88 \times 10^{-15}
\]

14. \( E_C^{Cu^{2+}/Cu} = 0.337 \) and \( E_A^{Ag^+/Ag} = 0.799 \) V
\[
E_c^{Ag^+/Ag} + E_c^{Cu/Cu^{2+}} = 0.799 - 0.337 = 0.462 \text{ V}
\]
\[
\therefore Cu + 2Ag^+ \rightarrow Cu^{2+} + 2Ag; \quad E_c^{cell} = 0.462 \text{ V}
\]
Hence the galvanic cell in question will consist of anode of copper and cathode of silver.
**Calculation of concentration:**
\[
E_{cell} = E^0_c - \frac{0.059}{n} \log \frac{[\text{Products}]}{[\text{Reactants}]}
\]
\[
E_c^{0} = \frac{RT}{nF} \log \frac{[\text{Products}]}{[\text{Reactants}]}
\]
\[
0.462 = \frac{0.059}{2} \log \frac{0.01}{[Ag^{2+}]^2}
\]
\[
\frac{462 \times 2}{0.059} = \log (10^{-2}) - \log [Ag^{2+}]^2
\]
\[
\frac{924}{59} = -2 + 2 \log [Ag^{2+}] \Rightarrow [Ag^{2+}] = 1.48 \times 10^{-9} \text{ M}
\]

15. \( C_6H_5NO_2 + 6H^+ + 6e^- \rightarrow C_6H_5NH_4 + 2H_2O \)
\[
\text{Eq. wt of } C_6H_5NO_2 = \frac{M \text{ wt.}}{6} = \frac{123}{6} = 20.5 \text{ g/mol}
\]
\[
w = \frac{E_{cell}}{96500} \quad \therefore \text{current efficiency} = 50\%\)
\[
\therefore i = \frac{50i_0}{100}
\]
\[
\therefore 12.3 = \frac{123 \times 1 \times t \times 50}{6 \times 100 \times 96500}
\]
\[
i \times t = Q = 115800 \text{ Coulomb}
\]
Energy used = 115800 \times 3 = 347.4 \text{ kJ.}

16. The following chemical cell sets up:
\[
\text{Zn} | \text{Zn}^{2+} \parallel \text{Ni}^{2+} | \text{Ni}
\]
The net cell reaction is: \( \text{Zn} + \text{Ni}^{2+} \rightleftharpoons \text{Zn}^{2+} + \text{Ni} \)
The e.m.f. is given by
\[
E_{cell} = E_c^{0_{\text{Ni}^{2+}/\text{Ni}}} - E_c^{0_{\text{Zn}^{2+}/\text{Zn}}} - \frac{0.059}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Ni}^{2+}]}
\]
\[
= -0.24 - (-0.75) - 0.0295 \log \frac{[\text{Zn}^{2+}]}{[\text{Ni}^{2+}]}
\]
\[
= 0.51 - 0.0295 \log \frac{[\text{Zn}^{2+}]}{[\text{Ni}^{2+}]}
\]
At equilibrium \( E_{cell} = 0 \)
Let \( x \) mol \( t \) be the concentration of \( \text{Ni}^{2+} \) at equilibrium.
Then \( [\text{Zn}^{2+}] = 1 - x \) \( \therefore 1 \) mole of \( \text{Ni}^{2+} \) gives 1 mole of \( \text{Zn}^{2+} \)
\[
\therefore 0.0295 \log \frac{1-x}{x} = 0.51
\]
\[
\therefore \log \frac{1-x}{x} = \frac{0.51}{0.0295} = 17.29 \quad \therefore \frac{1-x}{x} = 1.95 \times 10^{17}
\]
or \( x = \frac{1}{1.95 \times 10^{17}} = 5.128 \times 10^{-18} \) mol \( t \)

17. \( i = 1.70 \times 90 = \frac{100}{100} \text{ ampere} \)
No. of equivalents of \( \text{Zn}^{2+} \) which are lost
\[
= \frac{i \times t}{96500} = \frac{1.70 \times 90 \times 230}{96500} = 3.646 \times 10^{-3}
\]
\( \therefore \) Milli equivalents of \( \text{Zn}^{2+} \) which are lost 3.646
\( \therefore \) Initial value of \( \text{Zn}^{2+} = 300 \times 0.160 \times 2 = 96 \)
\( \therefore \) Milli equivalents of \( \text{Zn}^{2+} \) left in solution
\( 96 - 3.646 = 92.354 \)
\[
[ZnSO_4] = \frac{92.354}{2 \times 300} = 0.154 \text{ M}
\]
\( \therefore \) Molarity of \( \text{Zn}^{2+} = 0.154 \text{ M} \)

18. \( \text{Ag} | \text{AgCl(s), KCl(0.2M) || KBr(0.001M), AgBr(s)} | \text{Ag} \)
\( \text{Anode:} \) \text{Cathode:} \text{K}_p(\text{AgCl}) = 2.8 \times 10^{-10} \quad \text{K}_p(\text{AgBr}) = 3.3 \times 10^{-13}
\( \therefore \) At anode, \( \text{Ag} \rightarrow \text{Ag}^+ + e^- \)
\( \therefore \) At cathode, \( \text{Ag}^+ + e^- \rightarrow \text{Ag} \)
\( \therefore \) Cell reaction \( \text{Ag} + \text{Ag}^+ \rightarrow 2\text{Ag} \)

\( \text{NOTE:} \) The subscripts 1 and 2 on \( \text{Ag} \) denote the species concerned with anode and cathode respectively.
Applying Nernst equation
\[
E = E^0 - \frac{0.059}{n} \log \frac{[\text{Products}]}{[\text{Reactants}]}
\]
21. CrO$_3$ + 6H$^+$ + 6e$^-$ $\rightarrow$ Cr + 3H$_2$O

Eq. wt. of Cr

At. wt.

\[ \text{No. of Electrons lost or gained by one molecule of Cr} = \frac{52}{6} \]

(i) \[ \therefore 96500 \text{ coulomb deposit} = \left( \frac{52}{6} \right) \text{ g Cr} \]

\[ \therefore \text{24000 coulomb deposit} = \frac{52}{6} \times \frac{24000}{96500} = 2.1554 \text{ g of Cr} \]

(ii) Also given, \( w_{Cr} = 1.5 \text{ g} \), \( i = 12.5 \text{ ampere} \), \( t = ? \), \( E_{Cr} = \frac{52}{6} \)

\[ \therefore \text{w} = \frac{Eit}{96500} \text{ or } 1.5 = \frac{52 \times 12.5 \times t}{6 \times 96500} \]

\[ \therefore t = 1336.15 \text{ second} \]

22. \( E^o = \text{Standard reduction potential of the Ag}^+ / \text{Ag electrode} = 0.799 \text{V} \)

\( \text{AgI (s)} \rightleftharpoons \text{Ag}^+ + \text{I}^- \)

\( K_sp = [\text{Ag}^+] [\text{I}^-] = 8.7 \times 10^{-17} \) (given)

\( \text{I}^- \text{S}^+ \) is the solubility of AgI, then \( K_sp = S^2 \)

\[ \therefore S = \sqrt{K_sp} = \sqrt{8.7 \times 10^{-17}} \times 9.327 \times 10^{-8} \text{mol L}^{-1} \]

\[ \therefore [\text{Ag}^+] = [\text{I}^-] = 9.327 \times 10^{-9} \text{M} \]

Reaction : \( \text{Ag}^+ + e^- \rightarrow \text{Ag} \)

\[ \therefore E = E^o - \frac{0.059}{n} \log \frac{\text{[Products]}}{\text{[Reactants]}} \]

\[ = 0.799 \text{V} - \frac{0.059}{1} \log \frac{1}{9.327 \times 10^{-9}} \]

\[ = 0.799 - 0.059 \times 1.072 \times 10^9 \]

\[ = 0.799 - 0.474 = 0.325 \text{V} \]

Again,

L.H.S. Electrode reaction :
\( \text{Ag} \rightarrow \text{Ag}^+ + e^- \)

R.H.S. Electrode reaction :
\( \text{AgI(s)} \rightarrow \text{Ag}^+ + \text{I}^- \)

Cell reaction :
\( \text{AgI(s)} \rightarrow \text{Ag} + \text{I}^- \)

\[ K = \text{Equilibrium constant} = [\text{Ag}^+] [\text{I}^-] = 8.7 \times 10^{-17} \]

The standard cell emf \( E^o \) and the equilibrium constant \( k \) are related by the expression.

\[ E^o_{cell} = \frac{0.059}{n} \log K \text{ at } 298 K, \text{ Here, } n = 1, K = 8.7 \times 10^{-17} \]

\[ E^o_{cell} = 0.059 \log 8.7 \times 10^{-17} = 0.059 [0.9395 - 17] = -0.948 \text{ V} \]

But \( E^o_{cell} = E^o_{R,H.S.} - E^0_{L,H.S.} \)

\[ \therefore E^o_{R,H.S.} = E^o_{cell} + E^0_{L,H.S.} = -0.948 + 0.799 = -0.149 \text{ V} \]
23. (i) Given \( E^{\circ}_{\text{Ni}_2\text{O}_3/\text{NiO}} = +0.40 \text{ V} \), \( E^{\circ}_{\text{FeO}/\text{Fe}} = -0.87 \text{ V} \)

\[
E^{\circ}_{\text{NiO}/\text{Ni}_2\text{O}_3} = -0.40 \text{ V}, \quad E^{\circ}_{\text{Fe}/\text{FeO}} = +0.87 \text{ V}
\]

Since \( E^{\circ}_{\text{ox}} \) for Fe/FeO > \( E^{\circ}_{\text{ox}} \) for NiO/Ni2O3.

Redox changes can be written as

- **At anode**: \( \text{Fe}(s) + 2\text{OH}^- \rightarrow \text{FeO}(s) + \text{H}_2\text{O}(l) + 2\text{e}^- \)
- **At cathode**: \( \text{Ni}_2\text{O}_3(s) + \text{H}_2\text{O}(l) + 2\text{e}^- \rightarrow 2\text{NiO}(s) + 2\text{OH}^- \)

**Cell reaction**: \( \text{Fe}(s) + \text{Ni}_2\text{O}_3(s) \rightarrow \text{FeO}(s) + 2\text{NiO}(s) \)

(ii) \( E^{\circ}_{\text{cell}} = E^{\circ}_{\text{OP Fe}/\text{FeO}} + E^{\circ}_{\text{RP Ni}_2\text{O}_3/\text{NiO}} \)

\[
= 0.87 + 0.40 = 1.27 \text{ V}
\]

It is independent of conc. of KOH

(iii) Electrical energy = \( nFE^{\circ}_{\text{cell}} = 2 \times 96500 \text{ J} \times 1.27 \text{ V} = 2.45 \times 10^5 \text{ J} \)

24. The thin protective layer of oxides of aluminium is formed which protects the metal from further attack of water and air and make it stable.

25. \( 2\text{Hg} + 2\text{Fe}^{3+} \rightarrow \text{Hg}_2^{2+} + 2\text{Fe}^{2+} \)

Initial conc. \( 1.0 \times 10^{-3} \)

Eqib. conc. \( 0.05 \times 10^{-3} \)

\[
E = E^{\circ}_{\text{Fe}^{3+}/\text{Fe}^{2+}} - \frac{0.059}{n} \log \left( \frac{[\text{Fe}^{2+}]^2}{[\text{Hg}_2^{2+}]} \right)
\]

\[\text{NOTE: At equilibrium, } E = 0\]

\[
\Rightarrow 0 = 0.77 - \frac{E^{\circ}_{\text{Hg}_2^{2+}/\text{Hg}}}{2} - \frac{0.059}{2} \log \left( \frac{0.95 \times 10^{-3}}{0.95 \times 10^{-3}} \right)^2
\]

On usual calculations, \( E^{\circ}_{\text{Hg}_2^{2+}/\text{Hg}} = 0.792 \text{ V} \)

26. At pH = 14; \( [\text{H}^+] = 1 \times 10^{-14} \text{ M} \); \( [\text{OH}^-] = 10^0 = 1 \text{ M} \)

\( \therefore [\text{H}^+] \times [\text{OH}^-] = 1 \times 10^{-14} \)

\( \therefore \text{Cu(OH)}_2 \text{ ionises as follows:} \)

\( \text{Cu(OH)}_2 \rightarrow \text{Cu}^{2+} + 2\text{OH}^- \)

\( \therefore K_{sp} \text{ of Cu(OH)}_2 = [\text{Cu}^{2+}] \times [\text{OH}^-]^2 \)

\( = 1.0 \times 10^{-19} \times [\text{Cu}^{2+}] \times (1.0 \times 10^{-19}) \)

\( \text{The standard reduction potential of Cu}^{2+}/\text{Cu} \text{ is represented in the form of following equation:} \)

\( \text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}^{(s)} \)

On applying Nernst equation

\[
E = E^{\circ} - \frac{0.0591}{n} \log \left( \frac{1}{[\text{Cu}^{2+}]} \right)
\]

\[
= +0.34 - \frac{0.0591}{2} \log \left( \frac{1}{1 \times 10^{-19}} \right)
\]

\[
= +0.34 - \frac{0.0591}{2} \times 19 = 0.34 - 0.56 = -0.22 \text{ V}
\]

27. \( W_{\text{Ag}} = \frac{E_{\text{in}}}{96500} = \frac{107.8 \times 8.46 \times 8 \times 60 \times 60}{96500} = 34.02 \text{ g} \)

Volume of \( \text{Ag} = \frac{34.02}{10.5} = 3.24 \text{ ml} \)

\( \therefore \) Surface area = \( \frac{3.24}{0.00254} = 1275.6 \text{ cm}^2 \)

28. \( \text{Fe}^{2+}_{(aq)} \rightarrow \text{Fe}^{3+}_{(aq)} + \text{e}^- \); \( E^{\circ} = 0.68 \text{ V} \)

\( \text{Ce}^{3+}_{(aq)} + \text{e}^- \rightarrow \text{Ce}^{4+}_{(aq)} \); \( E^{\circ} = 1.44 \text{ V} \)

\( E^{\circ}_{\text{cell}} = 1.44 - 0.68 = +0.76 \text{ V} \)

at equilibrium, \( E_{\text{cell}} = 0 \)

\[
E_{\text{cell}} = \frac{0.0591}{n} \log_{10} K_c ; \quad 0.76 = \frac{0.0591}{1} \log_{10} K_c
\]

or \( \log_{10} K_c = 0.76 \); \( K_c = 12.859 \)

\( \therefore K_c = 7.6 \times 10^{12} \)

29. For the change \( 2\text{Fe}^{2+} + 3\text{I}^- \rightarrow 2\text{Fe}^{3+} + \text{I}_3^- \)

\( E = E^{\circ} - \frac{0.059}{2} \log K_c \) or \( E = \frac{0.059}{2} \log K_c \)

\( (\therefore \text{at equilibrium, } E = 0) \)

Also \( E^{\circ}_{\text{cell}} = E^{\circ}_{\text{RP Fe}^{3+}/\text{Fe}^{2+}} + E^{\circ}_{\text{OP Fe}^{2+}/\text{I}_3^-} \)

\( = 0.77 - 0.54 = 0.23 \text{ V} \)

\( E_{\text{cell}} = \frac{0.059}{2} \log K_c \)

At equilibrium, \( E_{\text{cell}} = 0 \) (Using Nernst equation)

Thus, \( 0.23 = \frac{0.059}{2} \log K_c \); \( K_c = 6.26 \times 10^7 \)

30. The cell reaction can be written as

\( \text{Ag} \mid \text{Ag}^{+} (\text{Ag}_2\text{CrO}_4 \text{Sat.}) \parallel \text{Ag}^{+} (0.1 \text{ M}) \mid \text{Ag} ; \quad E = 0.164 \text{ V} \)

At cathode: \( \text{Ag}^{+} \text{cathode} + \text{e}^- \rightarrow \text{Ag} \)

At anode: \( \text{Ag} \rightarrow \text{Ag}^{+} \text{anode} + \text{e}^- \)

Net reaction: \( \text{Ag}^{+} \text{cathode} \rightarrow \text{Ag}^{+} \text{anode} ; \quad E = 0.164 \text{ V} \)

Thus here, \( n = 1, E = 0.164 \text{ V} \); \( [\text{Ag}^{+}]_{\text{cathode}} = 0.1 \text{ M} \)

Let the solubility of \( \text{Ag}_2\text{CrO}_4 \) be \( S \text{ M} \)

Since \( \text{Ag}_2\text{CrO}_4 \) gives 2 \( \text{Ag}^{+} \)

\( \therefore \) Here concentration of \( [\text{Ag}^{+}]_{\text{anode}} = 2 \text{ S M} \)

\( \therefore 0.164 = -\frac{0.059}{1} \log \frac{[\text{Ag}^{+}]_{\text{anode}}}{[\text{Ag}^{+}]_{\text{cathode}}} \)

\( 0.164 = -\frac{0.059}{1} \log \frac{2S}{0.1} \)

or \( 0.164 = -\frac{0.059}{1} \log \frac{0.1}{2S} \)

\( \therefore 2S = 1.697 \times 10^{-4} \text{ M} \)

Hence \( S = 0.8485 \times 10^{-4} \text{ M} \)

For \( \text{Ag}_2\text{CrO}_4 \rightarrow 2\text{Ag}^{+} + \text{CrO}_4^{2-} \)

\( K_{sp} = (2S)^2 (S) = 4S^3 \)

\( \therefore K_{sp} = 4 \times (0.8485 \times 10^{-4})^3 = 2.44 \times 10^{-12} \)
31. Note that the given cell will not work as electrochemical cell since \( E^\circ_{\text{OCu}} > E^\circ_{\text{OAg}} \).

The equation for electro-chemical cells will be:

\[
\begin{align*}
\text{Cu} & \rightarrow \text{Cu}^{2+} + 2e^- \\
2\text{Ag}^+ + 2e^- & \rightarrow 2\text{Ag}
\end{align*}
\]

Thus, e.m.f. of cell \( \text{Cu} \mid \text{Cu}^{2+} \parallel \text{Ag}^+ \mid \text{Ag} \) will be

\[
E_{\text{cell}} = E^\circ_{\text{OCu}} + E^\circ_{\text{ORP}} + \frac{0.059}{2} \log \frac{[\text{Ag}^+]}{[\text{Cu}^{2+}]} \]

\( \therefore [\text{Ag}^+] = 1 \text{ M and [Cu}^{2+}]= 1 \text{ M} \)

\[
\therefore E_{\text{cell}} = E^\circ_{\text{OCu}} + E^\circ_{\text{ORP}}
\]

\[
\left( E^\circ_{\text{cell}} = E^\circ_{\text{OCu}} + E^\circ_{\text{ORP}} \right) \Rightarrow E_{\text{cell}} = E^\circ_{\text{cell}}
\]

After the passage of 9.65 amperes for 1 hr i.e. \( 9.65 \times 60 \times 60 \) Coulomb charge, during which the cell reactions are reversed, the Ag metal passes in solution state and Cu\(^{2+}\) ions are discharged. The reactions during the passage of current are:

\[
2\text{Ag} \rightarrow 2\text{Ag}^+ + 2e^- \quad \text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}
\]

Thus, \( \text{Ag}^+ \) formed \( \frac{9.65\times60\times60}{96500} = 0.36 \text{ eq.} = 0.36 \text{ mole} \)

\( \text{Cu}^{2+} \) discharged \( \frac{9.65\times60\times60}{96500} = 0.36 \text{ eq.} = 0.18 \text{ mole} \)

Thus \( [\text{Ag}^+] \) left = 1 + 0.36 = 1.36 mole \[\text{Cu}^{2+}] \) left = 1 - 0.18 = 0.82 mole.

Now e.m.f. can be given as:

\[
E_{\text{cell}} = E^\circ_{\text{cell}} + \frac{0.059}{2} \log \frac{0.36}{0.82} = E^\circ_{\text{cell}} + 0.010 \text{ V}
\]

Thus \( E_{\text{cell}} \) increases by 0.010 V.

32. \( m = Z \alpha \)

\[
Z \text{ for Cu} = \frac{63.5/2}{96500} ; t = 16 \times 60 \text{ sec}
\]

\[
\therefore m = \frac{63.5}{2 \times 96500} \times 2 \times 10^{-3} \times 16 \times 60
\]

\[
= \frac{63.5 \times 16 \times 60 \times 10^{-3}}{96500}
\]

Wt. of Cu at 50\% electrolysis of CuSO\(_4\)

\[
= \frac{63.5 \times 16 \times 60 \times 10^{-3}}{96500} \text{ g}
\]

Wt. of Cu at 100\% electrolysis of CuSO\(_4\)

\[
= \frac{63.5 \times 2 \times 16 \times 60 \times 10^{-3}}{96500} \text{ g}
\]

\[
= 0.198 \times 63.5 \times 10^{-4} \text{ g}
\]

\[
\text{CuSO}_4 = \text{Cu} = 0.198 \times 10^{-4} \text{ mol.}
\]

\[
\therefore \text{Conc. of CuSO}_4 = \frac{0.198 \times 10^{-4} \times 1000}{250} = 7.95 \times 10^{-5} \text{ mol/L}
\]

33. Given, \( E^\circ_{\text{Ce}^{4+}/\text{Ce}^{3+}} = 1.61 \text{ V} \); \( E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 0.77 \text{ V} \)

Thus for \( E^\circ_{\text{cell}} \) to be positive, following reaction should occur

\[
\text{Ce}^{4+} + \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{Ce}^{3+}
\]

Hence \( \text{Ce}^{4+} / \text{Ce}^{3+} \) electrode will act as cathode and \( \text{Fe}^{3+} / \text{Fe}^{2+} \) electrode will act as anode.

Therefore \( \text{current will flow from Ce electrode to iron electrode.} \)

Current will \( \text{decrease with time.} \)

34. (i) The half cell reactions are

\[
\text{At anode: } \frac{1}{2} \text{H}_2(g) \rightarrow \text{H}^+(aq) + e^- 
\]

\[
\text{At cathode: } \text{AgCl}(s) + e^- \rightarrow \text{Ag}(s) + \text{Cl}^{-}(aq)
\]

The cell reaction \( \frac{1}{2} \text{H}_2(g) + \text{AgCl}(s) \rightarrow \text{H}^+(aq) + \text{Ag}(s) + \text{Cl}^{-}(aq) \)

(ii) \text{TIPS/FORMULAE:}

We know that \( \Delta S = nF \frac{dE}{dT} \)

\( n \rightarrow \text{No. of transferred electrons} = 1 \)

\( F \rightarrow \text{faraday number} = 96500 \text{ coulombs} \)

\( dE \rightarrow \text{Difference of electrode potential at two different temperatures} = (0.21 - 0.23) = -0.02 \text{ V} \)

\( dT \rightarrow \text{Difference of two temperatures} \)

\( = (35^\circ\text{C} - 15^\circ\text{C}) = 20^\circ\text{C} \)

\( \therefore \Delta S^\circ = 1 \times 96500 \times \frac{-0.02}{20} = -96.5 \text{ J/K mole} \)

\( \therefore E_{15} = 0.23 \text{ V} ; \Delta G^\circ = -nE^\circ F \)

so \( \Delta G^\circ_{15} = -1 \times 0.23 \times 96500 = -22195 \text{ J/mole} \)

\( \Delta H^\circ = \Delta G^\circ - T\Delta S^\circ = -22195 - 288 \times (-96.5) = -49987 \text{ J/mole} \)

(iii) \( E^\circ_{\text{Cu}^{2+}/\text{Cu}} \) of cell

\[
= E_{15} - \frac{dE}{d\Delta T} 
\]

\[
= \frac{0.23 - 0.02}{20} \times 10 = 0.22 \text{ V}
\]

The corresponding cell is represented as:

\[
\text{Ag(s)} \parallel \text{Ag}^+(aq) \parallel \text{Cl}^{-}(aq) \mid \text{AgCl}(s) \parallel \text{Ag}(s)
\]

In form of oxidised electrode potential

\[
E^\circ_{\text{cell}} = E^\circ_{\text{anode}} - E^\circ_{\text{Cathode}} = E^\circ_{\text{Ag/Ag}^+} - E^\circ_{\text{Ag/AgCl/Cl}^-}
\]

\[
= -0.80 - (0.22) = 0.58 \text{ V}
\]

\[
E^\circ_{\text{cell}} = \frac{0.0591}{n} \log_{10} K_{\text{eq}} 
\]

\[
\text{AgCl(s)} \rightarrow \text{Ag}^+ + \text{Cl}^-
\]

\[
E^\circ_{\text{cell}} = \frac{0.0591}{n} \log_{10} [\text{Ag}^+] \times [\text{Cl}^-] = \frac{0.0591}{n} \log_{10} K_{\text{sp}}
\]

Therefore \( -0.58 = \frac{0.0591}{1} \log_{10} K_{\text{sp}} \)

or \( \log_{10} K_{\text{sp}} = -9.8139 = 10.1861 ; K_{\text{sp}} = 1.54 \times 10^{-10} \)

\( K_{\text{sp}} \) of AgCl = \( 1.54 \times 10^{-10} \) (mole litre\(^{-1}\))\(^2\)

Solubility of AgCl

\[
= \sqrt{K_{\text{sp}}} = 1.24 \times 10^{-5} \text{ mole/L}
\]
35. **Daniel cell is**: \( Zn \mid Zn^{2+} || Cu^{2+} \mid Cu \)
   Let there be two Daniel cells with their \( E_{cell} \) as given below:
   \( Zn \mid Zn^{2+} (C_1) || Cu^{2+} (C = ?) \mid Cu \)
   \( E_{cell} = E_1 \)
   \( Zn \mid Zn^{2+} (C_2) || Cu^{2+} (C = 0.5 \text{ M}) \mid Cu \)
   \( E_{cell} = E_2 \), where \( E_2 > E_1 \)
   According to question, \( E_2 - E_1 = 0.03 \) and \( C_2 = C_1 \)
   The cell reaction is
   \[ Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu \]
   \( \text{So, } E_{cell} = E_{cell}^0 - \frac{0.06}{2} \log \left( \frac{[Zn^{2+}]}{[Cu^{2+}]} \right) \)
   \[ \text{Thus, } E_1 = E_{cell}^0 - \frac{0.06}{2} \log \left( \frac{C_1}{C} \right) \]
   \[ \text{and } E_2 = E_{cell}^0 - \frac{0.06}{2} \log \left( \frac{C_2}{0.5} \right) \]
   Since same \( ZnSO_4 \) is used in both cells \( C_1 = C_2 \)
   \[ \text{So, } E_2 - E_1 = \frac{0.06}{2} \left( \log \left( \frac{C_1}{C} \right) - 0.5 \right) \]
   \[ \Rightarrow 0.03 = \frac{0.06}{2} \log \left( \frac{0.5}{C} \right) \Rightarrow \log \left( \frac{0.5}{C} \right) = 1 \text{ or } C = 0.05 \text{ M} \]

36. **The required reaction can be obtained in the following way:**
   \[ Cu^{2+} + e^- \rightarrow Cu^+ \quad \Delta G^o = -0.15 \text{ F} \]
   \[ (\Delta G^o = -n FE^o) \]
   \[ In^{2+} + e^- \rightarrow In^+, \quad \Delta G^o = +0.40 \text{ F} \]
   \[ In^+ \rightarrow In^{3+} + 2e^-, \quad \Delta G^o = -0.84 \text{ F} \]
   On adding, \( Cu^{2+} + In^{2+} \rightarrow In^{3+} + Cu^+ \), \( E^o = -0.59 \text{ F} \)
   Now we know that \(-n FE^o = -0.59 \text{ F} \)
   or \(-E_{cell}^o = -0.59 \text{ V} \) or \( E_{cell}^o = 0.59 \text{ V} \)
   \[ E_{cell} = E_{cell}^0 - \frac{0.0591}{n} \log K_c \]
   \[ E_{cell}^0 = 0, \text{then } E_{cell} = \frac{0.0591}{n} \log K_c \]
   \[ 0.59 = \frac{0.0591}{n} \log K_c \]
   \[ \log K_c = \frac{0.59}{0.0591} = 10 ; \quad K_c = 10^{10} \]

37. **(a)** From the given details, the reactions can be written as:
   At anode: \( Ag(s) + Cl^- (aq) \rightarrow AgCl(s) + e^- \)
   At anode: \( Ag^+ (aq) + e^- \rightarrow Ag(s) \)
   Complete reaction: \( Ag^+ (aq) + Cl^- (aq) \rightarrow AgCl(s) \)
   Hence cell representation is
   \[ Ag (s) \mid AgCl (s) \mid Cl^- (aq) || Ag^+ (aq) || Ag(s) \]
   \[ \Delta G^o = \Delta G^o (AgCl) - [\Delta G^o (Ag^+) + \Delta G^o (Cl^-)] \]
   \[ = -109 - (-129 + 77) = -57 \text{ kJ/mol} = -57000 \text{ J/mol} \]
   We know that, \( \Delta G^o = -n FE_{cell} \)

38. **Given:** \( \lambda_m (Ag^+)^{-1} = 6 \times 10^{-3}; \lambda_m (Br^-)^{-1} = 8 \times 10^{-3}; \)
   \( \lambda_m (NO_3^-) = 7 \times 10^{-3} \) and \( K_{sp} (AgBr) = 12 \times 10^{-14} \)

**NOTE THIS STEP:** To find the specific conductivity \( \kappa \) of the final solution of \( AgBr \) in which \( AgNO_3(10^{-7} \text{ M}) \) is mixed we must find the individual \( \kappa \) of the ions.

or \( \kappa_{so ln} = \kappa_{Ag^+} + \kappa_{Br^-} + \kappa_{NO_3^-} \)

Again, \( \kappa = \lambda_m \times \text{molar concentration} \)
Calculation of molar concentration of ions:

Concentration,

\[ [\text{NO}_3^-] = 10^{-7} \text{ moles/l} = 10^{-4} \text{ moles/m}^3 \]

Let \( x \) be the molar concentration of \( Ag^+ \) from \( AgBr \)

\[ (x + 10^{-7})x = 12 \times 10^{-14} \]

or \( x^2 + 10^{-7}x - 12 \times 10^{-14} = 0 \)

or, \( (x + 4 \times 10^{-7})(x - 3 \times 10^{-7}) = 0 \Rightarrow x = 3 \times 10^{-7} \text{ M} \)

\[ [\text{Br}^-] = 3 \times 10^{-7} \text{ M} = 3 \times 10^{-4} \text{ moles/m}^3 \] and

\[ [\text{Ag}^+] = 3 \times 10^{-7} + 10^{-7} = 4 \times 10^{-7} \text{ M} = 4 \times 10^{-4} \text{ moles/m}^3 \]

\[ \kappa_{\text{Ag}^+} = 6 \times 10^{-3} \times 4 \times 10^{-4} \]

\[ = 24 \times 10^{-7} \text{ (Sm}^2 \text{ mol}^{-1} \times \text{mol/m}^3) = 24 \times 10^{-7} \text{ S/m} \]

Similarly, \( \kappa_{\text{Br}^-} = 8 \times 10^{-3} \times 3 \times 10^{-4} = 24 \times 10^{-7} \text{ S/m} \) and

\[ \kappa_{\text{NO}_3^-} = 7 \times 10^{-3} \times 10^{-4} = 7 \times 10^{-7} \text{ S/m} \]

\[ \Rightarrow \kappa = (24 + 24 + 7) \times 10^{-7} \text{ S/m} = 55 \times 10^{-7} \text{ S/m} \]

So the correct answer is 55.

F. Match the Following

1. (A - p, s); (B - r); (C - p, q); (D - p).
   \( A \rightarrow p, s; \) The reaction is redox reaction because the O.N. of O in \( O_2 \) is −0.5 and that in \( O_2^- \) is zero. It involves reduction oxidation reaction. Since here a part of molecule is oxidised and a part is reduced so it is disproportionation.
   \( B \rightarrow r; \) The structure of \( Cr_2O_7^{2-} \) is given below

\[
\begin{array}{c}
\text{C} \\
\text{O} \\
\text{O} \\
\text{O} \\
\text{O} \\
\text{O}
\end{array}
\]

\[ 2^{-} \]

\[ \text{[NOTE : In any solution dichromate ions and chromate ions exist in equilibrium. In alkali solution, dichromate ions are converted into chromate ions and on acidification chromate ions are converted back into dichromate ion.]} \]

C \( \rightarrow p, q; \) The reaction is

\[ 2MnO_4^- + 6H^+ + 5NO_2^- \rightarrow 2Mn^{2+} + 3H_2O + 5NO_3^- \]

In involves change in O.N of Mn (from +7 in MnO_4^-) to +2 (in Mn^{2+}). So Mn is reduced and NO_2^- is oxidised to NO_3^- it is a redox reaction.

The structure of NO_3^- (one of the products is trigonal planar)

D \( \rightarrow p; \) It is a redox reaction.

2. (a) (P) \( (\text{C}_2\text{H}_5)_3\text{N+CH}_3\text{COOH} \rightarrow \]

\[
\begin{array}{c}
\text{C}_2\text{H}_5 \\
\text{C} \\
\text{CH}_3 \\
\text{N} \\
\text{O}
\end{array}
\]

\[ (\text{C}_2\text{H}_5)_3\text{NH}^+\text{CH}_3\text{COO}^- \]

\[ \text{Topic-wise Solved Papers - CHEMISTRY} \]

Initially conductivity increases because on neutralisation ions are created. After that it becomes practically constant because X alone can not form ions.

\[ (Q) \quad K\text{I}(0.1\text{M}) + \text{AgNO}_3(0.01\text{M}) \rightarrow \text{AgI} \downarrow + \text{KNO}_3 \]

Number of ions in the solution remains constant as only AgNO_3 precipitated as AgI. Thereafter conductance increases due to increase in number of ions.

(R) Initially conductance decreases due to the decrease in the number of OH^- ions as OH^- is getting replaced by CH_3COO^- which has poorer conductivity thereafter it slowly increases due to the increase in number of H^+ ions.

(S) Initially it decreases due to decrease in H^+ ions and then increases due to the increase in OH^- ions.

3. (d) \( \text{Fe}^{3+} \rightarrow (\text{Fe}^{2+} \rightarrow \text{Fe} \)

\[
\begin{array}{c}
\text{Fe}^{3+} \rightarrow +0.77V \\
\text{n=1} \rightarrow \text{Fe}^{2+} \rightarrow -0.44V \\
\text{n=2} \rightarrow \text{Fe} \\
\end{array}
\]

\[ \Delta G^{0}_{\text{Fe}^{3+}/\text{Fe}} = \Delta G^{0}_{\text{Fe}^{3+}/\text{Fe}^{2+}} + \Delta G^{0}_{\text{Fe}^{2+}/\text{Fe}} \]

\[ -3 \times \text{FE}^{0}_{\text{Fe}^{3+}/\text{Fe}} = -1 \times \text{FE}^{0}_{\text{Fe}^{3+}/\text{Fe}^{2+}} + (2 \times \text{FE}^{0}_{\text{Fe}^{2+}/\text{Fe}}) \]

\[ 3 \times x = 1 \times 0.77 + 2 \times (-0.44) \]

\[ x = \frac{0.11}{3} \quad V = -0.04 \text{ V.} \]

\[ \text{(Q)} \quad 2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \quad E^o = -1.23 \text{ V} \]

\[ 4\text{e}^- + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{OH}^- \quad E^o = +0.40 \text{ V} \]

\[ 4\text{H}_2\text{O} \rightarrow 4\text{H}^+ + 4\text{OH}^- \quad E^o = -0.83 \text{ V} \]

\[ \text{(R)} \quad \text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu} \quad E^o = +0.34 \text{ V} \]

\[ 2\text{Cu} \rightarrow 2\text{Cu}^\text{2+} + 2\text{e}^- \quad E^o = -0.52 \text{ V} \]

\[ \text{Cu}^{2+} + \text{Cu} \rightarrow 2\text{Cu}^\text{2+} \quad E^o = -0.18 \text{ V} \]

\[ \text{(S)} \quad \text{Cr}^{3+} \rightarrow \text{Cr}^{2+} \rightarrow \text{Cr} \]

\[
\begin{array}{c}
\text{Cr}^{3+} \rightarrow \frac{x}{n=1} \rightarrow \text{Cr}^{2+} \rightarrow \frac{-0.91V}{n=2} \rightarrow \text{Cr} \\
\end{array}
\]

\[ -0.74V, \quad n = 3 \]

\[ x \times 1 + 2 \times (-0.91) = 3 \times (-0.74) \]

\[ x - 1.82 = -2.22 \Rightarrow x = -0.4 \text{ V} \]

G. Comprehension Based Questions

In the given reaction, Ag ions are reduced to Ag and Glucose is oxidised to gluconic acid as per the given reactions,

\[ \text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}; \quad E^\text{red} = +0.800 \text{ V} \quad \text{and} \]

\[ \text{C}_6\text{H}_12\text{O}_6 + \text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_12\text{O}_7 + 2\text{H}^\text{2+} + 2\text{e}^-; \quad \text{Gluconic acid} \]
2. (a) For the reaction,
\[ \text{C}_6\text{H}_12\text{O}_6 + \text{H}_2\text{O} \longrightarrow \text{C}_6\text{H}_12\text{O}_7^- + 2\text{H}^+ + 2e^- \]
Gluconic acid
\[ E = E^o - \frac{0.0591 \ln [P]}{n} = E^o - \frac{0.0591 \ln (\text{H}^+) \times 2 \ln (\text{pH})}{2} = 0.0591 \times 11 = 0.65 \]

So, \( E^o_\text{oxidation} \) increases over \( E^o_\text{reduction} \) by 0.65 V.

3. (b) During Tollens' test, oxidation of silver ion requires an alkaline medium. Under these conditions it forms insoluble silver oxide, hence to dissolve this oxide a complexing agent, ammonia is added, which brings silver ion as diammoniosilver (I) ion, \([\text{Ag(NH}_3]_2]^-\). It is a soluble complex.

4. (b) Reaction at anode: \( 2\text{Cl}^- \longrightarrow \text{Cl}_2 + 2e^- \)

mole of \( \text{Cl}^- = 4 \times 500 \times 10^{-3} = 2 \)

mole of \( \text{Cl}_2 = \frac{1}{2} = 1 \)

5. (d) 500 ml of 4.0 molar NaCl has 2 mole of NaCl.
By electrolysis we can get a maximum of 2 moles of sodium which can combine with exactly 2 moles of mercury to give amalgam.
\[ \therefore \text{The maximum weight of amalgam which can be formed from this solution} \]
= weight of 2 mole of sodium + weight of 2 mole of mercury = \( 2 \times 23 + 2 \times 200 = 446 \text{g} \)

6. (d) \( \text{Na}^+ + e^- \longrightarrow \text{Na} \)

Total number of moles of \( \text{Na}^+ \) discharged at cathode = 2 mole
\[ \therefore \text{The number of electron required for this purpose} = 2 \text{ mole} \]
\[ \therefore \text{Total charge required} = 2 \times \text{faraday} = 2 \times 96500 = 193000 \text{ coulombs} \]

7. (c) \( 2\text{I}^- + \text{Cl}_2 \longrightarrow \text{I}_2 + 2\text{Cl}^- \)
\[ E^o = E^o^- + E^o_{\text{Cl}_2 / \text{Cl}^-} = -0.54 + 1.36; E^o = 0.82 \text{ V} \]

\( E^o \) is positive hence, iodide ion is oxidized by chlorine.

8. (d) \( 4\text{Mn}^{3+} + 2\text{H}_2\text{O} \longrightarrow 4\text{Mn}^{2+} + \text{O}_2 + 4\text{H}^+ \)
\[ E^o_{\text{Mn}^{3+} / \text{Mn}^{2+}} + E^o_{\text{H}_2\text{O} / \text{O}_2} = 1.50 + (-1.23) = 0.27 \text{ V} \]

Reaction is feasible. \[ \therefore \text{E}^o \text{ is positive} \]

9. (a) The precipitate formed in this reaction is of \( \text{Fe}_5(\text{FeCN})_6)_{\text{L}_3} \)

10. (b) \( \text{M}_{(s)} + \text{M}^{\text{aq}}_{(aq)} \longrightarrow \text{M}^{\text{aq}}_{(aq)0.55} + \text{M}_{(s)} \)
According to Nernst equation,
\[ E_{\text{cell}} = -\frac{2.303RT}{F} \log \frac{\text{M}^{\text{aq}}_{(aq)0.55}}{\text{M}_{(s)}} \]
\[ = -\frac{2.303RT}{F} \log(5 \times 10^{-2}) = +ve \]

Hence, \( |E_{\text{cell}}| = 0.70 \text{ V} \) and \( \Delta G < 0 \) for the feasibility of the reaction.

11. (c) From above equation \[ \frac{2.303RT}{F} = 0.0538 \]
So, \[ E_{\text{cell}} = \frac{E^o_{\text{cell}}}{F} \log 0.0025 \]
\[ = 0 \]
\[ \therefore \text{log} 0.0025 = 0.13988V \approx 140 \text{ mV} \]

12. (d) At anode: \( \text{M}(s) + 2\text{X}^-_{(aq)} \longrightarrow \text{MX}_2_{(aq)} + 2e^- \)
At cathode: \( \text{M}^{2-}_{(aq)} + 2e^- \longrightarrow \text{M}(s) \)
Thus, here \( n = 2 \)
\[ \Delta G = -nF \text{E}_{\text{cell}} \]
\[ = -2 \times 96500 \times 0.059 \times 10^{-3} \text{ kJ/mole} = -11.4 \text{ kJ/mole} \]

13. (b) \[ \text{M}[\text{M}^{2+} _{(aq)} ] \| \text{M}^{2+} _{(aq)} ][\text{M}] \]
\[ 0.001 \text{ M} \]

Anode: \[ \text{M} \longrightarrow \text{M}^{2+} _{(aq)} + 2e^- \]
Cathode: \[ \text{M}^{2+} _{(aq)} + 2e^- \longrightarrow \text{M} \]
\[ \text{E}_{\text{cell}} = -\frac{0.059}{2} \log \left( \frac{\text{M}^{2+} _{(aq)} }{10^{-3}} \right) \]
\[ \Rightarrow 0.059 = -\frac{0.059}{2} \log \left( \frac{\text{M}^{2+} _{(aq)}}{10^{-3}} \right) \]
\[ -2 = \log \left( \frac{\text{M}^{2+} _{(aq)}}{10^{-3}} \right) \]
\[ \Rightarrow \frac{10^{-2} \times 10^{-3} = \text{M}^{2+} _{(aq)} = \text{solubility} = s } \]
\[ K_{sp} = 4s^3 = 4 \times (10^{-5})^3 = 4 \times 10^{-15} \]

**I. Integer Value Correct Type**

1. (4) \( \text{X} \longrightarrow \text{Y} \)
\[ \Delta G^o = -193 \text{ kJ mol}^{-1} \]
\[ \text{M}^+ \longrightarrow \text{M}^{3+} + 2e^- \]
\[ E^o = -0.25 \text{ V} \]
Hence \( \Delta G^o \) for oxidation will be
\[ \Delta G^o = -nFE^o \]
\[ = -2 \times 96500 \times (-0.25) = 48250 \text{ J} = 48.25 \text{ kJ} \]
48.25 kJ energy oxidises one mole \( \text{M}^+ \)
\[ \therefore \text{193 kJ energy oxidises } 193 \text{ mole } \text{M}^+ = 4 \text{ mole } \text{M}^+ \]

2. (3) \( 1 \rightarrow \text{HX} \quad 2 \rightarrow \text{HY} \)
\[ \alpha_1 = \frac{(\lambda_m)_{\text{HX}}}{\lambda_m} \]
\[ \alpha_2 = \frac{(\lambda_m)_{\text{HY}}}{\lambda_m} \]
\[ K_{a1} = C_1 \alpha_1^2 \quad K_{a2} = C_2 \alpha_2^2 \]
\[ = 0.01 \left( \frac{(\lambda_m)_{\text{HX}}}{(\lambda_m)_{\text{HY}}} \right)^2 \]
\[ = 0.1 \left( \frac{(\lambda_m)_{\text{HX}}}{(\lambda_m)_{\text{HY}}} \right)^2 \]
\[ K_{a1} = 0.01 \left( \frac{(\lambda_m)_{\text{HX}}}{(\lambda_m)_{\text{HY}}} \right)^2 \]
\[ K_{a2} = 0.1 \left( \frac{(\lambda_m)_{\text{HX}}}{(\lambda_m)_{\text{HY}}} \right)^2 \]
\[ \therefore \]
Section-B  JEE Main/ AIEEE

1. (b) given \( S \propto \frac{\text{area} \times \text{conc}}{\ell} = \frac{\text{kmol}}{\text{m} \times \text{m}^2} \) \( \therefore \kappa = \text{Smol}^{-1} \)

2. (c) \( E_{\text{cell}} = \text{Reduction potential of cathode (right)} - \text{Reduction potential of anode (left)} \)

3. (b) Oxidation half cell:
\[ \text{H}_2(\text{g}) \longrightarrow 2\text{H}^+(1\text{M}) + 2e^- \]

Reduction half cell:
\[ 2\text{H}^+(1\text{M}) + 2e^- \longrightarrow \text{H}_2(\text{g}) \]

The net cell reaction:
\[ \text{H}_2(\text{g}) \longrightarrow 2\text{H}^+(\text{aq}) \]

\[ E_{\text{cell}} = 0.00 \text{ V} \]
\( n = 2 \)

\[ E_{\text{cell}} = E^0_{\text{cell}} - \frac{RT}{nF} \log K = 0 - \frac{RT}{nF} \log \frac{P_2}{P_1} \]

or \( E_{\text{cell}} = \frac{RT}{2F} \log \frac{P_2}{P_1} \)

4. (a) \( 2\text{Cr}^{3+} + 7\text{H}_2\text{O} \longrightarrow \text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ \)

O.S. of Cr changes from +3 to +6 by loss of electrons.
At anode oxidation takes place.

5. (d) Pure metal always deposits at cathode.

6. (d) \( \text{Zn}^0 + 2\text{Ag}^+ + 2\text{CN}^- \longrightarrow 2\text{Ag}^0 + \text{Zn}^{2+} (\text{CN})_2 \)

The oxidation state shows a change only in (d)

7. (c) The equilibrium constant is related to the standard emf of cell by the expression

\[ \log K = E^0_{\text{cell}} \times \frac{n}{0.059} = 0.295 \times \frac{2}{0.059} \]

\[ \log K = \frac{590}{59} = 10 \text{ or } K = 1 \times 10^{10} \]

8. (d) \( A \quad B \quad C \)

\( +0.5 \text{C} \quad -3 \text{V} \quad -1.2 \text{V} \)

NOTE: The higher the negative value of reduction potential, the more is the reducing power.
Hence \( B > C > A \).

9. (a) When 96500 coulomb of electricity is passed through the electroplating bath the amount of \( \text{Ag} \) deposited is 108g

\( \therefore \) when 9650 coulomb of electricity is passed deposited

\[ = \frac{108}{9650} \times 9650 = 10.8 \text{ g} \]

10. (b) \( E_{\text{cell}} = E^0_{\text{cell}} + \frac{0.059}{n} \log \frac{[\text{Cu}^{2+}]}{[\text{Zn}^{2+}]} \)

\[ = 1.10 + \frac{0.059}{2} \log[0.1] = 1.10 - 0.0295 = 1.07 \text{ V} \]

11. (b) Magnesium provides cathodic protection and prevent rusting or corrosion.

12. (b) In \( \text{H}_2 - \text{O}_2 \) fuel cell, the combustion of \( \text{H}_2 \) occurs to create potential difference between the two electrodes

\[ \text{Fe}^{3+} + e^- \longrightarrow \text{Fe}^{2+} \]

\[ \text{Sn}^{2+} + 2e^- \longrightarrow \text{Sn}^{0} \]

\[
\begin{align*}
\text{Sn}^{2+} + 2e^- & \longrightarrow \text{Sn}^{0} \Delta G^o = -2 \times \text{F}(-0.14) \\
\text{Sn}^{0} + 2\text{Fe}^{3+} (\text{aq}) & \longrightarrow 2\text{Fe}^{2+} (\text{aq}) + \text{Sn}^{2+} (\text{aq}) \\
\end{align*}
\]

\( \therefore \) Standard potential for the given reaction

\[ E_{\text{cell}}^o = E_{\text{Sn}/\text{Sn}^{2+}}^o + E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^o = 0.14 + 0.77 = 0.91 \text{ V} \]

14. (a) \( E_{\text{cell}}^o = E_{\text{cell}}^o - \frac{0.059}{n} \log K_{\text{c}} \)

or \( 0 = 0.591 - \frac{0.0591}{1} \log K_{\text{c}} \)

or \( \log K_{\text{c}} = \frac{0.591}{0.0591} = 10 \text{ or } K_{\text{c}} = 1 \times 10^{10} \)

15. (c) \( \lambda^0 \text{NaCl} = \lambda^0 \text{Na}^+ + \lambda^0 \text{Cl}^- \) .....(i)

\( \lambda^0 \text{KBr} = \lambda^0 \text{K}^+ + \lambda^0 \text{Br}^- \) .....(ii)

\( \lambda^0 \text{KCl} = \lambda^0 \text{K}^+ + \lambda^0 \text{Cl}^- \) .....(iii)

operating (i) + (ii) - (iii)

\( \lambda^0 \text{NaBr} = \lambda^0 \text{Na}^+ + \lambda^0 \text{Br}^- \)

\[ = 126 + 152 - 150 = 128 \text{ S cm}^2 \text{ mol}^{-1} \]

16. (a) \( \text{Zn}(s) + 2\text{H}^+ (aq) \longrightarrow \text{Zn}^{2+} (aq) + \text{H}_2 (g) \)

\[ E_{\text{cell}} = E_{\text{cell}}^o - \frac{0.059}{2} \log \frac{[\text{Zn}^{2+}][\text{H}_2]}{[\text{H}^+]^2} \]

Addition of \( \text{H}_2\text{SO}_4 \) will increase [\( \text{H}^+ \)] and \( E_{\text{cell}} \) will also increase and the equilibrium will shift towards RHS

17. (c) The given values show that Cr has maximum oxidation potential, therefore its oxidation will be easiest. (Change the sign to get the oxidation values)

18. (d) NOTE: For spontaneous reaction \( \Delta G \) should be negative. Equilibrium constant should be more than one

\( \Delta G = -2.303 \text{RT} \log K_{\text{c}} \) \( \text{If } K_{\text{c}} = 1 \text{ then } \Delta G = 0; \text{If } K_{\text{c}} < 1 \text{ then } \Delta G = +ve \).

Again \( \Delta G = -nE_{\text{cell}}^o \).

\( E_{\text{cell}}^o \) must be +ve to have \( \Delta G \) -ve.
19. (a) Thus difluoro acetic acid being strongest acid will furnish maximum number of ions showing highest electrical conductivity. The decreasing acidic strength of the carboxylic acids given is difluoro acetic acid > fluoro acetic acid > chloro acetic acid > acetic acid.

20. (d) 1 mole of e⁻ = 1F = 96500 C
27 g of Al is deposited by 3 x 96500 C
5120 g of Al will be deposited by

\[
\frac{3 \times 96500 \times 5120}{27} = 5.49 \times 10^7 C
\]

21. (b) \( \Lambda_{HCl}^\infty = 426.2 \)

(ii) \( \Lambda_{AcO\text{Na}}^\infty = 91.0 \)

(iii) \( \Lambda_{NaCl}^\infty = 126.5 \)

\( \Lambda_{AcOH}^\infty = (i) + (ii) - (iii) = [426.2 + 91.0 - 126.5] = 390.7 \)

22. (c) \( 2\text{HI}^{-} + \text{H}_2\text{SO}_4 \rightarrow \text{I}_2 + \text{SO}_2 + 2\text{H}_2\text{O} \) in this reaction oxidation number of S is decreasing from +6 to +4 hence undergoing reduction and for HI oxidation Number of I is increasing from -1 to 0 hence undergoing oxidation therefore \( \text{H}_2\text{SO}_4 \) is acting as oxidising agent.

23. (b) \( \Lambda_{CH_{3}COOH}^\infty \) is given by the following equation

\[
\Lambda_{CH_{3}COOH}^\infty = \left( \Lambda_{CH_{3}COO\text{Na}}^\infty + \Lambda_{HCl}^\infty \right) - \left( \Lambda_{NaCl}^\infty \right)
\]

Hence \( \Lambda_{NaCl}^\infty \) is required.

24. (b) \( R = 100 \Omega \), \( \kappa = \frac{1}{R} \times \frac{1}{a} \) (cell constant) = 1.29 x 100 m⁻¹

Given, \( R = 520 \Omega \), \( C = 0.2 \text{ M} \), \( \mu \) (molar conductivity) = ?

\( \mu = \kappa \times V \) (can be calculated as \( \kappa = \frac{1}{R} \) \( \frac{1}{a} \))

Hence, \( \mu = \frac{1}{520} \times 129 \times \frac{1000}{0.2} \times 10^{-6} \text{ m}^3 = 12.4 \times 10^{-4} \text{Sm} \text{mol}^{-1} \)

25. (b) \( \text{NOTE} : \) According to Kohlrausch’s law, molar conductivity of weak electrolyte acetic acid (CH₃COOH) can be calculated as follows:

\( \Lambda_{CH_{3}COOH}^\infty = \left( \Lambda_{CH_{3}COO\text{Na}}^\infty + \Lambda_{HCl}^\infty \right) - \Lambda_{NaCl}^\infty \)

\( \therefore \) Value of \( \Lambda_{NaCl}^\infty \) should also be known for calculating value of \( \Lambda_{CH_{3}COOH}^\infty \).

26. (d) \( E_{cell} = 0 \); when cell is completely discharged.

\[
E_{cell} = E^\infty - \frac{0.059}{2} \log \left( \frac{Zn^{2+}}{Cu^{2+}} \right)
\]

or \( 0 = 1.1 - \frac{0.059}{2} \log \left( \frac{Zn^{2+}}{Cu^{2+}} \right) \)

\[
\log \left( \frac{Zn^{2+}}{Cu^{2+}} \right) = \frac{2 \times 1.1 - 0.059}{0.059} = 37.3 \therefore \left( \frac{Zn^{2+}}{Cu^{2+}} \right) = 10^{37.3}
\]

27. (d) From the given representation of the cell, \( E_{cell} \) can be found as follows.

\[
E_{cell} = E^\infty_{Fe^{2+}/Fe} - E^\infty_{Cr^{3+}/Cr} - \frac{0.059}{6} \log \left( \frac{[Cr^{3+}]^2}{[Fe^{2+}]^3} \right)
\]

[Nernst-Equation]

\[
= -0.42 - (-0.72) - \frac{0.059}{6} \log \frac{(0.1)^2}{(0.01)^3}
\]

\[
= -0.42 + 0.72 - \frac{0.059}{6} \log \frac{0.1 \times 0.1}{0.01 \times 0.01 \times 0.01}
\]

\[
= 0.3 - \frac{0.059}{6} \log \frac{10^{-2}}{10^{-6}} = 0.3 - \frac{0.059}{6} \times 4
\]

\[
= 0.30 - 0.0393 = 0.26 \text{ V}
\]

Hence option (d) is correct answer.

28. (c) \( CH_{3}OH(l) + \frac{3}{2} O_2(g) \rightarrow CO_2(g) + 2H_2O(l) \)

\[
\Delta G = \Delta G_f(CO_2,g) + 2\Delta G_f(H_2O,l) - \Delta G_f(CH_3OH,l) - \frac{3}{2} \Delta G_f(O_2,g)
\]

\[
= -394.4 + 2(-237.2) = 166.2 - 0
\]

\[
= -394.4 - 474.4 + 166.2 = -702.6 \text{ kJ}
\]

% efficiency = \( \frac{702.6}{726} \times 100 = 97\% \)

29. (b) Given

\( Fe^{3+} + 3e^- \rightarrow Fe \), \( E^\infty_{Fe^{3+}/Fe} = -0.036 \text{ V} \) (i)

\( Fe^{2+} + 2e^- \rightarrow Fe \), \( E^\infty_{Fe^{2+}/Fe} = -0.439 \text{ V} \) (ii)

we have to calculate

\( Fe^{3+} + e^- \rightarrow Fe^{2+} \), \( \Delta G = ? \)

To obtain this equation subtract (ii) from (i) we get

\( Fe^{3+} + e^- \rightarrow Fe^{2+} \) (iii)

As we know that \( \Delta G = -nFE \)

Thus for reaction (iii)

\( \Delta G = \Delta G_1 - \Delta G = -nF \) \( E^\circ = -0.770 \text{ V} \)

\( O^{2-} > F^- > Na^+ > Mg^{++} > Al^{3+} \)
30. (c) $\Delta G = -nFE$

or $E = \frac{\Delta G}{-nF} = \frac{966 \times 10^3}{4 \times 96500} = -2.5 \text{ V}$

$\therefore$ The potential difference needed for the reduction is 2.5 V.

31. (a) The value of $E^\circ_{\text{Mn}^{2+}/\text{Mn}}$ for given metal ions are

$E^\circ_{\text{Mn}^{2+}/\text{Mn}} = -1.18 \text{ V}$, $E^\circ_{\text{Cr}^{2+}/\text{Cr}} = -0.9 \text{ V}$,

$E^\circ_{\text{Fe}^{2+}/\text{Fe}} = -0.44 \text{ V}$ and $E^\circ_{\text{Co}^{2+}/\text{Co}} = -0.28 \text{ V}$.

The correct order of $E^\circ_{\text{M}^{2+}/\text{M}}$ values without considering negative sign would be

$\text{Mn}^{2+} > \text{Cr}^{2+} > \text{Fe}^{2+} > \text{Co}^{2+}$.

32. (c) $\text{H}^+ + \text{e}^- \rightarrow \frac{1}{2} \text{H}_2$; $E = E^\circ - \frac{0.059}{1} \log \frac{P_{\text{H}_2}^{1/2}}{[\text{H}^+]}$

Now if $P_{\text{H}_2} = 2 \text{ atm}$ and $[\text{H}^+] = 1\text{ M}$

then $E = 0 - \frac{0.059}{1} \log \frac{2^{1/2}}{1} = -2$

33. (d) For a spontaneous reaction $\Delta G$ must be $-ve$

Since $\Delta G = -nFE^\circ$

Hence for $\Delta G$ to be $-ve$, $\Delta E^\circ$ has to be positive. Which is possible when $X = \text{Zn}$, $Y = \text{Ni}$

$\text{Zn} + \text{Ni}^{++} \rightarrow \text{Zn}^{++} + \text{Ni}$

$E^\circ_{\text{Zn}/\text{Zn}^{2+}} + E^\circ_{\text{Ni}^{2+}/\text{Ni}} = 0.76 + (-0.23) = +0.53$

(positive)

34. (d) The higher the value of standard reduction potential stronger will be the oxidising agent, hence MnO$_4^-$ is the strongest oxidising agent.

35. (a) Given for 0.2 M solution

$R = 50 \Omega$

$\kappa = 1.4 \text{ S m}^{-1} = 1.4 \times 10^{-2} \text{ S cm}^{-1}$

Now, $R = \rho \frac{\ell}{a} = \frac{1}{\kappa} \frac{\ell}{a}$

36. (a) (i) $\text{Mn}^{2+} + 2\text{e}^- \rightarrow \text{Mn}$; $E^\circ = -1.18 \text{ V}$

(b) $\text{Mn}^{3+} + \text{e}^- \rightarrow \text{Mn}^{2+}$; $E^\circ = -1.51 \text{ V}$

Now multiplying equation (ii) by two and subtracting from equation (i)

$3\text{Mn}^{2+} \rightarrow \text{Mn}^{3+} + 2\text{Mn}^{3+}$;

$E^\circ = E_{\text{Ox}} + E_{\text{Red}} = -1.18 + (-1.51) = -2.69 \text{ V}$

$[-ve$ value of EMF (i.e., $\Delta G = +ve$) shows that the reaction is non-spontaneous$]$

37. (c) According to Debyes Huckle onsager equation,

$\lambda_C = \lambda_{\infty} - B\sqrt{C}$

38. (d) $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$

2F i.e. $2 \times 96500 \text{ C deposit Cu} = 1 \text{ mol} = 63.5 \text{ g}$

39. (b) Galvanization is the process by which zinc is coated over corrosive (easily rusted) metals to prevent them from corrosion.
Chemical Kinetics & Nuclear Chemistry

Section-A: JEE Advanced/ IIT-JEE

A 1. $A^{-4}_M$ 2. Product of active masses of reactants at that temperature
3. 8 4. acidic, first (or basic, second) 5. isotope
6. $1.765 \times 10^{-4}$ kg/hr 7. very high temperature or zero activation energy


C 1. (b) 2. (a) 3. (d) 4. (c) 5. (d) 6. (d) 7. (b) 8. (b) 9. (d) 10. (d)
11. (b) 12. (a) 13. (c) 14. (a) 15. (c) 16. (d) 17. (b) 18. (d) 19. (c) 20. (a)
21. (d) 22. (a) 23. (d) 24. (d) 25. (b)

D 1. (b, c) 2. (b, c) 3. (a, d) 4. (a, d) 5. (a, b, d) 6. (a, b, d) 7. (a, b) 8. (b, c, d) 9. (b, d)

E 1. 1.0, 1.386 min 2. $1.2 \times 10^{-4}$ yrs$^{-1}$, 1/4 3. first order
4. 7.6 5. 5.2%, 128.33 hours 6. 0.0231 min$^{-1}$, 43.848 kJ mol$^{-1}$ 7. $3.451 \times 10^{-18}$ mol
8. 311.35 K 9. $5.2 \times 10^{-3}$ min$^{-1}$ 10. $3.267 \times 10^{-2}$ min$^{-1}$ 11. 5.624 x $10^{5}$ atoms
12. 67.17% 13. 0.749 atm 14. (i) 2, (ii) 1.2 M, (iii) 0.1 mol/l/hr
15. (i) 2, 1; (ii) $2.66 \times 10^{8}$ mol$^{-2}$ P$^{-1}$ s$^{-1}$; (iii) $5.54 \times 10^{4}$ J; (iv) $1.175 \times 10^{18}$ P$^{-2}$ mol$^{-2}$ sec
16. 0.061 µg
17. 20.34 min 18. $3.81 \times 10^{4}$ yr$^{-1}$, 3.14 x $10^{-2}$ yr$^{-1}$ 19. $6.07 \times 10^{6}$
20. (i) 239 kJ mol$^{-1}$, (ii) 669 K 22. $5.42 \times 10^{10}$ sec$^{-1}$, 2.2 x $10^{4}$ mol$^{-1}$
23. $3.4354 \times 10^{-3}$ M min$^{-1}$ 24. $7.097 \times 10^{8}$ yrs 25. 100 kJ mol$^{-1}$
26. 24.14 min 27. $1.005 \times 10^{-4}$ min$^{-1}$ 29. (a) $R_0 = k [A_0]$; (b) 0.5 sec$^{-1}$
31. (i) 1, (ii) 6.93 x $10^{-3}$ min$^{-1}$, (iii) 200 min, (iv) 950 mm Hg

F 1. (c) 2. (b) 3. (a)

G 1. (a)

H 1. (a)

I 1. 8 2. 5 3. 3 4. 9 5. 8 6. 9 7. 8

Section-B: JEE Main/ AIEEE

1. (a) 2. (b) 3. (d) 4. (d) 5. (a) 6. (c) 7. (b)
8. (d) 9. (b) 10. (c) 11. (b) 12. (c) 13. (d) 14. (b)
15. (a) 16. (b) 17. (d) 18. (d) 19. (b) 20. (c) 21. (a)
22. (c) 23. (c) 24. (b) 25. (a) 26. (b) 27. (a) 28. (b)
29. (b) 30. (b) 31. (c) 32. (d) 33. (c) 34. (b) 35. (a)
36. (d) 37. (c) 38. (d)
Section-A

A. Fill in the Blanks

1. **TIPS/Formulae:**
   When an element emits \( \alpha \)-particle atomic mass decreases by four and atomic number decreases by two. Loss of \( \beta \)-particle results in increase in atomic number by 1 and no change in atomic mass.

\[
\begin{array}{cccc}
\text{A} & \text{M} & \xrightarrow{\alpha} & \text{A-4} & \text{X} & \xrightarrow{\beta} & \text{A-4} & \text{Y} & \xrightarrow{\beta} & \text{A-4} & \text{M} \\
\text{Z} & & & & & & & & & & \text{Z-2} & & & & & & & & & & \text{Z-1} & & & & & & & & & & \text{Z} \\
\end{array}
\]

2. **Product of active masses of reactants at that time**

3. **8; \text{ }^{14}_6\text{C} \rightarrow ^{14}_7\text{N} + ^{0}_1\text{e} \text{ i.e. 2 particles. }**

**NOTE:** Due to emission of the \( \beta \) particle atomic number increases by 1.

4. **acidic, first (or basic, second).**

5. **Isotope:** (because new atom has same atomic number but different atomic mass). [Refer to Q. 1 above]

6. **1.765 \times 10^{-4} \text{ kg/hr;}**

\[
\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})
\]

Here Rate of reaction = \( \frac{1}{3} \) [Rate of disappearance of \( \text{H}_2 \)] = \[ \frac{1}{2} \] [Rate of appearance of \( \text{NH}_3 \)]

or \[ \frac{1}{3} \frac{\text{d}[\text{H}_2]}{\text{dt}} = \frac{1}{2} \frac{\text{d}[\text{NH}_3]}{\text{dt}} \Rightarrow \frac{\text{d}[\text{H}_2]}{\text{dt}} = \frac{3}{2} \frac{\text{d}[\text{NH}_3]}{\text{dt}} \]

\[ \frac{\text{d}[\text{NH}_3]}{\text{dt}} = 0.01 \text{ kg/hr} = \frac{0.001}{17} \times 1000 = \frac{1}{17} \text{ mole/hr} \]

\[ \therefore \frac{\text{d}[\text{H}_2]}{\text{dt}} = \frac{1}{17} \times \frac{3}{2} = \frac{3}{34} \text{ mole/hr} = \frac{3}{34} \times 2 \times 1000 = 1.765 \times 10^{-4} \text{ kg/hr} \]

7. **very high temperature** (T\( \approx \)\( \infty \)) or zero activation energy.

B. True/False

1. **True:** The rate of reaction of first order is directly proportional to the concentration of reacting substance.

2. **False:** Catalyst does not make a reaction more exothermic, but decreases the activation energy and hence increase the rate of reaction.

3. **False:** Catalyst lowers the energy of activation and therefore influences the rate as well as rate constant of the reaction.

4. **False:** In \( \beta \)-emission \((-1e^0\) the atomic number of the daughter nuclei increases by 1.

5. **True:** The rate of a reaction increases with increase in temperature because at higher temperature more number of molecules attain the activation energy.

C. MCQs with One Correct Answer

1. **(b)** \( _{92}^{238}\text{U} \rightarrow _{90}^{234}\text{U} + _{2}^{4}\text{He} \) (\( \alpha \)-particle)

2. **(a)** It is a constant of a particular reaction at a given temperature. It does not depend upon initial concentration of the reactants, time of reaction and extent of reaction.

3. **(d)** It is a characteristic constant of a particular reaction at a given temperature. It does not depend upon initial concentration of the reactants, time of reaction and extent of reaction.

4. **(c)** A catalyst decreases the activation energy of the reactants and thus shortens time of reaction. So (c) is the correct option.

5. **(d)** **NOTE:** \( \alpha \)- and \( \beta \)-rays, made up of positively & negatively charged particles and are deflected by a magnetic field in opposite directions; \( \gamma \)-rays remain undeflected. (as they do not have charge).

6. **(d)** **TIPS/Formulae:**

\[ N = N_0 \left( \frac{1}{2} \right)^n \]

where, \( N \) = Amount of radioactive substance which is left after certain number of half-life periods \( (n) \)

\( N_0 \) = Initial amount of radioactive substance.

No. of half-lives = \[ \frac{\text{total time}}{\text{half life period}} = \frac{560}{140} = 4 \]

In ‘n’ half-lives, the element will reduce to

\[ \left( \frac{1}{2} \right)^n \times \text{Initial wt.} = \left( \frac{1}{2} \right)^4 \times 1 = \frac{1}{16} \text{ g} \]

7. **(b)** The Arrhenius equation is: \( k = A \exp \left(-E_a/RT\right) \)

As \( T \rightarrow \infty \), \( \exp \left(-E_a/RT\right) \rightarrow 1 \). Hence, \( k = A \) where \( A \), the Arrhenius parameter, is \( 6.0 \times 10^{14} \text{ s}^{-1} \) [\( \text{NOTE : } 'A' \text{ is also known as frequency factor} \)]

8. **(b)** The species \( _{13}^{29}\text{Al} \) (No. of neutrons = 16) contains more neutrons than the stable isotope \( _{13}^{27}\text{Al} \) (No. of neutrons = 14).

Neutron on decomposition shows \( \beta \)-emission.

\[ _0^n\text{p} \rightarrow _{-1}^0\text{e} + _{0}^1\text{n} \]

9. **(d)** **TIPS/Formulae:**

The sum of mass number and atomic numbers of reactants = The sum of mass number and atomic no. of products in a nuclear reaction.

The given nuclear fission reaction is

\[ _{92}^{235}\text{U} + _0^1\text{n} \rightarrow _{54}^{139}\text{Xe} + _{38}^{94}\text{Sr} + 3_0^1\text{n} \]
10. (d) **TIPS/Formulae**:

Find the order of reaction and then use appropriate equation.

As unit of \( k \) is \( \text{sec}^{-1} \), reaction is of **first order**, \( r = k[N_2O_5] \).

\[
[N_2O_5] = \frac{2.4 \times 10^{-5}}{3 \times 10^{-5}} = 0.8 \text{ mol/L}
\]

11. (b) **NOTE**: The rate of photochemical process varies with the intensity of absorption.

Since greater the intensity of absorbed light more photons will fall at a point, and further each photon causes one molecule to undergo reaction.

12. (a) **NOTE**: Individual rates of reactants and products become equal when each of these is divided by their respective stoichiometric coefficient. With time concentration of reactants decreases and is represented by negative sign whereas concentration of products increases and is represented by positive sign.

The given reaction is:

\( N_2(g) + 3H_2(g) \rightarrow 2NH_3(g) \)

\( \therefore \) Correct relationship amongst the rate expression is shown in (a)

13. (c) **TIPS/Formulae**:

\[
k = \frac{2.303 \log [A]_0}{t} = \frac{800}{50} = 1.386 \times 10^{-4} \text{ s}^{-1}
\]

14. (a) \( n/p \) ratio of \( ^{24}\text{Na} \) nuclide is 13/11 i.e. greater than unity and hence \( ^{24}\text{Na} \) is radioactive. To achieve stability, it would tend to adjust its n/p ratio to the proper value of unity. This can be done by breaking a neutron into proton and electron.

\( \beta^+ \rightarrow p^+ + \: \: e^- \) or \( \beta^- \)

**NOTE**: The proton will stay inside the nucleus whereas electron which cannot exist in the nucleus, will be emitted out as \( \beta^- \) ray.

15. (c) **TIPS/Formulae**:

For first order reaction,

Rate \( = k \) [conc. of reactant]

Since 0.1 M of \( X \) changes to 0.025 M in 40 minutes,

\( t_{1/2} \) of reaction = 40/2 = 20 minutes

Rate of reaction of \( X = k[X] = \frac{0.693}{t_{1/2}} \times [X] = \frac{0.693}{20} \times 0.01 \)

\( = 3.47 \times 10^{-4} \text{ M min}^{-1} \)

16. (d) Order of a reaction can be fractional. Rest of all are true.

[**NOTE**: Order of a reaction can be determined experimentally]

17. (b) The required reaction is

\( \text{Ag}^+ + 2\text{NH}_3 \rightleftharpoons [\text{Ag(NH}_3)_2]^+ \); \( K = ? \)

From the given equations, we have

\[
k_1 = \frac{[\text{Ag(NH}_3)_2]^+}{[\text{Ag}^+][\text{NH}_3]} \quad \text{and} \quad k_2 = \frac{[\text{Ag(NH}_3)_2]^+}{[\text{Ag(NH}_3)_2]^+}[\text{NH}_3]
\]

\( \therefore \) The value of \( K \) is given by \( K = k_1 \times k_2 = 6.8 \times 10^{-3} \times 1.6 \times 10^{-3} = 1.08 \times 10^{-5} \).

18. (d) **TIPS/Formulae**:

Overall order = sum of orders w.r.t each reactant.

Let the order be \( x \) and \( y \) for \( G \) and \( H \) respectively.

<table>
<thead>
<tr>
<th>Exp.No.</th>
<th>([G]) mole litre(^{-1})</th>
<th>([H]) mole litre(^{-1})</th>
<th>rate(mole litre(^{-1}) time(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( a )</td>
<td>( b )</td>
<td>( r )</td>
</tr>
<tr>
<td>2</td>
<td>( 2a )</td>
<td>( 2b )</td>
<td>( 8r )</td>
</tr>
<tr>
<td>3</td>
<td>( 2a )</td>
<td>( b )</td>
<td>( 2r )</td>
</tr>
</tbody>
</table>

Applying \( r = k \) \([G]^x \) \([H]^y \) we get, \( x = 1, y = 2 \)

\( \therefore \) For (1) and (3), the rate is doubled when conc. of \( G \) is doubled keeping that of \( H \) constant i.e., rate \( \propto [G] \)

\( \therefore \) \( x = 1 \)

From (2) and (3), \( y = 2 \); \( \therefore \) Overall order is 3.

19. (c) \( _{23}^{11}\text{Na} \rightarrow _{10}^{23}\text{X} + _{1}^{0}\beta \)

20. (a) The values of rate constants \( k_p, k_n \) for zero order and first order reaction, respectively, are given by the following equation:

\[
k_0 = \frac{A_0}{2 \times t_{1/2}} \quad \text{[where} \ A_0 \text{= initial concentration, and} \ t_{1/2} \text{= half-life period]}
\]

and \( k_1 = \frac{0.693}{t_{1/2}} \)

substituting various given values, we get

\[
k_0 = \frac{1.386 \text{ mol litre}^{-1}}{2 \times 20 \text{ sec}} \quad \text{... (i)}
\]

and \( k_1 = \frac{0.693}{40 \text{ sec}} \quad \text{... (ii)}
\]

Dividing (ii) by (i), we get

\[
\frac{k_1}{k_0} = \frac{0.693}{40} \times \frac{2 \times 20}{1.386} \text{ mol}^{-1} \text{ litre}
\]

\[= 0.5 \text{ mol}^{-1} \text{ litre} = 0.5 \text{ mol}^{-1} \text{ dm}^{-3} \quad [1 \text{ litre} = 1 \text{ dm}^3]
\]

Thus the correct answer is (a).

21. (d) \( \log k = \log A - \frac{E_a}{2.303RT} \quad \text{... (i)} \)
Also given \( \log k = 6.0 - (2000) \frac{1}{T} \) \( \ldots(2) \)

On comparing equations, (1) and (2)

\[ \log A = 6.0 \Rightarrow A = 10^{6} \text{s}^{-1} \]

and \( \frac{E_a}{2.303 R} = 2000 \); 

\[ \Rightarrow E_a = 2000 \times 2.303 \times 8.314 = 38.29 \text{ kJ mol}^{-1} \]

22. (a) As per Arrhenius equation \( (k = Ae^{-E_a/RT}) \), the rate constant increases exponentially with temperature.

23. (a) \[ 13\text{Al}^{27} + 2\alpha = 14\text{Si}^{30} + \frac{1}{2}\text{P}^{1} \] (X)

\[ 13\text{Al}^{27} + 2\alpha = 15\text{P}^{30} + 0\text{n} \] (Y)

\[ 15\text{P}^{30} = 14\text{Si}^{31} + 1\beta \] (Z)

24. (d) For P, if \( \frac{1}{50}\% = x \) then \( \frac{1}{75}\% = 2x \)

This is true only for first order reaction.

So, order with respect to P is 1.

Further the graph shows that concentration of Q decreases with time. So, rate, with respect to Q, remains constant. Hence, it is zero order w.r.t Q.

So, overall order is \( 1 + 0 = 1 \)

25. (b) \( M \rightarrow N \)

\[ r = k [M]^x \]

when \( M = 2M; r = 8r \), thus

\[ 8 = k[2M]^x \]

\[ 8 = (2)^x \]

\[ x = 3 \]

D. MCQs with One or More Than One Correct

1. (b, c) A catalyst provides a new path of lower activation energy. The catalyst reacts with the reactants to form an intermediate of low activation energy. The intermediate then decomposes to form the products along with regeneration of catalyst. Thus the reaction mechanism changes completely.

2. (b, c) As rate \( = k [\text{RCI}] \), so it is first order reaction. On decreasing the concentration of RCI to half, the rate will also be halved. Rate will also increase with temperature.

3. (a, d) TIPS/Formulae:

Balance various given nuclear reactions.

(a) \( 13\text{Al}^{27} + 2\he^{4} \rightarrow 15\text{P}^{30} + 0\text{n} \)

(d) \( 96\text{Am}^{241} + 2\he^{4} \rightarrow 97\text{Bk}^{244} + 1\text{e}^{0} + 0\text{n} \)

4. (a, d) In first order reaction, if \( \alpha \) is the degree of dissociation then

\[ kt = \log_{e} \frac{1}{(1 - \alpha)} = -\log_{e} (1 - \alpha) \text{ or } e^{-kt} = 1 - \alpha \]

\[ \therefore \alpha = 1 - e^{-kt} \]

The Arrhenius equation is, \( k = Ae^{-E_a/RT} \)

Plot of reciprocal concentration of the reactant vs time is linear. Dimensions of pre-exponential factor \( \theta A' \) are equivalent to dimensions of \( k \), which is \( T^{-1} \) for a first order reaction.

5. (a, b, d) The relevant expressions are as follows.

Choice (a) \( \log K_p = -\frac{\Delta H}{R} \frac{1}{T} + l \)

Choice (b) \( \log [X] = \log [X]^0 + k t \)

Choice (c) \( PT = \text{constant } (V \text{ constant}) \)

Choice (d) \( PV = \text{constant } (T \text{ constant}) \)

6. (a, b, d) For first order reaction

\[ [A] = [A]^0 e^{-kt} \]

Hence concentration of \([\text{NO}_2] \) decreases exponentially.

Also, \( t_{1/2} = \frac{0.693}{K} \). Which is independent of concentration and \( t_{1/2} \) decreases with the increase of temperature.

\[ t_{99.6} = \frac{2.303}{K} \log \left( \frac{100}{0.4} \right) \]

\[ t_{99.6} = \frac{2.303}{K} (2.4) = 8 \times \frac{0.693}{K} = 8 t_{1/2} \]

7. (a, b) The reaction can occur by following two ways.

\[ \frac{9}{4}\text{Be} + \gamma \rightarrow \frac{8}{4}\text{Be} + \frac{0}{4}\text{n} \quad \frac{9}{4}\text{Be} + \frac{1}{4}\text{H} \rightarrow \frac{5}{4}\text{H} + \frac{4}{4}\text{Be} \]

8. (b, c, d)

(A) High activation energy usually implies a slow reaction.

(B) Rate constant of a reaction increases with increase in temperature due to increase in number of collisions whose energy exceeds the activation energy.

(C) \( k = P \times Z \times e^{-E_a/RT} \)

(D) So, pre-exponential factor \( (A) = P \times Z \) and it is independent of activation energy or energy of molecules.

9. (b, d) When N/P ratio is less than one, then proton changes into neutron.

Position emission: \( \frac{1}{4}\text{H} \rightarrow \frac{0}{4}\text{n} + \frac{1}{0}\beta \)

k-electron capture: \( \frac{1}{4}\text{H} + \frac{0}{0}\text{e} \rightarrow \frac{0}{4}\text{n} + \text{X-rays} \)

E. Subjective Problems

1. From data (i) and (ii) it is obvious that when the concentration of \( B \) is kept constant (0.01 mol litre\(^{-1}\)) and the concentration of \( A \) is doubled (0.01 to 0.02 mol litre\(^{-1}\)), the rate of reaction is also doubled (0.005 to 0.010 mol litre\(^{-1}\) min\(^{-1}\)). This shows that the rate of reaction varies directly as the first power of the concentration. Hence the order of reaction with respect to \( A \) is 1.

Similarly, from data (i) and (iii) it is obvious that when the concentration of \( A \) is kept constant (0.01 mol litre\(^{-1}\)) and the concentration of \( B \) doubled (0.01 to 0.02 mol litre\(^{-1}\)), the rate of reaction remains constant (0.005 mol litre\(^{-1}\) min\(^{-1}\)). This shows that the order of reaction with respect to \( B \) is zero.

Now we know that the rate of reaction, \( A + B \rightarrow \) Products, is given by

\[ \text{Rate } r = k [A][B]^0 \Rightarrow r = k [A] \]
Chemical Kinetics & Nuclear Chemistry

2. TIPS/Formulae:

\[ N = N_0 \left( \frac{1}{2} \right)^n \]

Half-life, \( t_{1/2} = 5770 \) years
Let the original sample be 1 gram.
\[ \therefore \text{After every } 5770 \text{ years one-half of radioactive carbon would decay or disintegrate.} \]
Thus, 1 g sample becomes \( \frac{1}{2} \) g after 5770 years and
\[ \frac{1}{2} \times \frac{1}{2} = \frac{1}{4} \text{ left after } 11,540 \text{ years.} \]
\[ \therefore 25\% \text{ of radioactive carbon remains after } 11540 \text{ years.} \]
Rate constant, \( k \) for first order reaction,

\[ k = \frac{0.693}{t_{1/2}} = \frac{0.693}{5770} = 1.2 \times 10^{-4} \text{ year}^{-1}. \]

3. Assuming that the decomposition of \( \text{N}_2\text{O}_3 \) is a first order reaction, then

\[ k \frac{2.303}{t} \log \frac{a}{(a-x)} = \frac{2.303}{t} \log \frac{P_0}{P} \]

or \( \log P = \frac{-kt}{2.303} + \log P_0 \)

Thus \( \log P \) vs time graph is linear with slope \( \frac{-k}{2.303} \) if the given reaction is of first order which is in accordance with the given statement. Thus the reaction obeys first order reaction.

4. \( ^{234}_{90}\text{Th} \rightarrow ^{206}_{82}\text{Pb} \)

**NOTE:** For emission of one \( \alpha \)-particle, atomic mass decreases by 4 and atomic number by 2. Further for the emission of one \( \beta \)-particle, the atomic mass does not change but the atomic number increases by 1.
So we first find the \( \alpha \)-particles:
Decrease in atomic mass = 234 – 206 = 28

No. of \( \alpha \)-particles emitted = \( \frac{28}{4} \) = 7

Hence, atomic number should have decrease to 90 – (7 x 2) = 76
Now, atomic number of Pb = 82, which is more by (82 – 76) = 6
This increase is due to ionisation of \( \beta \)-particles.
Therefore, \( \beta \)-particles emitted = 6

5. TIPS/Formulae:

For a first order reaction we know that

\[ k = \frac{2.303}{t} \log \frac{a}{(a-x)} \]

Here, \( t = 10 \times 60 \times 60 \text{ sec. and let } a = 1 \), then substituting the values, we get

\[ 1.5 \times 10^{-6} = \frac{2.303 \times 10 \times 3600 \log \frac{1}{(1-x)}}{10 \times 3600} \]

\[ 1.5 \times 10^{-6} \times \frac{10 \times 3600}{2.303} = \log \frac{1}{(1-x)} \]

\[ 0.0234 = \log \frac{1}{(1-x)} \]

Taking antilog, \( 1.055 = \frac{1}{(1-x)} \)

or \( 1.055 - 1.055x = 1 \Rightarrow x = \frac{(1.055 - 1)}{1.055} = 0.052 \)

Thus, 5.2% of the initial concentration has changed into product.
Again we know that

\[ t_{1/2} = \frac{0.693}{k} = \frac{0.693}{1.5 \times 10^{-6}} = 462000 \text{ second} = 128.33 \text{ hours} \]

6. TIPS/Formulae:

\[ k = \frac{0.693}{t_{1/2}} ; \frac{k_1}{k_2} = \frac{E_a}{2.303R} \left[ \frac{T_2 - T_1}{T_1 T_2} \right] \]

Substituting the value at the two given conditions

\[ k_{27} = \frac{0.693}{30} = 0.0231 \text{ min}^{-1} ; k_{47} = \frac{0.693}{10} = 0.0693 \text{ min}^{-1} \]

We also know that log

\[ \frac{k_{47}}{k_{27}} = \frac{E_a}{2.303R} \times \frac{T_2 - T_1}{T_1 T_2} \]

or \( E_a = \frac{2.303 \times R \times T_2 \times \log \frac{k_{47}}{k_{27}}}{T_2 - T_1} \)

\[ = \frac{2.303 \times 8.314 \times 10^{-3} \times 300 \times 320}{320 - 300} \times \log \frac{0.0693}{0.0231} \]

\[ = 43.848 \text{ kJ mol}^{-1} \]

7. Minimum number of \( \beta \)-particles required in one minute = 346

No. of \( \beta \)-particles required for carrying out the experiment for 6.909 x 60 minutes = 346 x 6.909 x 60 = 143431
\[ \therefore \text{Amount of } \beta \text{-particles required} \]

\[ = \frac{143431}{6.023 \times 10^{23}} = 2.3814 \times 10^{-19} \text{ mol} \]

Now we know that, \( \lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{66.6} = 0.0104 \text{ hr}^{-1} \)
Further we know that, 
\[ \lambda = \frac{2.303}{t} \log \frac{a}{a-x} \]
where \( a \) = Initial concentration of \( \beta \)-particles
\( x \) = Consumed concentration of \( \beta \)-particles
\[ \log \frac{a-x}{a} = -\frac{\lambda t}{2.303} = -\frac{0.0104 \times 6.909}{2.303} = -0.0312 \]
\[ = 1.9688 \]
or \[ \frac{a-x}{a} = 0.931 \quad [\text{Taking antilog}] \]
or \[ \frac{a-2.3814 \times 10^{-19}}{a} = 0.931 \quad [:: x=2.3814 \times 10^{-19}] \]
On usual calculations, \( a = 3.451 \times 10^{-18} \) mol

8. **TIPS/Formulae**
According to Arrhenius equation
\[ \log k = \log A - \frac{E_A}{2.303 \cdot RT} \]
We know that \( k = \frac{0.693}{t_{\frac{1}{2}}} = \frac{0.693}{10 \times 60} \quad (t_{\frac{1}{2}} = 10 \times 60 \text{ sec.}) \]
\[ = 1.555 \times 10^{-3} \]
Substituting the various values in the above equation, we get
\[ \log 1.155 \times 10^{-3} = \log 4 \times 10^{13} - \frac{98.6}{2.303 \times 8.314 \times 10^{-3} \times T} \]
On usual calculations, \( T = 311.35 \text{ K} \)

9. \( 2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g) \)
2 mol of gaseous nitrogen pentoxide on complete decomposition gives 5 mol of gaseous products.

Therefore, initial pressure of \( N_2O_5 \) = \( \frac{584.5 \times 2}{5} \)
\[ = 233.8 \text{ mm Hg} \]
Let \( x \) be the amount of \( N_2O_5 \) decomposed after 30 min.
\[ \therefore \text{After 30 min.} \]
\( \text{Pressure due to } N_2O_5 = 233.8 - x; \quad \text{Pressure due to } NO_2 = 2x \)
and pressure due to \( O_2 = \frac{x}{2} \)
Total pressure after 30 min
\[ = 284.5 \text{ mm Hg} = 233.8 + 2x + \frac{x}{2} \]
or \[ 233.8 + \frac{3x}{2} = 284.5 \quad \text{or} \quad x = 33.8 \text{ mm Hg} \]
Hence pressure of \( N_2O_5 \) after 30 min.
\[ = 233.8 - 33.8 = 200 \text{ mm Hg} \]

\[ k = \frac{2.303}{t} \log \left( \frac{a}{a-x} \right) = \frac{2.303}{30} \log \frac{233.8}{200} \]
\[ k = \frac{2.303}{30} \times 0.0679 = 5.2 \times 10^{-3} \text{ min}^{-1} \]

10. \( A \rightarrow \text{Products} \quad \ldots(i) \]
\( B \rightarrow \text{Product} \quad \ldots(ii) \]
Half-life of (i) reaction at 310 \( k = 30 \text{ min.} \)
\[ \therefore \frac{k_{310}}{k_{300}} = \frac{0.693}{30} \quad \ldots(1) \]
Also given, \( \frac{A_{k_{310}}}{A_{k_{300}}} = 2 \quad \ldots(2) \]
Also at 310 \( k, B_{k_{310}} = 2A_{k_{310}} \quad \ldots(3) \]
Also \( E_B = \frac{1}{2} E_A \)
According to Arrhenius equation, \( k = Ae^{-E/RT} \quad \ldots(4) \)
or \[ \log \frac{k_2}{k_1} = \frac{E}{2.303 \cdot RT} \left[ \frac{T_2 - T_1}{T_1 \cdot T_2} \right] \]

For reaction (i),
\[ \log \frac{A_{k_{310}}}{A_{k_{300}}} = \frac{E_A}{2.303 \cdot R} \left[ \frac{10}{300 \times 310} \right] \quad \ldots(5) \]

For reaction (ii),
\[ \log \frac{B_{k_{310}}}{B_{k_{300}}} = \frac{E_B}{2.303 \cdot R} \left[ \frac{10}{300 \times 310} \right] \quad \ldots(6) \]
Dividing (6) by (5),
\[ \log \frac{B_{k_{310}}}{B_{k_{300}}} = \frac{E_B}{E_A} = \frac{1}{2} \quad \left( \because E_B = \frac{1}{2} E_A \right) \]
or \[ \log \frac{B_{k_{310}}}{B_{k_{300}}} = 2 \log \frac{B_{k_{310}}}{B_{k_{300}}} = \log \left( \frac{B_{k_{310}}}{B_{k_{300}}} \right)^2 \]
or \[ \frac{A_{k_{310}}}{A_{k_{300}}} = \left( \frac{B_{k_{310}}}{B_{k_{300}}} \right)^2 \quad \ldots(7) \]
Combining (7), (2) and (3), we get
\[ \left( \frac{2A_{k_{310}}}{B_{k_{300}}} \right)^2 = 2 \]
\[ 2A_{k_{310}} = \sqrt{2} \times B_{k_{300}}; \quad B_{k_{300}} = \sqrt{2} \times A_{k_{310}} \]
\[ B_{k_{300}} = 1.414 \times \frac{0.693}{30} = 3.267 \times 10^{-2} \text{ min}^{-1} \]
Chemical Kinetics & Nuclear Chemistry

11. The ratio of $\text{H}^3 : \text{H}^1 : 8 \times 10^{-18} : 1$
   \[ \therefore \text{No. of H atoms in 18 g H}_2\text{O} = 2N \]
   \[ \therefore \text{No. of H}^3\text{ atoms in 18 g of H}_2\text{O} = 2N \times 8 \times 10^{-18} = 2 \times 6.023 \times 10^{23} \times 8 \times 10^{-18} \text{ atoms} \]
   \[ \therefore \text{No. of H}^3\text{ atoms in 10 g H}_2\text{O} = \frac{2 \times 6.023 \times 10^{23} \times 8 \times 10^{-18} \times 10}{18} \text{ atoms} \]
   \[ = 5.354 \times 10^6 \text{ atoms} \]
   No. of atoms left after 40 years are derived as follows using the relation
   \[ t = \frac{2.303}{3.693} \log N_0 \]
   \[ 40 = \frac{2.303 \times 12.3}{0.693} \log \frac{5.354 \times 10^6}{N} \]
   \[ \therefore N = 5.624 \times 10^5 \text{ atoms} \]

12. **TIPS/Formules**:

   According to Arrhenius equation
   \[ \log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \]
   \[ Calculation \ of \ k \ at \ 25^\circ \text{C} (298 \text{ K}), \ i.e. \ k_1 \]
   Here \( a = 100, a-x = 100 - 25, t = 20 \text{ mts.} \]
   Thus \[ k_1 = \frac{2.303}{20} \log \frac{100}{75} = 0.014386 \text{ min}^{-1} \]
   \[ Calculation \ of \ k \ at \ 40^\circ \text{C} (313 \text{ K}) \ i.e., k_2 \]
   Substituting various values, we get
   \[ \log \frac{k_2}{0.014386} = \frac{70 \times 10^3}{2.303 \times 8.314} \times \left( \frac{1}{298} - \frac{1}{313} \right) \]
   \[ = \frac{70 \times 10^3 \times 15}{2.303 \times 8.314 \times 298 \times 313} = 0.587 \]
   \[ \log k_2 = 0.014386 \times 0.587, k_2 = 0.05570 \text{ min}^{-1} \]
   \[ Calculation \ of \ % \ decomposition \ at \ 40^\circ \text{C} \]
   Thus here \( a = 100, a-x = 100 - x, t = 20 \text{ mts.} \), \( k_2 = 0.05570 \text{ min}^{-1} \)
   Substituting the values in the first order reaction equation:
   \[ k_2 = 0.05570 = \frac{2.303}{20} \log \frac{100}{100 - x} \]
   On usual calculations, \( x = 67.169 = 67.17\% \)

13. $\text{CH}_3\text{O} - \text{CH}_2(g) \rightarrow \text{CH}_4(g) + \text{CO(g)} + \text{H}_2(g)$
   Given \( \tau = 14.5 \text{ min}, \text{ initial pressure} = 0.40 \text{ atm}, \tau = 12 \text{ min} \).
   Now, \[ k = \frac{0.693}{14.5} = 4.78 \times 10^{-2} \text{ min}^{-1} \]
   Writing first order equation and substituting the given values, we get
   \[ 4.78 \times 10^{-2} = \frac{2.303}{12 \text{ min}} \log \frac{0.4}{0.4 - x} \]
   which gives \( x = 0.175 \text{ atm} \)

Since volume and temp. are constant, final pressure:\
$\text{CH}_3\text{O} - \text{CH}_2(g) \rightarrow \text{CH}_4(g) + \text{CO(g)} + \text{H}_2(g)$
\[ 0.4 \]
\[ 0.4 - 0.175 \]
\[ 0.175 \]
\[ 0.175 \]
\[ 0.175 \]
Hence total pressure $0.4 - 0.175 + 3 \times 0.175 = 0.749 \text{ atm}$

14. (i) According to Fig. in the given time of 4 hours (1 to 5) concentration of $A$ falls from 0.5 to 0.3 M, while in the same time concentration of $B$ increases from 0.2 M to 0.6 M.
   Decrease in concentration of $A$ in 4 hours
   \[ = 0.5 - 0.3 = 0.2 \text{ M} \]
   Increase in concentration of $B$ in 4 hours
   \[ = 0.6 - 0.2 = 0.4 \text{ M} \]
   Thus increase in concentration of $B$ in a given time is twice the decrease in concentration of $A$. Thus \( n = 2 \).

(ii) \[ K = \frac{[B]_{eq}^2}{[A]_{eq}} = \frac{(0.6)^2}{0.3} = 1.2 \text{ M} \]

(iii) Initial rate of conversion of $A$
   \[ \text{Change in conc. of } A \text{ during 1 hour} \]
   \[ = \frac{0.6 - 0.5}{1} = 0.1 \text{ mole litre}^{-1} \text{ hour}^{-1} \]

15. Let the order with respect to $A$ is $x$ and the order with respect to $B$ is $y$
   Then, Rate $= k[A]^x[B]^y$
   \[ 5.0 \times 10^{-4} = k[2.5 \times 10^{-4}]^x[3.0 \times 10^{-5}]^y \quad \ldots(i) \]
   \[ 4.0 \times 10^{-3} = k[5.0 \times 10^{-3}]^x[6.0 \times 10^{-5}]^y \quad \ldots(ii) \]
   \[ 1.6 \times 10^{-2} = k[1.0 \times 10^{-3}]^x[6.0 \times 10^{-5}]^y \quad \ldots(iii) \]
   From (ii) and (iii), we get \( 2^x = 4; \ x = 2 \)
   From (i) and (ii), we get \( 2^x \cdot 3^y = 8; \ x + y = 3; y = 1 \)
   \[ \therefore \text{ The rate equation for the reaction is} \]
   Rate $= k[A]^2[B]$  
   (i) Thus order of reaction with respect to $A = 2$ and order of reaction with respect to $B = 1$.

(ii) Rate constant ($k_1$) at 300 K
   \[ k_1 = \frac{\text{Rate}}{[A]^2[B]} = \frac{5.0 \times 10^{-4} \text{ mol}^{-1} \text{ s}^{-1}}{(2.5 \times 10^{-4} \text{ mol}^{-1})^2 (3.0 \times 10^{-5} \text{ mol}^{-1})} \]
   \[ = 2.66 \times 10^4 \text{ mol}^{-2} \text{ s}^{-1} \]

(iii) Determination of energy of activation:
   Rate constant ($k_2$) at 320 K
   \[ k_2 = \frac{\text{Rate}}{[A]^2[B]} = \frac{2.0 \times 10^{-3} \text{ mol}^{-1} \text{ s}^{-1}}{(2.5 \times 10^{-4} \text{ mol}^{-1})^2 (3.0 \times 10^{-5} \text{ mol}^{-1})} \]
   \[ = 1.066 \times 10^9 \text{ mol}^{-2} \text{ s}^{-1} \]
\[
\log \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left[ \frac{T_2 - T_1}{T_1 T_2} \right]
\]
\[
\text{or } E_a = 2.303 R \log \frac{k_2}{k_1} \left[ \frac{T_1 T_2}{T_2 - T_1} \right]\]
\[
= 2.303 \times 8.314 \left[ \log \frac{1.066 \times 10^9}{2.66 \times 10^8} \right] \left[ \frac{320 \times 300}{20} \right]
\]
\[
= 5.54 \times 10^4 \text{ J}
\]

(iv) Determination of the pre-exponential factor

\[
\log k = -\frac{E_a}{2.303 R} \times \frac{1}{T} + \log A
\]
\[
\log 2.66 \times 10^8 = \frac{5.54 \times 10^4}{2.303 \times 8.314} \times \frac{1}{300} + \log A
\]
\[
\therefore A = 1.175 \times 10^{18} \text{ l mol}^{-2} \text{ sec}
\]

16. Wt. of $^{90}$Sr at start, $N_0 = 1$ mg, Wt. of $^{90}$Sr after 20 years, $N_t = ?$, Time $t = 20$ years

Half-life of $^{90}$Sr, $T_{1/2} = 28.1$ years

Calculation of decay constant,

\[
\lambda = \frac{0.693}{T_{1/2}} = \frac{0.693}{28.1} = 0.0247 \text{ years}^{-1}
\]

Substituting the values in the relation

\[
N_t = N_0 e^{-\lambda t} = 1 \times e^{-0.0247 \times 20} = 0.061 \mu g
\]

17. $k_{653K} = \frac{0.693}{360} = 1.925 \times 10^{-3} \text{ min}^{-1}$

Calculation of $k_{723K}$

\[
E_a = 200 \text{ kJ mol}^{-1} = 200 \times 10^3 \text{ J mol}^{-1}
\]
\[
T_2 = 723 \text{ K}, T_1 = 653 \text{ K}
\]
\[
k_{653} = 1.925 \times 10^{-3} \text{ min}^{-1}
\]

We know that,

\[
\frac{k_2}{k_1} = e^{-\frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)}
\]

or

\[
k_{723K} = \frac{200 \times 10^3}{8.314} \left[ \frac{1}{723} - \frac{1}{653} \right]
\]

On usual calculations, $k_{723K} = 6.81 \times 10^{-2} \text{ min}^{-1}$

Calculation of time for 75% decomposition at 723 K

Let the initial amount of $\text{H}_2\text{O}_2$, $a = 1$

\[
\therefore \text{Amount at the required time, } (a-x) = 0.25
\]

Substituting the values in the given relation,

\[
t = \frac{2.303}{k_{723K}} \log \frac{a}{a-x} = \frac{2.303}{6.81 \times 10^{-2}} \log \frac{1}{0.25} = 20.34 \text{ min}
\]

18. $\lambda_{\text{Ac}} = \frac{0.693}{21.8} = 3.18 \times 10^{-2} \text{ year}^{-1}$

Since the decay involves two parallel paths

$\text{Th}^{227} \longleftrightarrow \text{Ac}^{227} \longrightarrow \text{Fr}^{223}$

$\lambda_{\text{Ac}} = \lambda_{\text{Th}} + \lambda_{\text{Fr}}$

Thus, Fractional yield of Th = $\frac{\lambda_{\text{Th}}}{\lambda_{\text{Ac}}}$

or $\lambda_{\text{Th}} = 3.18 \times 10^{-2} \times \frac{1.2}{100} = 3.81 \times 10^{-4} \text{ yr}^{-1}$

Similarly, Fractional yield of Fr = $\frac{\lambda_{\text{Fr}}}{\lambda_{\text{Ac}}}$

\[
\therefore \lambda_{\text{Fr}} = 3.18 \times 10^{-2} \times \frac{98.8}{100} = 3.14 \times 10^{-2} \text{ yr}^{-1}
\]

19. $\text{NH}_3 + \text{H}_2\text{O} \xrightleftharpoons[k_b]{K_b} \text{NH}_4^+ + \text{OH}^-$, $K_b = 3.4 \times 10^{10}$

$\text{NH}_4^+ + \text{H}_2\text{O} \xrightleftharpoons[K_w]{K_w} \text{NH}_2\text{OH} + \text{H}^+$, $K_w = 5.6 \times 10^{-10}$

$K_{\text{base}} = \frac{K_f}{K_b} = K_{\text{acid}}$ or $K_f = K_{\text{acid}} \times 3.4 \times 10^{10} = 10^{-14}$

\[
\therefore K_f = 6.07 \times 10^5
\]

20. (i) The Arrhenius equation is

$k = A \exp(-E_a / RT)$

Taking natural logarithm, we get

\[
\ln k = \ln A - \frac{E_a}{2.303 R} \frac{1}{T}
\]

Comparing this expression with the given one, we get

\[
\frac{E_a}{2.303} = 1.25 \times 10^4 \text{ K}
\]

Hence, $E_a = (1.25 \times 10^4 \text{ K})(2.303)(8.314 \text{ JK}^{-1} \text{ mol}^{-1}) = 2.39 \times 10^5 \text{ J mol}^{-1} = 239 \text{ kJ mol}^{-1}$

(ii) The reaction is first order as the unit of rate constant is s$^{-1}$. For a first order reaction,

\[
t_{1/2} = \frac{0.693}{k}
\]

Hence, $k = \frac{0.693}{256 \times 60} = 4.51 \times 10^{-5} \text{ s}^{-1}$

Substituting this in the given expression, we get

\[
\log \left(4.51 \times 10^{-5}\right) = 14.34 - \frac{1.25 \times 10^{-4} \text{ K}}{T}
\]

or $-4.346 = 14.34 - \frac{1.25 \times 10^{-4} \text{ K}}{T}$

or $T = \frac{1.25 \times 10^{-4} \text{ K}}{18.686} = 669 \text{ K}$
21. \[ \gamma^{14}N + 2\, ^{1}H \rightarrow ^{18}F + ^{17}O + ^{1}H \]

22. \[
\frac{k_2}{k_1} = \frac{E_a}{2.303 \times R \left[ \frac{T_2 - T_1}{T_1 T_2} \right]}
\]

\[ \therefore \log \frac{4.5 \times 10^{7}}{1.5 \times 10^{7}} = \frac{E_a}{8.314 \times 2.303} \left[ \frac{373 - 323}{373 \times 323} \right] \]

\[ \therefore E_a = 2.2 \times 10^{4} \text{ J mol}^{-1} \]

Now \( k = Ae^{-E_a/RT} \)

\[ \therefore 4.5 \times 10^{7} \text{ J mol}^{-1} = Ae^{8.314 \times 373} \quad \therefore A = 5.42 \times 10^{10} \text{ sec}^{-1} \]

23. \( A \rightarrow B; k = 4.5 \times 10^{-3} \text{ min}^{-1}; \) \([A]_0 = 1 \text{ M}\)

For first order reaction, \( k = \frac{2.303}{t} \log \frac{a}{(a-x)} \)

Find \((a-x)\) at \( t = 60 \text{ min} \).

\[ 4.5 \times 10^{-3} = \frac{2.303}{60} \log \frac{1}{(a-x)} \quad \therefore (a-x) = 0.7634 \]

Thus rate after 60 minute = \( k \, (a-x) = 4.5 \times 10^{-3} \times 0.7634 = 3.4354 \times 10^{-3} \text{ M min}^{-1} \)

24. Let the number of \( \alpha \)-particles emitted = \( a \)

and number of \( \beta \)-particles emitted = \( b \)

\[ ^{92}U^{238} \rightarrow 4a^{4} + b_{1}^{0} + 82^{206} \text{ Pb} \]

Thus \( 4a + 206 = 238; \) Therefore \( a = 8 \)

Further \( 2a - b + 82 = 92; \) Therefore \( b = 6 \)

Composition of the ore indicates that it has 1 gm of U and 0.1 gm of Pb; thus here \( N_{i} = 1 \text{ gm} \)

Determination of \( N_{0} \)

206 g Pb is obtained from 238 g of U

0.1 g Pb is obtained from = \( \frac{238}{206} \times 0.1 \text{ g} = 0.1155 \text{ g} \)

Therefore initial amount of U (\( N_{0} \)) = 1 + 0.1155 = 1.1155

Now we know that \( t = \frac{2.303}{k} \log \frac{N_{0}}{N_{t}} = \frac{2.303}{0.693 / 4.5 \times 10^{9}} \log \frac{1.1155}{1} \)

By usual calculations, \( t = 7.097 \times 10^{8} \text{ years} \).

25. According to Arrhenius equation \( k = Ae^{-E_a/RT} \)

Let \( E_{a} \) of the reaction in absence of catalyst = \( x \text{ kJ mol}^{-1} \)

Therefore \( E_{a} \) of the reaction in presence of catalyst = \( x - 20 \text{ kJ mol}^{-1} \)

The Arrhenius equations in the two conditions can thus be written as

\[ k = Ae^{-\frac{x}{R \times 500}} \quad \ldots (i) \]

\[ k = Ae^{-\frac{x-20}{R \times 400}} \quad \ldots (ii) \]

Dividing equation (i) by (ii), we get \[ \frac{x}{500} = e^{-\frac{x-20}{R \times 400}} \Rightarrow \frac{x}{500} = \frac{x-20}{400} \quad \text{or} \quad x = 100 \text{ kJ mol}^{-1} \]

26. \( r_2 = k_1c_1 \) and \( r_2 = k_2c_2 \)

Since rate of first order reaction is directly proportional to the concentration of its reactant,

\[ \frac{r_1}{c_1} = \frac{r_2}{c_2} = \frac{0.04}{c_2} = \frac{0.03}{c_2} \]

According to first order reaction

\[ k = \frac{2.303}{t_{20} - t_{10}} \log \frac{c_{1}}{c_{2}} \]

On substituting the various values \( k = 0.0287 \text{ min}^{-1} \)

\[ t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.0287} = 24.14 \text{ min} \]

27. Let the number of moles of A left after 100 min = \( x \)

Total number of moles after 100 min = \( x + 12 + 0.525 \)

\[ P_{mix} = P_{A} + P_{B} \]

\[ \frac{(x + 12 + 0.525) \times 300}{12 + x} = \frac{6000 + 300x}{12 + x} \]

According to Raoult’s law

\[ \frac{6000 + 300x}{12 + x} = \frac{0.525}{x + 12 + 0.525} \]

On solving we get, \( x = 9.9 \)

Now according to first order kinetics,

\[ k = \frac{2.303}{100} \log \frac{10}{9.9} = 1.005 \times 10^{-4} \text{ min}^{-1} \]

28. \( ^{64}Cu \rightarrow ^{64}Zn \quad \text{ or } ^{64}Ni \)

\( ^{64} \text{ Zn} \quad ^{64} \text{Ni} \)

\( ^{64} \text{ Zn} \quad ^{64} \text{Zn} \)

\[ ^{64}Cu → ^{64}Zn \quad ^{64}Ni \]

Let the rate constants of the above emission processes be \( k_1, k_2 \) and \( k_3 \) respectively and the overall rate constant be \( k \). Then

\[ k = k_1 + k_2 + k_3 = \frac{0.693}{12.8} = 0.693 \text{ h}^{-1} \]

Also, \( k_1 = 0.38 \text{ k} = 0.38 \times 0.693 \text{ h}^{-1} \)

\[ t_1 = \frac{0.693 \times 12.8}{0.38 \times 0.693} = 33.68 \text{ h} \]
Similarly,
\[ t_2 = \frac{0.693}{k_2} = \frac{0.693}{0.19k} = \frac{0.693}{0.19 \times 0.693} \times 12.8 = 67.36h , \]
\[ t_3 = \frac{0.693}{k_3} = \frac{0.693}{0.43k} = \frac{12.8}{0.43} = 29.76h \]

where \( t_1 \), \( t_2 \) and \( t_3 \) are the partial half-lives for \( \beta^- \) emission, \( \beta^+ \) emission and electron capture processes, respectively.

29. (a) From the rate law expression, \( R_0 = k[A_0]^a[B_0]^b \) and from the table it is clear that:

(i) when the concentration of \([A_0]\) is doubled, keeping \([B_0]\) constant (see readings 1 and 2), the rate also doubles i.e. rate is directly proportional to \([A_0]\) or \( a = 1 \).

(ii) when the concentration of \([B_0]\) is reduced, keeping \([A_0]\) constant (see readings 1 and 3), the rate remains constant. i.e. rate is independent of \([B_0]\) or \( b = 0 \)

Thus, rate equation becomes \( R_0 = k[A_0] \)

(b) \( k = \frac{R_0}{[A_0]} = \frac{0.05}{0.10} = 0.5 \text{ sec}^{-1} \)

30. **TIPS/Formulæ:**

(i) Sum of atomic masses of reactant = sum of atomic masses of products

(ii) Sum of atomic numbers of reactant = sum of atomic numbers of products

(iii) The atomic number of the final stable product \( = 90 - 7 \times 2 + 1 \times 6 = 82 \) & the mass number of the final stable product \( = 234 - 7 \times 4 + 0 \times 0 = 206 \). Thus the element \( X \) should be \( ^{82}\text{Pb}^{206} \).

(ii) \( ^{92}\text{U}^{235} + _0^1\text{e} \rightarrow ^{52}\text{Te}^{137} + ^{40}\text{Zr}^{97} + _2^0\text{He} \)

(iii) \( ^{34}\text{Se}^{86} \rightarrow _{-1}^2\text{e}^0 + ^{36}\text{Kr}^{86} \)

31. (i) From the given data, it is evident that the \( t_{1/2} \) (half-life period) for the decomposition of \( X(g) \) is constant (100 minutes) therefore the order of reaction is one.

(ii) Rate constant, \( k = \frac{0.693}{t_{1/2}} = \frac{0.693}{100} = 6.93 \times 10^{-3} \text{ min}^{-1} \)

(iii) Time taken for 75% completion of reaction
\[ = 2t_{1/2} = 2 \times 100 = 200 \text{ minutes} \]

(iv) \( 2X \rightarrow 3Y + 2Z \)

Initial pressure \( = 800 \)

After time \( t \)
\[ (800 - 2P) \quad 3P \quad 2P \]

when the pressure of \( X \) is 700 mm of Hg then, \( 800 - 2P = 700 \)
\[ 2P = 100 \quad \text{P} = 50 \text{ mm of Hg} \]

Total pressure \( = 800 - 2P + 3P + 2P = 800 + 150 = 950 \text{ mm of Hg} \)

\[ t_{1/8} = \frac{2.303 \log 8}{k} = \frac{2.303 \times 3 \log 2}{k} \]

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**Topic-wise Solved Papers - CHEMISTRY**

**G. Comprehension Based Questions**

1. (c) It is clear from the 3rd paragraph, which states that in living organisms a dynamic equilibrium is established whereby the ratio of \(^{14}\text{C} / ^{12}\text{C} \) remains constant. The \(^{14}\text{C} \) which decays into \(^{14}\text{N} \) is replenished by the production of new isotopes.

2. (b) As the half-life of \(^{14}\text{C} \) is 5760 years, so a 6 year old fossil’s age can’t be determined. Further this technique cannot be used to date objects older than 30,000 years. After this length of time the radioactivity is too low to be measured.

3. (a) \( T_1 = \frac{1}{\lambda} \ln C_1 \), \( T_2 = \frac{1}{\lambda} \ln C_2 \)

Let the concentration of \(^{14}\text{C} \) in the fossil be \( C \). In nearby areas concentration of \(^{14}\text{C} \) in living beings will be \( C_1 \) and in far off places \( C_2 \), obviously \( C_1 > C_2 \). Hence, age of fossil in nearby areas,

\[ T_1 = \frac{1}{\lambda} \ln \frac{C_1}{C} \] .... (i)

And age in far off places, \( T_2 = \frac{1}{\lambda} \ln \frac{C_2}{C} \) .... (ii)

From (i) and (ii), \( T_1 - T_2 = \frac{1}{\lambda} \ln \frac{C_1}{C_2} \)

Since, \( C_1 > C_2 \), R.H.S. is positive i.e., \( T_1 > T_2 \).

**H. Assertion & Reason Type Questions**

1. (a) Assertion is correct as for every 10°C raise in temperature, the specific rate constant, \( K \) nearly doubles. (Although it is not correct for all reactions. For some reactions \( K \) even gets tripled for 10°C raise).

[NOTE : The value of temperature coefficient is the ratio of rate constants at two different temperature (which differ by 10°C) generally lies between 2 and 3] The statement is clearly true and it explains the assertion, as the rate of collision among the molecules doubles for 10° rise in temperature.

1. **Integer Value Correct Type**

1. \( ^{92}\text{U}^{238} \rightarrow _6^6\text{He} \rightarrow _{80}^{214}\text{X} \rightarrow _{82}^{214}\text{Pb} \)

Hence total number of particles emitted are \( 2 + 6 = 8 \)

2. The integrated form of a zero-order reaction is
\[ [A_0] - [A_t] = k_0 t \]
\[ 1.0 - 0.75 = k_0 \times 0.05 \quad k_0 = 5 \]
Again, \( 1.0 - 0.4 = k_0 \times 0.12 \quad k_0 = 5 \)

3. \( ^{92}\text{U}^{235} \rightarrow _{34}^{54}\text{Xe}^{142} \rightarrow _{38}^{82}\text{Sr}^{90} + _0^1\text{He} \)

\[ 235 = 142 + 90 + 1 \Rightarrow y = 3 \]

The number of neutrons emitted are 3.

4. \( t_{1/8} = \frac{2.303 \log 8}{k} = \frac{2.303 \times 3 \log 2}{k} \)

---
6. (9) Number of moles in gas phase, at start \( n_i = 1 \)
\[
\frac{238}{92} \text{U} \rightarrow \frac{206}{82} \text{Pb} + \frac{82}{2} \text{He} + \frac{6}{0} \text{N}
\]
Now number of moles in gas phase, after decomposition \( n_f \)
\( = 1 + 8 = 9 \) mole
at constant temperature and pressure
\[
\frac{P_e}{P_m} = \frac{n_e}{n_m} = \frac{9}{1} = 9
\]

7. (8) \( 8 \text{H}^+ + 5[\text{Fe(H}_2\text{O}_2\text{O}_2\text{X}])]^2^- + \text{MnO}_4^- \rightarrow \text{Mn}^{2+} + \]
\[+ 5[\text{Fe(H}_2\text{O}_2\text{O}_2\text{X}])]^+ + 4\text{H}_2\text{O}
\]
Rate = \( \frac{1}{8} \frac{d[\text{H}^+]}{dt} = - \frac{d[\text{MnO}_4^-]}{dt} \)

Hence, \( \frac{\text{rate of [H}^+\text{] decay}}{\text{rate of [MnO}_4^-\text{] decay}} = 8 \)

8. (d) \( t_{1/2} = 3 \) hrs. \( T = 18 \) hours \( \therefore T = n \times t_{1/2} \)
\[\therefore n = \frac{18}{3} = 6
\]
Initial mass \( (C_0) = 256 \) g
\[\therefore C_n = \frac{C_0}{2^n} = \frac{256}{2^6} = \frac{256}{64} = 4 \text{g.}
\]

9. (b) In equation \( K = A e^{-E_a / RT} \), \( A = \) Frequency factor
\( K = \) velocity constant, \( R = \) gas constant and \( E_a = \) energy of activation

10. (c) \( \text{Rate}_1 = k[A]^n [B]^m \), \( \text{Rate}_2 = k[2A]^n [B]^m \)
\[\therefore \frac{\text{Rate}_2}{\text{Rate}_1} = \frac{k[2A]^n [B]^m}{k[A]^n [B]^m} = 2^n [\frac{1}{2}]^m = 2^n 2^{-m} = 2^{n-m}
\]

11. (b) \( r = k[\text{O}_2][\text{NO}]^2 \). When the volume is reduced to 1/2, the conc. will double
\[\therefore \text{New rate} = k[2\text{O}_2][2\text{NO}]^2 = 8 k[\text{O}_2][\text{NO}]^2 \]

The new rate increases to eight times of its initial.

12. (c) As the concentration of reactant decreases from \( 0.8 \) to \( 0.4 \) in 15 minutes hence the \( t_{1/2} \) is 15 minutes. To fall the concentration from \( 0.1 \) to \( 0.025 \) we need two half lives i.e., 30 minutes.

13. (d) The velocity constant depends on temperature only. It is independent of concentration of reactants.

14. (b) \( \frac{238}{92} \text{M} \rightarrow \frac{230}{88} \text{N} + 2\frac{4}{2} \text{He}
\]
\[\frac{230}{88} \text{N} \rightarrow \frac{230}{86} \text{L} + 2\beta^+
\]
The number of neutrons in element L = 230 - 86 = 144
15. (a) \( N_t = N_0 \left( \frac{1}{2} \right)^n \) where \( n \) is number of half life periods.

\[
\frac{\text{Total time}}{\text{half life}} = \frac{24}{4} = 6
\]

\[
.: N_t = 200 \left( \frac{1}{2} \right)^6 = 3.125 \text{g}
\]

16. (b) Such reaction in which two lighter nucleus are fused together to form a heavier nuclei is called nuclear fusion.

**NOTE:** In hydrogen bomb, a mixture of deuterium oxide \((\text{H}_2\text{O})\) and tritium oxide \((\text{T}_2\text{O})\) is enclosed in a space surrounding an ordinary atomic bomb. The temperature produced by the atomic bomb initiates the fusion reaction between \(\text{H}_3\text{H}^+\) and \(\text{H}_3\text{H}^-\) releasing a large amount of energy.

17. (d) The molecularity of a reaction is the number of reactant molecules taking part in a single step of the reaction.

**NOTE:** The reaction involving two different reactant can never be unimolecular.

18. (d) The graph show that reaction is exothermic.

\[
\log k = \frac{-\Delta H}{RT} + 1
\]

For exothermic reaction \(\Delta H < 0\)

\[
.: \log k \propto \frac{1}{T} \text{ would be negative straight line with positive slope.}
\]

19. (b) \(\text{Mg}^{24} \longrightarrow \text{Na}^{23} + \text{H}^1\).

20. (c) \(t_{1/4} = \frac{2.303}{K} \log \frac{1}{3/4} = \frac{2.303}{K} \log \frac{4}{3}
\]

\[
= \frac{2.303}{K} (\log 4 - \log 3) = \frac{2.303}{K} (2 \log 2 - \log 3)
\]

\[
= \frac{2.303}{K} (2 \times 0.301 - 0.4771) = 0.29
\]

21. (a) Since the reaction is 2nd order w.r.t CO. Thus, rate law is given as.

\[
r = k \left[ \text{CO} \right]^2
\]

Let initial concentration of CO is a i.e. \([\text{CO}] = a\)

\[
.: r_1 = k (a)^2 = k a^2
\]

when concentration becomes doubled, i.e. \([\text{CO}] = 2a\)

\[
.: r_2 = k (2a)^2 = 4ka^2
\]

So, the rate of reaction becomes 4 times.

22. (c) In Arrhenius equation \(K = A e^{-E/RT}\), \(E\) is the energy of activation, which is required by the colliding molecules to react resulting in the formation of products.

23. (c) \(\text{U}^{238}_{92} \rightarrow^{\alpha} \text{Th}^{234}_{90} \rightarrow^{28} \text{U}^{234}_{92}\)

24. (b) (i) \(\text{NO}(g) + \text{Br}_2(g) \rightleftharpoons \text{NOBr}_2(g)\)

(ii) \(\text{NOBr}_2(g) + \text{NO}(g) \rightarrow 2 \text{NOBr}(g)\)

Rate law equation = \(k[\text{NOBr}_2][\text{NO}]\)

But \(\text{NOBr}_2\) is intermediate and must not appear in the rate law equation

from 1st step \(K_C = \frac{[\text{NOBr}_2]}{[\text{NO}][\text{Br}_2]}\)

\(\therefore [\text{NOBr}_2] = K_C \text{[NO]} \text{[Br}_2]\)

\(\therefore\) Rate law equation = \(k \cdot K_C \cdot \text{[NO]}^2 \cdot \text{[Br}_2]\)

hence order of reaction is 2 w.r.t NO.

25. (a) \(\Delta H_R = E_f - E_b = 180 - 200 = -20 \text{kJ/mol}\)

The nearest correct answer given in choices may be obtained by neglecting sign.

26. (b) For a first order reaction \(t_{1/2} = \frac{0.693}{K}\) i.e. for a first order reaction \(t_{1/2}\) does not depend up on the concentration. From the given data, we can say that order of reaction with respect to \(B = 1\) because change in concentration of \(B\) does not change half life.

Order of reaction with respect to \(A = 1\) because rate of reaction doubles when concentration of \(B\) is doubled keeping concentration of \(A\) constant.

\(\therefore\) Order of reaction = 1 + 1 = 2 and units of second order reaction are \(L\ \text{mol}^{-1} \text{sec}^{-1}\).

27. (a) Suppose activity of safe working = \(A\)

\(\lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{30}\)

\(t_{1/2} = \frac{2.303 \log A_0}{A} = \frac{2.303 \log 10A}{A}\)

\[= \frac{2.303 \times 30}{0.693} \times \log 10 = 100 \ \text{days.}\]

28. (b) **NOTE:** Isotopes are atoms of same element having same atomic number but different atomic masses. Neutron has atomic number 0 and atomic mass 1. So, loss of neutron will generate isotope. e.g.,

\[\text{U}^{238}_{92} + 0^1 \rightarrow \text{U}^{239}_{92}\]

29. (b) The rates of reactions for the reaction

\[\frac{1}{2} A \longrightarrow 2B\]

can be written either as

\[-2 \frac{d[A]}{dt}\] with respect to ‘A’

or \[\frac{1}{2} \frac{d[B]}{dt}\] with respect to ‘B’

From the above, we have

\[-2 \frac{d[A]}{dt} = \frac{1}{2} \frac{d[B]}{dt}\]

\(\therefore\) correct answer is (b)
30. (b) For a first order reaction,

\[ k = \frac{2.303}{t} \log \frac{100}{100 - 99} \]

\[ 0.693 = \frac{2.303}{t} \log \frac{100}{1} \]

\[ 0.693 = \frac{2.303 \times 2}{t} \Rightarrow t = 46.06 \text{ min} \]

31. (c) For the reaction

\[ A \rightarrow \text{Product} \], given \( t_{1/2} = 1 \text{ hour} \)

For a zero order reaction

\[ t_{\text{completion}} = \frac{[A_0]}{k} = \text{initial conc.} \text{rate constant} \]

\[ \therefore t_{1/2} = \frac{[A_0]}{2k} \text{ or } k = \frac{[A_0]}{2t_{1/2}} = \frac{2}{2 \times 1} = 1 \text{ mol max}^{-1} \text{ hr}^{-1} \]

Further for a zero order reaction

\[ k = \frac{dx}{dt} = \text{change in concentration} \text{time} \]

\[ 1 = \frac{0.50 - 0.25}{0.25} \therefore \text{time} = 0.25 \text{ hr} \]

32. (d) Since the slow step is the rate determining step hence if we consider option (1) we find

Rate = \( k \left[ \text{Cl}_2 \right] \left[ H^+ \right] \left[ S^2^- \right] \)

Now if we consider option (2) we find

Rate = \( k \left[ \text{Cl}_2 \right] \left[ H^+ \right] \left[ S^2^- \right] \) \quad (1)

From equation (i)

\[ k = \frac{\left[ H^+ \right] \left[ S^2^- \right]}{H^+} \left[ H^+ \right] \left[ S^2^- \right] = k \left[ H_2S \right] \]

Substituting this value in equation (1) we find

Rate = \( k \left[ \text{Cl}_2 \right] \left[ H_2S \right] \)

hence only, mechanism (1) is consistent with the given rate equation.

33. (e) Since for every 10°C rise in temperature rate doubles for 50°C rise in temp increase in reaction rate = \( 2^5 = 32 \text{ times} \)

34. (b) For a first order reaction

\[ k = \frac{2.303}{t} \log \frac{a}{a-x} \]

\[ = \frac{2.303}{40} \log \frac{0.1}{0.025} \]

\[ = \frac{2.303 \log 4}{40} = \frac{2.303 \times 0.6020}{40} = 3.47 \times 10^{-2} \]

\[ R = kA^1 = 3.47 \times 10^{-2} \times 0.01 = 3.47 \times 10^{-4} \]

35. (a) Activation energy can be calculated from the equation

\[ \log k_2 = \frac{E_a}{2.303R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \]

Given \( k_2 = 2 \quad T_2 = 310 \text{ K} \quad T_1 = 300 \text{ K} \)

\[ = \log 2 = \frac{-E_a}{2.303 \times 8.314} \left( \frac{1}{310} - \frac{1}{300} \right) \]

\[ E_a = 53598.6 \text{ J/mole} = 53.6 \text{ kJ/mole} \]

36. (d) Let rate of reaction = \( \frac{d[C]}{dt} = k[A]^x [B]^y \)

Now from the given data

\[ 1.2 \times 10^{-3} = k[0.1]^x[0.1]^y \quad \ldots(i) \]

\[ 1.2 \times 10^{-3} = k[0.1]^x[0.2]^y \quad \ldots(ii) \]

\[ 2.4 \times 10^{-3} = k[0.2]^x[0.1]^y \quad \ldots(iii) \]

Dividing equation (i) by (ii)

\[ \Rightarrow 1.2 \times 10^{-3} = \frac{k[0.1]^x[0.1]^y}{1.2 \times 10^{-3} = k[0.1]^x[0.2]^y} \]

We find, \( y = 0 \)

Now dividing equation (i) by (iii)

\[ \Rightarrow 1.2 \times 10^{-3} = \frac{k[0.1]^x[0.1]^y}{2.4 \times 10^{-3} = k[0.2]^x[0.1]^y} \]

We find, \( x = 1 \)

Hence \( \frac{d[C]}{dt} = k[A]^1 [B]^0 \)

37. (c) Reactions of higher order (>3) are very rare due to very less chances of many molecules to undergo effective collisions.

38. (d) \( \text{H}_2\text{O}_2(aq) \rightarrow \text{H}_2\text{O}(aq) + \frac{1}{2} \text{O}_2(g) \)

For a first order reaction\n
\[ k = \frac{2.303}{t} \log \frac{a}{(a-x)} \]

Given \( a = 0.5, (a-x) = 0.125, t = 50 \text{ min} \)

\[ \therefore \quad k = \frac{2.303}{50} \log \frac{0.5}{0.125} \]

\[ = 2.78 \times 10^{-2} \text{ min}^{-1} \]

\[ r = k[H_2O_2] = 2.78 \times 10^{-2} \times 0.05 \]

\[ = 1.386 \times 10^{-3} \text{ mol min}^{-1} \]

Now

\[ \frac{d[H_2O_2]}{dt} = \frac{d[H_2O]}{dt} = \frac{2d[O_2]}{dt} \]

\[ \therefore \quad \frac{2d[O_2]}{dt} = \frac{d[H_2O_2]}{dt} \]

\[ \therefore \quad \frac{d[O_2]}{dt} = \frac{1}{2} \frac{d[H_2O_2]}{dt} \]

\[ = \frac{1.386 \times 10^{-3}}{2} = 6.93 \times 10^{-4} \text{ mol min}^{-1} \]
Section-A : JEE Advanced/ IIT-JEE

C 1. (c) 2. (c) 3. (b) 4. (a) 5. (c) 6. (b)
D 1. (b, d) 2. (a, c, d) 3. (c, d) 4. (b, c, d) 5. (b, c, d) 6. (a, b, c)
F 1. (A) - p, r; (B) - p, r; (C) - q; (D) - s 2. (A) - p, (B) - q, (C) - p, r; (D) - p, s
3. (A) - p, q, s, (B) - t, (C) - q, r; (D) - r
Section-B : JEE Main/ AIEEE

1. (c) 2. (b) 3. (c) 4. (b) 5. (c) 6. (c) 7. (d) 8. (b)
9. (b) 10. (a)

Section-A

JEE Advanced/ IIT-JEE

A. Fill in the Blanks

1. Tin. It is SnO₂. [The formula of Casseterite ore in SnO₂]
2. Aluminium

Fe₂O₃ + 2Al → Al₂O₃ + 2Fe + Heat

[Thermite reaction]

3. Magnesia and lime; calcium silicate

NOTE: The lining of converter is made of magnesia & lime. Slag formed consists of CaSiO₃.

4. Sintering, smelting.

C. MCQs with One Correct Answer

1. (c) Malachite is CuCO₃. Cu (OH)_2 is ore of copper.
2. (c) Al reduces Fe₂O₃ or Cr₂O₃ to respective metals and acts as a reducing agent.

Fe₂O₃ + 2Al → Al₂O₃ + 2 Fe

3. (b) NOTE: During the extraction of copper, iron is present in the ore as impurity (FeS).

The ore together with a little coke and silica is smelted; FeS present as impurity in the ore is oxidized to iron oxide, which then reacts with silica to form fusible ferrous silicate which is removed as slag.

4. (a) MgCl₂ → Mg²⁺ + 2Cl⁻ (fused anhydrous)

At cathode: Mg²⁺ + 2e⁻ → Mg;
At anode: 2Cl⁻ → 2e⁻ → Cl₂ ↑

5. (c) Cuprite: Cu₂O; Chalcocite: Cu₉S₆; Chalcopyrite: CuFeS₂;

Malachite: Cu(OH)₂; CuCO₃. We see that CuFeS₂ contains both Cu and Fe.

6. (b) NOTE: Extraction of Zn from ZnS (Zinc blende) is achieved by roasting followed by reduction with carbon.

2ZnS + 3O₂ → 2ZnO + 2SO₂

ZnO + C → Zn + CO

7. (d) (i) Haematite is Fe₂O₃ in which Fe is present in III oxidation state.

(ii) Magnetite (Fe₃O₄) is an equimolar mixture of FeO and Fe₂O₃.

Oxidation state of Fe in FeO is II.

Oxidation state of Fe in Fe₂O₃ is III.

8. (b) The reactions involved in cyanide extraction process are:

Ag₂S + 4NaCN → 2Na[Ag(CN)₂] + Na₂S (argentite)

4Na₂S + 5O₂ + 2H₂O → 2Na₂SO₄ + 4NaOH + 2S

Oxidizing agent

2Na[Ag(CN)₂] + Zn → Na₂[Zn(CN)₄] + 2Ag ↓

(reducing agent)
9. **(a)** Silver, copper and lead are commonly found in earth's crust as Ag₂S (silver glance), CuFeS₂ (copper pyrites) and PbS (galena)

**D. MCQs with One or More Than One Correct**

1. **(b, d)** Both Mg and Al have their reduction potentials less than that of water \(E^\circ = -0.83 \text{ V} \). Hence, their ions in the aqueous solution cannot be reduced. Instead water will be reduced: \(2H_2O + 2e^- \rightarrow H_2 + 2OH^-\)

2. **(a, c, d)**

3. **(c, d)** Al from \(Al_2O_3\) and Mg from \(MgCO_3\), \(CaCO_3\) are separately extracted by electrolytic reduction.

4. **(b, c, d)**
\[
\begin{align*}
Cu_2S + 2Cu_2O & \rightarrow 6Cu + SO_2 \\
Cu_2S + 2CuO & \rightarrow 4Cu + SO_2 \\
Cu_2S + CuSO_4 & \rightarrow 3Cu + 2SO_2
\end{align*}
\]

5. **(b, c, d)** In electrolytic refining of blister Cu, acidified CuSO₄ is used as electrolyte, pure Cu deposits at cathode and impurities settle as anode mud.

6. **(a, b, c)**

Copper pyrite \([CuFeS_2]\)

\[
\begin{align*}
\text{Crushing into fine powder} \\
\text{Concentrated by froth floatation process} \\
\text{Roasting take place in reverberatory furnace}
\end{align*}
\]

\[
\begin{align*}
2CuFeS_2 + O_2 & \xrightarrow{\text{(air)}} Cu_2S + 2FeS + SO_2 \\
FeS + O_2 & \xrightarrow{\Delta} FeO + SO_2
\end{align*}
\]

\[
\begin{align*}
\text{Smelting:} & \quad \boxed{\text{Iron is removed as slag of FeSiO_3}} \\
& \quad \boxed{\text{FeO + SiO_2 (flux) } \xrightarrow{\Delta} \text{FeSiO}_3 (\ell)(\text{slag})}
\end{align*}
\]

Copper matte \((Cu_2S + FeS)\)

\[
\begin{align*}
\text{Self reduction occurs in Bessemer converter}
2Cu_2S + 3O_2 & \rightarrow 2Cu_2O + 2SO_2 \\
Cu_2S + 2CuO & \rightarrow 6Cu + SO_2
\end{align*}
\]

(Blister copper)

Refining of blister copper is done by poling followed by electrefining but not by carbon reduction method.

**E. Subjective Problems**

1. **(a)** Galena is roasted in excess of air in a reverberatory furnace

\[
2\text{PbS} + 3O_2 \rightarrow 2\text{PbO} + 2\text{SO}_2 \quad \text{(air)}
\]

\[
PbS + 2O_2 \rightarrow \text{PbSO}_4
\]

It is followed by self reduction

\[
PbS + \text{PbSO}_4 \rightarrow 2\text{Pb} + 2\text{SO}_2
\]

\[
PbS + 2\text{PbO} \rightarrow 3\text{Pb} + \text{SO}_2
\]

**F. Match the Following**

1. **(A)- p, r; (B)- p, r; (C)- q; (D)- s**

**NOTE:** The oxides and sulphides of less active metals like Hg, Cu & Pb are unstable to heat and hence no reducing agent is required. They undergo self reduction.

(A) \[
2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2
\]

(B) \[
2\text{PbS} + 3O_2 \rightarrow 2\text{PbO} + 2\text{SO}_2 \\
\text{PbS} + 2\text{PbO} \rightarrow 3\text{Pb} + \text{SO}_2
\]

Hence (A) \(\rightarrow\) (p), (r)

**NOTE:** The oxides of less electropositive metals like Pb, Zn, Fe, Sn, Cu, etc. are reduced by strongly heating them with coke or coal.
1. (c) Pure aluminium can be obtained by electrolysis of a mixture containing alumina, crayolite and fluor spar in the ratio 20 : 24 : 20. The fusion temperature of this mixture is 900°C and it is a good conductor of electricity.

2. (b) Silver ore forms a soluble complex with NaCN from which silver is precipitated using scrap zinc.

\[ \text{Ag}_2\text{S} + 2\text{NaCN} \rightarrow \text{Na}_2\text{Ag(CN)}_2 \] \[ \rightarrow \text{Zn} \] \[ \rightarrow \text{Na}_2[\text{Zn(CN)}_4] + 2\text{Ag} \downarrow \] sod argento-cyanide soluble

3. (c) NOTE: Galena is PbS and thus purified by froth flotation method.

Froth flotation method is used to concentrate sulphide ores. This method is based on the preferential wetting properties with the frothing agent and water.

4. (b) During the process of electrolytic refining Ag and Au are obtained as anode mud.

5. (c) NOTE: The reduction of metal sulphides by carbon reduction process is not spontaneous because \( \Delta G \) for such a process is positive. The reduction of metal oxide by carbon reduction process is spontaneous as \( \Delta G \) for such a process is negative.

From this we find that on thermodynamic considerations \( \text{CO}_2 \) is more stable than \( \text{CS}_2 \) and the metal sulphides are more stable than corresponding oxides.

In view of above the factor listed in choice (c) is incorrect and so is of no significance.

Hence the correct answer is (c)

6. (c) Moles of HCl taken = \( 20 \times 0.1 \times 10^{-3} = 2 \times 10^{-3} \) Moles of HCl neutralised by \( \text{NaOH} \) solution \( = 15 \times 0.1 \times 10^{-3} = 1.5 \times 10^{-3} \)

Moles of HCl neutralised by ammonia \( = 2 \times 10^{-3} - 1.5 \times 10^{-3} = 0.5 \times 10^{-3} \)

\( \% \) of nitrogen = \( \frac{1.4 \times N \times V}{\text{w.t. of Substance}} \times 100 \)

\( = \frac{1.4 \times 0.5 \times 10^{-3}}{29.5 \times 10^{-3}} \times 100 = 23.7\% \)

7. (d) Van Arkel is a method in which heat treatment is used to purify metal in this process metals are converted into other metal compound for loosely coupled like as iodine to make metal iodide which are easily decomposed and give pure metal.

The process is known as Van Arkel method.

8. (b) On electrolysis of aqueous solution of s-block elements \( \text{H}_2 \) gas discharge at cathode.

At cathode: \( \text{H}_2\text{O} + e^- \rightarrow \frac{1}{2} \text{H}_2 + \text{OH}^- \)

9. (b) In the metallurgy of aluminium, purified \( \text{Al}_2\text{O}_3 \) is mixed with \( \text{Na}_2\text{AlF}_6 \) or \( \text{CaF}_2 \) which lowers the melting point of the mix and brings conductivity.

10. (a) Froth flotation method is mainly applicable for sulphide ores.

(1) Malachite ore: \( \text{Cu(OH)}_2 \), \( \text{CuCO}_3 \)

(2) Magnetite ore: \( \text{Fe}_3\text{O}_4 \)

(3) Siderite ore: \( \text{FeCO}_3 \)

(4) Galena ore: \( \text{PbS} \) ( Sulphide Ore)
The p-Block Elements

Section-A : JEE Advanced/ IIT-JEE

   6. white/yellow  7. hypobromous, bromide  8. cross-linking  9. two
   15. I₃ complex ion  16. glass  17. inert-pair effect
C 1. (c)  2. (b)  3. (a)  4. (c)  5. (a)  6. (d)  7. (c)  8. (d)  9. (d)  10. (c)
   11. (b)  12. (b)  13. (a)  14. (c)  15. (b)  16. (b)  17. (d)  18. (a)  19. (b)  20. (d)
   21. (c)  22. (b)  23. (d)  24. (c)  25. (c)  26. (b)  27. (d)  28. (a)  29. (b)  30. (c)
   31. (d)  32. (c)  33. (b)  34. (c)  35. (c)  36. (c)  37. (d)  38. (c)  39. (a)  40. (a)
   41. (c)  42. (b)  43. (c)  44. (b)  45. (b)  46. (c)  47. (c)  48. (b)  49. (b)  50. (b)
   51. (d)  52. (b)  53. (b)  54. (d)  55. (b)  56. (c)  57. (d)  58. (b)  59. (a)  60. (c)
   61. (b)  62. (a)
D 1. (a, b)  2. (a, d)  3. (a, d)  4. (b, c)  5. (b)  6. (a, b, d)  7. (a, c, d)  8. (c)  9. (a, b)  10. (a, b, c)
   11. (a, c, d)  12. (b, d)  13. (a, c, d)  14. (a, b, c)  15. (b, d)  16. (b, c)  17. (b)  18. (a, c, d)  19. (b, d)
E 14. (i) HBr < HCl < HF,  (ii) HOCI < HOCIO < HOCIO₂ < HOCIO₃
       (iii) SiO₂ < CO₂ < N₂O₅ < SO₃,
       (iv) CCl₄ < MgCl₂ < AlCl₃ < SiCl₄ < PCl₅
   17. [A]-PbO, [B]-heat in the absence of air  19. 12, 4  22. M=As, N=AsH₃
   27. vanadium pentoxide  28. Ca(OH)₂, NH₄HCO₃, Na₂CO₃, NH₄Cl, CaCl₂
   32. BCl₃ or BB₃, B₂H₆
   36. O.N. of Pb in PbO is +2
   37. NaHSO₃ (OS = +4), Na₂SO₃ (OS = +4), Na₂S₂O₇ (OS = -2), Na₂S₄O₆ (OS = +2.5)
   39. 1008 g
   41. Conc. H₂SO₄, Br₂, NO₂⁺, TNT

Section-B : JEE Main/ AIEEE

A 1. (A)⁻; (B)⁻; (C)⁻; (D)⁺
   2. (A)⁻; (B)⁺; (C)⁺; (D)⁻
   3. (A)-p, r, t; (B)-s, t; (C)-p, q, r; (D)-p, r, s
   4. (d)

B 1. (a)  2. (c)  3. (a)  4. (c)  5. (c)  6. (b)  7. (a)  8. (c)  9. (a)  10. (a)
   11. (b)  12. (d)  13. (d)  14. (c)  15. (c)  16. (b)  17. (b)  18. (c)  19. (c)  20. (b)
   21. (d)  22. (d)  23. (b)  24. (b)  25. (b)  26. (d)  27. (a)  28. (c)  29. (d)  30. (a)
   31. (d)  32. (a)  33. (c)  34. (c)  35. (a)  36. (b)  37. (b)  38. (c)  39. (b)  40. (c)  41. (c)
A. Fill in the Blanks

1. $-3$;
2. NaIO$_3$
   $$3I_2 + 6NaOH \rightarrow 5NaI + NaIO_3 + 3H_2O$$ (hot)
3. HF; HF is the weakest of the three, because the ionisation (i.e. acidic character) of HX is a multistep process and when its $\Delta H$, heat of ionisation, is calculated it comes out to be the minimum. This is due to the strong H – F bond, large heat of hydration (because of H-bonding) and low value of electron affinity of F-atom.
4. KI$_3$; complexes are more soluble in water as compared to normal salts. [KI$+1_2 \rightarrow$ KI$_3$]
5. sodium hydroxide;
   $$Al + 2NaOH + 2H_2O \rightarrow 2NaAlO_2 + 3H_2$$
6. white/ yellow; NOTE: In white phosphorus, each phosphorus atom is linked to the other three atoms by covalent bonds. PPF bond angle is 60°, due to which the molecule remains under strain and hence is active in nature.
7. Hypobromous; bromite. HBrO $\rightarrow$ H$^+$ + BrO$^-$
8. cross-linking;
9. two; $\text{H}_3\text{P} \rightarrow \text{OH}$ [It contains two replaceable hydrogens.]
10. Silicones;
11. four.

In each P atom is linked to 4 oxygen atoms

12. Nitric oxide. [NO]
   The mixture containing SO$_2$, air and nitric oxide, when treated with steam, sulphuric acid is formed.
   $$2SO_2 + O_2 + 2H_2O + [\text{NO}] \rightarrow 2H_2SO_4 + [\text{NO}]$$ (Catalyst)
13. Trialkylchlorosilanol; The hydrolysis of R$_3$SiCl, yields R$_3$Si(OH) which condenses to give R$_3$Si – O – SiR$_3$
   $$R_3SiO – H + H – O^– \rightarrow R_3Si – O – Si – R_3$$
14. Fullerene
15. $I_3^–$ complex ion; $I_2 + I^– \rightarrow I_3^–$
16. glass
17. inert-pair effect; When ns$^2$ electrons of outermost shell do not participate in bonding it is called inert pair and the effect is called inert pair effect.

B. True/False

1. False: Red phosphorus is polymeric substance. It exist as chains of P$_4$ tetrahedra linked together. Therefore, it is less volatile than white phosphorus.
2. False: PbO$_2$ is a dioxide and it does not give hydrogen peroxide when it reacts with a dilute acid.
   $$\text{PbO}_2 + 4\text{HCl} \rightarrow \text{PbCl}_2 + \text{Cl}_2 + 2\text{H}_2\text{O}$$
3. False: CCl$_4$ gives phosgene with superheated steam.
   $$\text{CCl}_4 + \text{H}_2\text{O} \rightarrow \text{COCl}_2 + 2\text{HCl}$$
4. True: Fe + 2HCl $\rightarrow$ FeCl$_2$ + H$_2$ [In FeCl$_2$, Fe is in +2 state.]
5. False: Since halogens have high electron affinities, they easily pick up electrons from other substances. Hence halogens are oxidising agents. The oxidising power decreases from fluorine to iodine. Since fluoride is the strongest oxidising agent it will oxidise any of the other halide ions in solution or when dry. Similarly, Cl$_2$ will displace Br$^–$ and I$^–$ ions from their solutions and Br$_2$ will displace I$^–$ ions.
   NOTE: In general, a halogen of low atomic number will oxidise the halide ion of higher atomic number.
6. True:
   NOTE: The central element in the metal hydrides of group 15 elements is although in $sp^3$ hybrid state, the H – M – H bond angle is less than the normal tetrahedral bond angle of 109° 28’; e.g. the bond angle, H – N – H in NH$_3$ is 106° 45’. This is due to greater repulsion between a lone pair and a bond pair of electrons than between the two bond pairs of electrons.
   The decrease in bond angle from 106° 45’ in ammonia to about 90° in AsH$_3$ can be explained by the fact that in the latter case $sp^3$ hybridisation becomes less and less distinct with the increasing size of their electron clouds, i.e., pure $p$ orbitals (instead of $sp^3$ hybrid orbitals) are used for $M – H$ bonding and the lone pair of electrons is present in spherical $s$-orbital.
7. False: because of its high thermal stability. CCl$_4$ is most stable as compared to other tetrachlorides of the group.
8. True: Graphite is better lubricant on the moon than on the earth because of lack of gravitation pull on the moon, where friction is already less than earth.
9. False: The structure of Al$_2$Cl$_6$ is as under:

```
\begin{center}
\includegraphics[width=0.5\textwidth]{structure.png}
\end{center}
```

Structure of Al$_2$Cl$_6$
The p-Block Elements

Bond distance between aluminium-chlorine bond forming bridge is greater (2.21 Å) than the distance between aluminium-chlorine bond present in the end (2.06 Å).

10. True: The molecule of NO has eleven valence electrons (5 due to N and 6 due to O). It is impossible for all of them to be paired, hence the nitric oxide molecule contains an odd electron which makes gaseous nitric oxide paramagnetic.

\[ \text{N} \quad \quad \quad \text{O} \]

NOTE: In the liquid and solid states, nitric oxide is polymerised to a dimer which is diamagnetic.

11. True: In diamond, each carbon atom is in sp³ hybridised state and is linked to four other neighbouring carbon atoms held at the corners of a regular tetrahedron by covalent bonds. Owing to very strong covalent bonds by which the atoms are held together, diamond is the hardest substance known. Graphite has a two dimensional sheet like structure and carbon in sp² hybridised state is attached to three other carbon atoms by three \( \sigma \) bonds forming a hexagonal planar structure. Due to wide separation and weak interlayer bonds, the two adjacent layers can easily slide over each other; hence graphite is soft.

12. True: The property of catenation in carbon is due to the fact that in carbon atom, the number of valence electrons (4) is equal to the number of valence orbitals (one 2s + three 2p). Hence carbon in the tetravalent state is fully saturated, i.e., it has neither any vacant orbital nor any lone pair of electrons on its atom due to which the C – C bond is extremely stable.

NOTE: The reason for greater tendency of carbon for catenation than silicon may further be explained by the fact that the C – C bond energy is approximately of the same magnitude as the energies of the bond between C and other elements. On the other hand, the Si – Si bond is weaker than the bonds between silicon and other elements.

13. False: None amongst, HBr and HI, HI exhibit hydrogen bonding. HI is a stronger acid than HBr because of its higher dissociation constant, \( K_a \). HI has a stronger tendency to release protons to water molecules and hence is a stronger acid.

C. MCQs with One Correct Answer

1. (c) \( \text{NO} + \text{O}_2 \rightarrow \text{NO}_2 \)

Nitric oxide (colourless)

Nitrogen dioxide (reddish brown coloured)

2. (b) Temporary hardness of water is due to presence of bicarbonates of Ca and Mg and it is removed by adding Ca(OH)₂ to hard water and precipitating these soluble bicarbonates in the form of insoluble salts.

\[ \text{Ca(HCO}_3\text{)}_2 \xrightarrow{\Delta} \text{CaCO}_3\downarrow + \text{CO}_2\uparrow + \text{H}_2\text{O} \]

\[ \text{Mg(HCO}_3\text{)}_2 \xrightarrow{\Delta} \text{Mg(OH)}_2\downarrow + 2\text{CO}_2\uparrow \]

3. (a) Due to highest bond dissociation energy.

4. (c) \( \text{P}_4 + 3\text{NaOH} + 3\text{H}_2\text{O} \rightarrow \text{PH}_3 + 3\text{NaH}_2\text{PO}_2 \)

It is a redox reaction.

(i) Oxidation number increases during oxidation reaction and decreases during reduction reaction.

(ii) In a neutralisation reaction acids and bases react together to form salt and water.

5. (a) \( \text{Cl}_2 \) is more reactive than bromine.

6. (d) All are colourless gases.

7. (c)

8. (d) None; it reacts with all given compounds. It forms addition compounds with them.

It can be dried over any metal oxide.

9. (d) HI and HBr (in that order) are the strongest reducing hydrazides and hence they reduce \( \text{H}_2\text{SO}_4 \). HCl is quite stable and hence is oxidised by strong oxidising agent like KMnO₄. HF is not a reducing agent. In the smallest F⁻ ion, the electron which is to be removed during oxidation is closest to the nucleus and therefore most difficult to be removed. Therefore, HF is a poor reducing agent.

10. (c) \( \text{AlCl}_3 \) exists as a dimer (\( \text{Al}_2\text{Cl}_6 \)). It is a strong Lewis acid as it has an incomplete octet and has a tendency to gain electrons. \( \text{AlCl}_3 \) undergoes hydrolysis easily and forms an acidic solution.

\[ \text{AlCl}_3 + 3\text{H}_2\text{O} \rightarrow \text{Al(OH)}_3 + 3\text{HCl} \]

Option (c) is true that \( \text{AlCl}_3 \) sublimes at 100°C under vacuum.

\( \text{AlCl}_3 \) is a Lewis acid.

11. (b) Graphite shows moderate electrical conductivity due to the presence of unpaired or free fourth valence electron on each carbon atom.

12. (b) Bleaching action of chlorine is only in presence of moisture where nascent oxygen is displaced from \( \text{H}_2\text{O} \). \( \text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HCl} + \text{HClO} \) (unstable)

\[ \text{HClO} \rightarrow \text{HCl} + \text{O} \]

13. (a) Only nitrates of heavy metals and lithium decompose on heating to produce \( \text{NO}_2 \).

14. (c) \( \text{SO}_2 \) is highly soluble in water and therefore cannot be collected over water.

15. (b) \( 2\text{HgO} \xrightarrow{\Delta} 2\text{Hg} + \text{O}_2 \)

16. (b) The structure clearly shows the presence of covalent and co-ordinate bonds.

17. (d) \( \text{NO}_2 \) is reddish brown coloured gas. Rest of the oxides are colourless.

18. (a) Least basic trihalogen of nitrogen is \( \text{NF}_3 \) because of the highest electronegativity of fluorine.

19. (b) Chlorine is stronger oxidising agent than bromine, therefore, chlorine water will liberate bromine from KBr solution.

\[ 2\text{KBr} + \text{Cl}_2 \rightarrow 2\text{KCl} + \text{Br}_2 \]
20. (d) In $\text{S}_2\text{O}_5^{2-}$ there is an S–O–S bond unlike in other. So S–S bond is absent as can be seen from the structure drawn.

\[
\begin{align*}
\text{S}_2\text{O}_4^{2-} & \quad \text{S}_2\text{O}_7^{2-} \\
\text{S}_2\text{O}_5^{2-} & \quad \text{S}_2\text{O}_3^{2-}
\end{align*}
\]

21. (c) In $\text{P}_4\text{O}_{10}$, each P atom is linked to 4 oxygen atoms as can be confirmed by its structure. It is linked to three oxygen atoms by single bond and with one oxygen atom by double bond. [For structure refer to Q.11 of Section A]

22. (b) HBr is not prepared by heating NaBr with conc. $\text{H}_2\text{SO}_4$ because HBr is a strong reducing agent and reduce $\text{H}_2\text{SO}_4$ to $\text{SO}_2$ and is itself oxidised to bromine.

\[
\text{NaBr} + \text{H}_2\text{SO}_4 \rightarrow \text{NaHSO}_4 + \text{HBr}
\]

\[
\text{H}_2\text{SO}_4 + 2\text{HBr} \rightarrow \text{SO}_2 + \text{Br}_2 + 2\text{H}_2\text{O}
\]

23. (d) HO\text{S}=\text{O}–\text{O}=\text{S}–\text{OH} + 2 \text{H}_2\text{O}

peroxodisulphuric acid

\[
\rightarrow 2\text{HO}–\text{S}–\text{O}–\text{OH} + \text{H}_2\text{O}_2
\]

peroxomonosulphuric acid

hydrogen peroxide

24. (c) $\text{CsBr}_3$ may be represented as $\text{Cs}^+\text{Br}_3^-$

25. (c) $\text{KF} + \text{HF} \rightarrow \text{KHF}_2 \rightleftharpoons \text{K}^+ + (\text{HF}_2)^-$

26. (b) $\text{Na}_2\text{SO}_3 + \text{S} \xrightarrow{\text{In alkaline medium}} \text{Na}_2\text{S}_2\text{O}_3$

27. (d) Due to inert pair effect.

28. (a) CO is an example of neutral oxide.

29. (b) The species called as pseudohalide ions are these are monovalent and made by electronegative atoms. They possess properties similar to halide ion. The corresponding dimers of these pseudohalide ions are called pseudohalogens. $\text{RCO}_2^-$ is not is pseudohalide.

30. (c) $\text{Cs}_3\text{P}_2 + 6\text{H}_2\text{O} \rightarrow 3\text{Ca(OH)}_2 + 2\text{PH}_3$; i.e. 2 moles of phosphine are produced.

31. (d) $(\text{NH}_4)_2\text{Cr}_2\text{O}_7 \rightarrow \text{N}_2 + \text{Cr}_2\text{O}_3 + 4\text{H}_2\text{O}$

32. (c) $\text{Al}_2\text{O}_3$ is electrolyte, while $\text{Na}_2\text{AlF}_6$ is used to decrease the melting point of $\text{Al}_2\text{O}_3$ and to increase the conductivity.

33. (b) In $\text{BCl}_3$, $\text{H} = \frac{1}{2} (3 + 3 + 0 – 0) = 3$; sp$^2$ hybridization (bond angle = 120°) similarly $\text{PCl}_3$, $\text{AsCl}_3$ and $\text{BiCl}_3$ are found to have sp$^3$ hybridized central atom with one lone pair of electrons on the central atom. The bond angle ≤ 109°28’, since the central atoms belong to the same group, the bond angle of the chlorides decreases as we go down the group. Thus the order of bond angle is $\text{BCl}_3 > \text{PCl}_3 > \text{AsCl}_3 > \text{BiCl}_3$.

34. (c) Cryolite reduces the melting temperature.

35. (c) In cyclic metaphosphoric acid number of P–O–P bonds is three.

36. (c) $\text{NH}_3$ does not react with $\text{CaO}$ while other reacts with $\text{NH}_3$

\[
2\text{NH}_3 + \text{H}_2\text{SO}_4 \rightarrow (\text{NH}_4)_2\text{SO}_4
\]

\[
\text{P}_4\text{O}_{10} + 12\text{NH}_3 \rightarrow 4(\text{NH}_4)_3\text{PO}_4 + 6\text{H}_2\text{O}
\]

\[
\text{CaCl}_2 + 8\text{H}_2\text{O} \rightarrow \text{CaCl}_2\cdot 8\text{H}_2\text{O}
\]

37. (d) In sulphur trioxide trimer $\text{S}_3\text{O}_6$ (also called γ-sulphur trioxide) two sulphur atoms are linked to each other via O atoms, hence there is no S–S bond.

38. (c) $2\text{Ca}^{2+} + \text{Na}_2[\text{Na}_4(\text{PO}_3)_6] \rightarrow 4\text{Na}^+ + \text{Na}_2[\text{Ca}_2(\text{PO}_3)_6]$ water soluble

39. (a) The structure of $\text{H}_3\text{PO}_4$ is as follows: There are only two –OH groups and hence dibasic. The oxidation number of P in this acid is +3. Whereas P can have +5 oxidation state also. Therefore, $\text{H}_3\text{PO}_4$ can be oxidised which means $\text{H}_3\text{PO}_4$ is a reducing agent.

40. (a) The central boron atom in boric acid, $\text{H}_3\text{BO}_3$ is electron-deficient.

NOTE: Boric acid is a Lewis acid with one p-orbital vacant. There is no d-orbital of suitable energy in boron atom. So, it can accommodate only
The p-Block Elements

one additional electron pair in its outermost shell.

\[
\begin{align*}
H_2O + B(OH)_3 & \quad \xrightarrow{\text{Base, Acid}} \quad OH_2 \\
& \quad \xrightarrow{\text{Polymerisation}} \quad [B(OH)_4]^- + H_2O
\end{align*}
\]

41. (c) TIPS/FORMULAE:
It appears at the first sight that Me₂SiCl₂ on hydrolysis will produce Me₂Si(OH)₂ which ultimately upon loss of water, will form Me₂Si ≡ O.
But silicon atom, because of its very large size in comparison to oxygen, is unable to form π-bond. Thus, the product of hydrolysis is polymeric in nature.

\[
\begin{align*}
\text{Me} & \quad \text{Me} \\
\text{Me} & \quad \text{Me}
\end{align*}
\]

42. (b) In XeOF₄, Xenon is \( sp^3d^2 \) hybridised and has one lone pair.
43. (c) Among oxyacids of sulphur, only Caro’s acid (H₂SO₃) and Marshall’s acid (H₃S₂O₄) have the O–O linkage.
44. (b) Tin can be extracted only by carbon reduction method, while lead can be extracted by self as well as carbon reduction method.
\[
\text{SnO}_2 + C \quad \xrightarrow{\text{Sn + CO}_2} \quad \text{PbS + 2PbO} \quad \xrightarrow{\text{3PbO + SO}_2}
\]
45. (b) Two dimensional sheet structures are formed when three oxygen atoms of each \([\text{SiO}_4]^{4-}\) tetrahedral are shared.
46. (c) The ignition temperature of black phosphorus is highest among all its allotropes, hence is most stable.
47. (c) In KMnO₄ manganese is already present in its highest possible oxidation state i.e. +7. So no further oxidation is possible.
48. (b) NO (g) + NO₂ (g) \xrightarrow{-30^\circ C} N₂O₃ (blue liquid)
49. (b) PbO₂ is a powerful oxidizing agent and liberate O₂ when treated with acids.
\[
2\text{PbO}_2 + 4\text{HNO}_3 \quad \xrightarrow{} \quad 2\text{Pb(NO}_3)_2 + 2\text{H}_2\text{O} + \text{O}_2 \quad \uparrow
\]
50. (b) \text{cis}-1,2-diol forms chelated complex ion with the product, \([\text{B(OH)}_2]^-\) causing the reaction to proceed in forward direction.
\[
\begin{align*}
\text{CH}_2\text{-OH} + [\text{HO-B-OH}] + \text{HO-CH}_2 & \xrightarrow{\text{HO-CH}_2} \quad \left[\text{CH}_2\text{-O-B-O-CH}_2\right]^{-} \\
\text{Stable chelated complex ion}
\end{align*}
\]

51. (d) In P₄, the P–P linkage is formed by \( sp^3–sp^3 \) hybridised orbital overlapping. So the percentage of \( \pi \)-character will be 75%.
52. (b) The following reaction occurs
\[
\text{Na}_2\text{S}_2\text{O}_3 + 4\text{Cl}_2 + 5\text{H}_2\text{O} \quad \xrightarrow{} \quad 2\text{NaHSO}_4 + 8\text{HCl}.
\]
53. (b) \( P_4 + 3\text{O}_2 \) \( \text{in presence of N}_2 \) \( \xrightarrow{} \) \( P_4\text{O}_6 \)
Here \( \text{N}_2 \) acts as a diluent and thus retards further oxidation. Reaction of \( P_4 \) under other three conditions.
(a) \( P_4 + 3\text{O}_2 \xrightarrow{} P_4\text{O}_6 \xrightarrow{2\text{O}_2} P_5\text{O}_{10} \)
(c) In moist air, \( P_4\text{O}_6 \) is hydrolysed to form \( \text{H}_3\text{PO}_3 \)
\[
P_5\text{O}_{10} + 6\text{H}_2\text{O} \quad \xrightarrow{} \quad 4\text{H}_3\text{PO}_3
\]
(d) In presence of \( \text{NaOH} \), \( P_4 + 3\text{OH}^- + 3\text{H}_2\text{O} \xrightarrow{} \text{PH}_3 + 3\text{H}_2\text{PO}_2^- \\
54. (d) \( \text{Ba(N}_3)_2 \xrightarrow{} \text{Ba + 3N}_2 \)
55. (b) \( \text{HNO}_3, \text{NO}, \text{N}_2, \text{NH}_4\text{Cl} \)
56. (c) \( \text{Oxidation} \)
\[
\text{P}_4 + 3\text{NaOH} + 3\text{H}_2\text{O} \quad \xrightarrow{-3} \quad \text{PH}_3 + 3\text{NaH}_2\text{PO}_4
\]
\[
\text{Reduction} \quad \xrightarrow{2\uparrow} \quad \text{Na}_3\text{PO}_4 + \text{PH}_3
\]
57. (d) \( \text{XeO}_2\text{F}_2 \) has trigonal bipyramidal geometry, due to presence of lone pair of electrons on equitorial position, its shape is \text{see-saw}.
58. (b) The slow decomposition of \( \text{HNO}_3 \) is represented by the eqn.
\[
4\text{HNO}_3 \quad \xrightarrow{} \quad 4\text{NO}_2 + 2\text{H}_2\text{O} + \text{O}_2
\]
(yellow-brown)
59. (a) \( P_4 + 8\text{SOCl}_2 \xrightarrow{} 4\text{PCl}_3 + 4\text{SO}_2 + 2\text{S}_2\text{Cl}_2 \)
white phosphorus
60. (c) \( \text{XeF}_6 \) \( \xrightarrow{\text{Complete Hydrolysis}} \) \( \text{XeO}_3 + \text{H}_2\text{F}_2 \)
\[
\xrightarrow{\text{(P) O}} \quad \text{HxeO}_2^- \quad \xrightarrow{\text{(Q) OH}^- + \text{H}_2\text{O} + \text{O}_2(g)} \quad \text{XeO}_4^2+ + \text{Xe(g)}
\]
61. (b) Atomic radii increases on moving down a group. However due to poor shielding effect of d orbit, atomic radius of Ga is smaller than Al (anomaly). Thus the correct order is Ga < Al < In < Tl.

62. (a) 

\[
\text{S}_2\text{O}_3^{2-} \xrightarrow{\text{Ag}^+} \text{Ag}_2\text{S}_2\text{O}_3 \xrightarrow{\text{Y}} \text{Ag}_2\text{S}_2\text{O}_3 \xrightarrow{\text{Z}} \text{Ag}_2\text{S} \]

(X) clear solution

on standing

white precipitate

black precipitate

So, X, Y and Z are \([\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}\), \(\text{Ag}_2\text{S}_2\text{O}_3\) and \(\text{Ag}_2\text{S}\) respectively.

D. MCQs with One or More Than One Correct

1. (a, b) Because of high melting point (2050°C), pure alumina cannot be electrolysed. Hence a mixture of alumina, cryolite (m.p. 1000°C) and calcium fluoride (to lower the temperature of the melt) is electrolysed at about 900°C.

   NOTE: The function of cryolite is to increase the electrical conductivity of the electrolyte, and to lower the temperature of the melt.

2. (a, d) \(\text{NH}_3 \text{NO}_3 \rightarrow \text{N}_2 \text{O} + 2\text{H}_2\text{O}\)
   \(\text{NH}_2\text{OH} \cdot \text{HCl} + \text{NaNO}_2 \rightarrow \text{N}_2\text{O} + \text{NaCl} + 2\text{H}_2\text{O}\)

3. (a, d) \(\text{NH}_3\) and \(\text{CF}_2\text{Cl}_2\) (freon-12) are used as refrigerants.

4. (b, c) To make the fused mixture very conducting and to reduce the temperature of the melt.

5. (b) Silicon is used in solar cells.

6. (a, b, d) Sodium nitrate on decomposition up to 500°C gives \(\text{NaNO}_2\) and oxygen.

   \(2\text{NaNO}_3 \xrightarrow{\Delta} 2\text{NaNO}_2 + \text{O}_2 \uparrow\)

   While at higher temperature (i.e. above to 800°C), \(\text{NaNO}_2\) further decomposes into \(\text{Na}_2\text{O}, \text{N}_2\) and \(\text{O}_2\).

7. (a, c, d) The four atoms in a \(\text{P}_4\) molecule are situated at the corners of a tetrahedron. There are six P – P single bonds with PPP bond angle equal to 60°. Each phosphorus has a lone pair of electrons.

8. (c) \(2\text{NH}_3 + \text{OCl}^- \rightarrow \text{NH}_4\text{Cl} + \text{H}_2\text{O}\)

9. (a, b) When ammonium salt \(\text{NH}_4\text{NO}_3\) or \(\text{NH}_4\text{NO}_2\) (ammonium salts are colourless) is boiled with excess of \(\text{NaOH}\), ammonia (\(\text{NH}_3\)) gas is evolved as follows:

   \(\text{NH}_4\text{NO}_3 + \text{NaOH} \rightarrow \text{NaNO}_3 + \text{NH}_3 + \text{H}_2\text{O}\)

   \(\text{NH}_4\text{NO}_2 + \text{NaOH} \rightarrow \text{NaNO}_3 + \text{NH}_3 + \text{H}_2\text{O}\)

   The \(\text{NH}_3\) gas evolved is non-flammable gas.

   When the gas evolution ceases we are left with \(\text{NaNO}_2\) or \(\text{NaNO}_3\) in solution.

   These salts get reduced when \(\text{Zn}\) is added to this solution containing salt (\(\text{NaNO}_2\) or \(\text{NaNO}_3\)) and excess \(\text{NaOH}\) and \(\text{NH}_3\) gas is evolve.

   \(\text{NaNO}_2 + 6(\text{H}) \xrightarrow{\text{Zn/NaOH}} \text{NaOH} + \text{NH}_3 + \text{H}_2\text{O}\)

   \(\text{NaNO}_3 + 8(\text{H}) \rightarrow \text{Zn/NaOH} \rightarrow \text{NaOH} + \text{NH}_3 + 2\text{H}_2\text{O}\)

Thus the colourless salt \([\text{H}]\) is either \(\text{NH}_4\text{NO}_2\) or \(\text{NH}_4\text{NO}_3\).

Thus (a) and (b) are correct answers.

[NOTE: \(\text{NaCl}\) formed has no reaction with \(\text{NaOH}\)]

10. (a, b, c) \(\text{N} \equiv \text{N} \rightarrow \text{O}\)

   (a)

   (b)

   (c)

   (d)

11. (a, c, d) \(\text{HX} + \text{AgNO}_3 \rightarrow \text{AgX} \downarrow + \text{HNO}_3\) (\(X = \text{Cl}, \text{Br}, \text{I}\))

   \(\text{AgX} + 2\text{Na}_2\text{S}_2\text{O}_3 \rightarrow \text{Na}_3[\text{Ag(S}_2\text{O}_3)_2] + \text{NaX}\)

12. (b, d)

   (a) Diamond is harder than graphite.

   (b) Graphite is good conductor of electricity as each carbon is attached to three C-atoms leaving one valency free, which is responsible for electrical conduction, while in diamond, all the four valencies of carbon are satisfied, hence insulator.

   (c) Diamond is better thermal conductor than graphite. Whereas electrical conduction is due to availability of free electrons; thermal conduction is due to transfer of thermal vibrations from atom to atom. A compact and precisely aligned crystal like diamond thus facilitates fast movement of heat.

   (d) In graphite, C – C bond acquires double bond character, hence higher bond order than in diamond.

13. (a, c, d)

\[
\text{O} = \text{O} \rightarrow \text{O} = \text{O} \rightarrow \text{O} = \text{O} \rightarrow \text{O} = \text{O}
\]

Ozone is diamagnetic in nature (due to presence of paired electron) and both the O – O bond length are equal. It has a bent structure.

14. (a, b, d) Balanced chemical equation is

\[
\text{6I}^- + \text{ClO}_3^- + 6\text{H}_2\text{SO}_4 \rightarrow \text{Cl}^- + 6\text{HSO}_4^- + 3\text{I}_2 + 3\text{H}_2\text{O}
\]

15. (b, d) \(\text{H}_2\text{BO}_3\) does not undergo self ionization. However, it acts as a weak acid in water (hence it is a weak electrolyte in water).

   \(\text{H}_2\text{BO}_3 + \text{H}_2\text{O} \rightarrow \text{B(OH)}_4^- + \text{H}^+\)

Addition of \(\text{cis}-\text{dilis}\) (e.g., ethylene glycol) to aqueous solution of orthoboric acid leads to complex formation, thus acidity of aqueous solution of orthoboric acid is increased.
The p-Block Elements

\[ \text{B(OH)}_4^- + 2 \text{CH}_2\text{OH} \rightarrow \left[ \begin{array}{c} \text{CH}_2\text{OH} \\ \text{CH}_2\text{OH} \\ \text{CH}_2\text{OH} \\ \text{CH}_2\text{OH} \end{array} \right] + 4\text{H}_2\text{O} \]

It arranges to planner sheets due to H-bonding.

16. (b, c)

(i) \[
\begin{array}{c}
\text{Cl-O-H} \\
\text{Cl-OH}
\end{array}
\]

(ii) \[
\begin{array}{c}
\text{Cl-O-H} \\
\text{Cl-OH}
\end{array}
\]

(iii) \[
\begin{array}{c}
\text{Cl-O-H} \\
\text{Cl-OH}
\end{array}
\]

(iv) \[
\begin{array}{c}
\text{Cl-O-H} \\
\text{Cl-OH}
\end{array}
\]

Number of Cl = O bonds in (ii) and (iii) together is 3
Number of lone pairs on Cl in (ii) and (iii) together is 3
Hybridisation of Cl in all the four is \(sp^3\)
Strongest acid is \(\text{HClO}_4\)

17. (b) \((\text{CH}_3)_2\text{SiCl}_2\) form linear polymer on hydrolysis and \((\text{CH}_3)_2\text{SiCl}_2\) is a chain terminator.

18. (a, c, d) Structure of borax

Correct formula of borax is \(\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 8\text{H}_2\text{O}\)
(A) Borax has tetraneurac. \([\text{B}_4\text{O}_5(\text{OH})_4]^{2-}\) unit
(B) Only two 'B' atom lie in same plane
(C) two Boron are \(sp^2\) and two are \(sp^3\) hybridised.
(D) one terminal hydroxide per boran atom.

19. (b, d)

\[
P_{4}\text{O}_{10} + 4\text{HNO}_3 \rightarrow 4(\text{HPO}_3)^2^- + 2\text{N}_2\text{O}_5
\]

(required product)

(A) \(P_4 + 20\text{HNO}_3 \rightarrow 4\text{H}_3\text{PO}_4 + 20\text{NO}_2 \uparrow + 4\text{H}_2\text{O}\)
(B) \(\text{N}_2\text{O}_5\) is diamagnetic in nature
(C) \(\text{N}_2\text{O}_5 \rightarrow \text{O} = \text{O} = \text{O}\)

\(\text{N}_2\text{O}_5\) contains one \(\text{N-O-N}\) bond not \(\text{N-N}\) bond.
(D) \(\text{Na} + \text{N}_2\text{O}_5 \rightarrow \text{NaNO}_3 + \text{NO}_2 \uparrow\)
(Brown gas)

E. Subjective Problems

1. (i) \(\text{HBr}\) is a reducing agent and it reduces \(\text{H}_2\text{SO}_4\) to \(\text{SO}_2\).
(ii) Acids turn blue litmus red, so \(\text{HClO}\) also turns blue litmus red. The colour of litmus is decolourised because \(\text{HClO}\) is also a strong oxidising agent.

2. (i) \(\text{Al}_2\text{O}_3 + 3\text{C} + 3\text{Cl}_2 \rightarrow 2\text{AlCl}_3 + 3\text{CO}\)
Alumina \(\rightarrow\) Aluminium chloride
(ii) \(\text{Ca(OH)}_2 + \text{Cl}_2 \rightarrow \text{CaOCl}_2 + \text{H}_2\text{O}\)
Slaked lime \(\rightarrow\) bleaching powder
(iii) \(\text{SnO}_2 + 2\text{C} \rightarrow \text{Sn} + 2\text{CO}\)
Cassiterite \(\rightarrow\) Tin
(iv) \(2\text{NaCl} + \text{MnO}_2 + 2\text{H}_2\text{SO}_4\)
Sodium chloride

\[
\text{Na}_2\text{SO}_4 + \text{MnSO}_4 + 2\text{H}_2\text{O} + \text{Cl}_2
\]
\(\Delta\)

(v) \(3\text{Cu} + 8\text{HNO}_3 \rightarrow 2\text{NO} + 3\text{Cu(NO}_3)_2 + 4\text{H}_2\text{O}\)
Nitric acid \(\rightarrow\) Nitric oxide

3. (i) \(\text{Sn} + 4\text{HNO}_3 \rightarrow \text{H}_2\text{SnO}_3 + 4\text{NO}_2 + \text{H}_2\text{O}\)
Metastatic acid
(ii) \(2\text{Al} + 2\text{NaOH} + 2\text{H}_2\text{O} \rightarrow 2\text{NaAlO}_2 + 3\text{H}_2\)
Sod. aluminate

4. (i) \(\text{HO} \rightarrow \text{P} \rightarrow \text{OH}\)
(ii) \(\text{O} = \text{P} \rightarrow \text{P} = \text{O}\)

5. (i) \(\text{HCO}_3^- + \text{Al}^{3+} \rightarrow \text{Al(OH)}_3 + \text{CO}_3^{2-}\)
(ii) \(\text{AlBr}_3 + \text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{PO}_4\)
\(\rightarrow\) \(\text{K}_3\text{PO}_4 + \text{AlPO}_4 + \text{H}_2\text{O} + \text{Br}_2 + \text{Cr}^{3+}\)

6. (i) Carbon exists in various allotropes forms like diamond, graphite, coal, etc. Diamond consists of a three-dimensional structure of \(sp^3\) hybridised carbon atoms bonded through very strong covalent bonds. It makes it hard and useful as an abrasive.
Graphite, on the other hand, is made up of a two-dimensional sheet like structure made of \(sp^2\) hybridised carbon atoms. These layers of carbon atoms are held together by relatively weak van der Waal’s forces and can, therefore, slip over one another imparting lubricating properties to graphite.
(ii) Sulphur consists of \(S_8\) rings held together by weak van der Waal’s forces. As sulphur melts at 119°C, these van der Waal’s forces are overcome and \(S_8\) rings slip and roll over one another giving rise to a clear mobile liquid. Above 160°C, the \(S_8\) rings begin to open up and form long chains which gets tangled with each other, thereby gradually increasing the viscosity.
(iii) **NOTE:** HI cannot be prepared by heating hydrogen iodide with conc. \(\text{H}_2\text{SO}_4\) because it is a strong reducing agent and reduces \(\text{H}_2\text{SO}_4\) to \(\text{SO}_2\) and is itself oxidised to iodine.
H$_2$SO$_4$ + 2HI → SO$_2$ + I$_2$ + 2H$_2$O

Hence HI is prepared by heating iodides with conc. phosphoric acid.

3KI + H$_3$PO$_4$ → K$_3$PO$_4$ + 3HI

(iv) In H$_3$PO$_4$ and H$_2$PO$_3$, the P atom is attached to 3 and 2 OH groups respectively. The H atom of these P – OH bonds are ionisable. This clearly shows that H$_3$PO$_4$ is tribasic and H$_2$PO$_3$ is dibasic.

(v) Liquor ammonia possesses high vapour pressure at room temperature and thus before opening a bottle of liquor ammonia, it should be cooled to lower the pressure of NH$_3$ inside the bottle, otherwise NH$_3$ will bump out of the bottle.

(vi) Solid CO$_2$ is technically known as dry ice because it sublimes without leaving any stain on surface.

(vii) Anhydrous HCl, being a non-polar covalent compound, is a bad conductor however an aqueous solution of HCl is ionised (Fajan’s rule) to give H$^+$ and Cl$^-$ ions and is a good conductor.

(viii) In graphite, out of four valence electrons, only three form covalent bonds (sp$^2$ hybridisation) with three other carbon atoms. This forms hexagonal rings as sheets of one atom thickness. These sheets are held together by weak attractive forces. One electron of each carbon atom is free and this enables these thin sheets to slide over one another. For this reason graphite is a soft material with lubricating properties.

(ix) The standard reduction potential of fluorine is highest and thus it cannot be oxidised by any reagent.

\[
\left(\frac{1}{2}\right) F_2 + e \rightarrow F^-; \quad E^*_{RP} = \text{maximum}
\]

(x) The mixture of N$_2$H$_4$ and H$_2$O$_2$ (in presence of Cu(II) catalyst) is used as a rocket propellant because the reaction is highly exothermic and large volume of gases are evolved, which can propel a rocket.

N$_2$H$_4$ + 2H$_2$O$_2$ $\xrightarrow{\text{Cu(II)}}$ N$_2$(g)$\uparrow$ + 4H$_2$O(g)$\uparrow$

Hydrazine Hydrogen peroxide

(xi) Orthophosphorus acid is a dibasic acid as it has 2-OH groups in its formula:

\[
\begin{array}{c}
\text{O} \\
\text{HO} \quad \text{P} \quad \text{OH} \\
\text{H}
\end{array}
\]

(xii) In MgCl$_2$, Mg is sp hybridised while in SnCl$_2$, Sn is sp$^3$ hybridised (hence the molecule is angular).

(xiii) NOTE : Oxygen is the 2nd most electronegative element after the fluorine and thus invariably show negative oxidation state.

\[
\text{Further more, it has } 2s^22p^4 \text{ configuration and thus requires only two electrons to complete its octet to show } -2 \text{ oxidation state. Although sulphur also possess } ns^2np^4 \text{ configuration but due to availability of } d\text{-orbitals in their outer most shell } -2, +2, +4, +6
\]

7. Phosphine gas (PH$_3$) is evolved when white phosphorus is boiled with aqueous NaOH or alcoholic solution of potassium hydroxide.

\[
P_4 + 3\text{NaOH} + 3\text{H}_2\text{O} \rightarrow \text{NaH}_2\text{PO}_4 + \text{PH}_3 \uparrow
\]

Sod. Hypophoshte

(ii) This is a method used to prepare I$_2$.

5NaHSO$_3$ + 2NaI$_2$O$_3$ → 3NaHSO$_4$ + 2Na$_2$SO$_4$ + I$_2$ + H$_2$O

(iii) 4Sn + 10HNO$_3$ → 4Sn(NO$_3$)$_2$ + N$_2$O$_5$ + 3H$_2$O (dilute)

 oxidation state are also shown. Oxygen, however, shows only –2 oxidation state due to non-availability of d-orbitals in its outermost shell.

(xiv) NOTE : H$_3$PO$_4$ is a dibasic acid because it contains two OH groups in its molecule. In the two P–OH bonds, the hydrogen is ionisable. [For structure see part (xi)]

(xv) NOTE : As compared to P, N atom has higher electronegativity and small size and shows H-bonding. Thus ammonia molecule show association where as phosphine does not.

(xvi) It is due to self ionization of NH$_3$, the reaction is

2NH$_3$ → NH$_4^+$ + NH$_2^-$

Thus on addition of NH$_4$Cl the concentration of NH$_4^+$ radical decreases and therefore NH$_4$Cl acts as an acid in liquid NH$_3$.

(xvii) In excess of NaOH the hydroxide of Al becomes soluble due to the formation of meta-aluminate.

(xviii) The repulsive forces between fluorine atoms are high due to its small size and high electronegativity. It makes dissociation of F – F bond easy. So bond dissociation energy of F$_2$ is less than Cl$_2$.

(xix) The reducing nature of SO$_2$ is represented as

SO$_2$ + 2OH$^-$ → SO$_4^{2-}$ + 2H$^+$ + 2e$^-$

Hence the increase of OH$^-$ (alkalinity) the forward reaction is favoured.

(xx) Nitrogen and fluorine both are small and have high electron density, they repel the bonded pair of electrons leading to larger bond length than expected.

(xxi) N$^{3-}$ being smaller in size and high charge present on it make it more susceptible to hydrolysis :

N$^{3-}$ + 3H$_2$O → NH$_3$ + 3OH$^-$

Cl$^-$ being a weak conjugate base does not undergo hydrolysis. MgCl$_2$ is stronger electrolyte and so it is not hydrolysed.

(xxii) In (SiH$_3$)$_3$N, lone pair of electrons on nitrogen is involved in $p\pi – d\pi$ back bonding, while in (CH$_3$)$_2$N no such $p\pi – d\pi$ back bonding is possible because of absence of d orbitals in carbon so (CH$_3$)$_2$N is more basic than (SiH$_3$)$_3$N.

(i) Phosphine gas (PH$_3$) is evolved when white phosphorus is boiled with aqueous NaOH or alcoholic solution of potassium hydroxide.

\[
P_4 + 3\text{NaOH} + 3\text{H}_2\text{O} \rightarrow \text{NaH}_2\text{PO}_4 + \text{PH}_3 \uparrow
\]

Sod. Hypophoshte

(ii) This is a method used to prepare I$_2$.

5NaHSO$_3$ + 2NaI$_2$O$_3$ → 3NaHSO$_4$ + 2Na$_2$SO$_4$ + I$_2$ + H$_2$O

(iii) 4Sn + 10HNO$_3$ → 4Sn(NO$_3$)$_2$ + N$_2$O$_5$ + 3H$_2$O (dilute)
The p-Block Elements

(iv) \( 2 \text{KMnO}_4 + 3 \text{H}_2\text{SO}_4 \rightarrow \text{K}_2\text{SO}_4 + 2 \text{MnSO}_4 + 3 \text{H}_2\text{O} + 5[\text{O}] \)

5 \( \text{H}_2\text{C}_2\text{O}_4 + 5[\text{O}] \rightarrow 10\text{CO}_2 \uparrow + 5\text{H}_2\text{O} \)

(v) \( 2\text{IO}_3^- + 5\text{HSO}_3^- \rightarrow \text{I}_2 + \text{H}_2\text{O} + 3\text{HSO}_4^- + 2\text{SO}_4^{2-} \)

(vi) \( 4\text{P} + 10\text{HNO}_3 + \text{H}_2\text{O} \rightarrow 5\text{NO} + 5\text{NO}_2 + 4\text{H}_3\text{PO}_4 \)

(vii) \( 2\text{H}_3\text{PO}_4 \xrightarrow{\text{Heat}} \text{PH}_3 + \text{H}_3\text{PO}_4 \)

(ix) \( \text{NaBrO}_3 + \text{F}_2 + 2\text{NaOH} \rightarrow \text{NaBrO}_4 + 2\text{NaF} + \text{H}_2\text{O} \)

(x) \( 3\text{SiCl}_4 + 4\text{Al} \xrightarrow{\Delta} 4\text{AlCl}_3 \uparrow + 3\text{Si} \)

(molten)

(xi) \( 15\text{CaO} + 4\text{P} \xrightarrow{\Delta} 5\text{Ca}_2\text{P}_2 + 3\text{P}_2\text{O}_5 \uparrow \)

\( \text{Ca}_2\text{P}_2 + 6\text{H}_2\text{O} \rightarrow 3\text{Ca(OH)}_2 + 2\text{PH}_3 \uparrow \) \( \times 5 \)

\( 15\text{CaO} + 4\text{P} + 30\text{H}_2\text{O} \rightarrow 15\text{Ca(OH)}_2 + 3\text{P}_2\text{O}_5 + 10\text{PH}_3 \uparrow \)

(xii) \( \text{CaSO}_4 + 2\text{NH}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{CaCO}_3 \downarrow + (\text{NH}_3)\text{SO}_4 \)

(xvii) \( \text{P}_4 + 20\text{HNO}_3 \xrightarrow{1\text{as catalyst}} 4\text{H}_3\text{PO}_4 + 20\text{NO}_2 + 4\text{H}_2\text{O} \)

(xviii) \( 2\text{H}_2\text{S} + \text{NaHSO}_3 + \text{H}^+ \rightarrow 3\text{S} \downarrow + 3\text{H}_2\text{O} + \text{Na}^+ \)

(xix) \( [2\text{HNO}_3 \rightarrow \text{H}_2\text{O} + 2\text{NO}_2 + [\text{O}] ] \times 10 \)

\( \text{P}_4 + 10[\text{O}] \rightarrow \text{P}_4\text{O}_{10} \)

\( \frac{\text{P}_4\text{O}_{10} + 6\text{H}_2\text{O} \rightarrow 4\text{H}_3\text{PO}_4}{\text{P}_4 + 20\text{HNO}_3 \rightarrow 4\text{H}_3\text{PO}_4 + 20\text{NO}_2 + 4\text{H}_2\text{O}} \)

(xx) \( 2\text{Al} + 2\text{NaOH} + 6\text{H}_2\text{O} \rightarrow 2\text{NaAlO}_2 + 2\text{H}_2\text{O} + 3\text{H}_2\text{O} \)

Sodium meta-aluminate

(xx) \( \text{Al}_2\text{S}_3 + 6\text{H}_2\text{O} \rightarrow 2\text{Al(OH)}_3 \downarrow + 3\text{H}_2\text{S} \uparrow \)

(foul odour)

Foul odour, on damping of AlS_3, is due to formation of H_2S gas, which smells like rotten eggs.

(xxii) \( \text{P}_4\text{O}_{10} + 6\text{PCl}_3 \rightarrow 10\text{POCl}_3 \)

(xxiii) \( \text{SnCl}_4 + 2\text{CH}_3\text{CH}_2\text{Cl} + \text{Na} \rightarrow \text{CH}_3\text{H}_10 + \text{Na}_2[\text{SnCl}_4] \)

8. By boiling Na_2SO_3 solution with powder of sulphur in absence of air sodium thiosulphate is prepared. Unreacted S is removed, filtrate is evaporated to give crystals of sod. thiosulphate.

Na_2SO_3 + S \rightarrow Na_2S_2O_3

9. Extraction of aluminium from bauxite:

\( 4\text{AlF}_3 + \text{(from cryolite)} \Leftrightarrow 4\text{Al}^{3+} + 12\text{F}^- \)

At cathode: \( 4\text{Al}^{3+} + 12\text{e}^- \rightarrow 4\text{Al} \)

At anode: \( (i) 12\text{F}^- \rightarrow 6\text{F}_2 + 12\text{e}^- \)

\( (ii) 2\text{Al}_2\text{O}_3 + 6\text{F}_2 \rightarrow 4\text{AlF}_3 + 3\text{O}_2 \)

10. \( \text{Al} + \text{NaOH} \xrightarrow{\text{aq}} \text{NaAlO}_2 \)

\( \text{2H}_2\text{O} \xrightarrow{\text{heat}} \text{Al(OH)}_3 \)

Al(OH)_3(Alumina)

11. \( \text{N}_2\text{O} \) has two principal resonance structures:

\( \text{N} = \text{N} = \text{O} ; \quad \text{N} = \text{N} \rightarrow \text{O} \)

12. \( (i) \text{KClO}_3 + 2\text{H}_2\text{C}_2\text{O}_4 + \text{H}_2\text{SO}_4 \rightarrow \text{KHSO}_4 + \text{HCl} + 6\text{CO}_2 + 3\text{H}_2\text{O} \)

\( (ii) (\text{NH}_4)_2\text{SO}_4 + \text{NO} + \text{NO}_2 \rightarrow 2\text{N}_2 + 3\text{H}_2\text{O} + \text{H}_2\text{SO}_4 \)

13. \( (i) \text{H}_2\text{S} \) oxidises into \( \text{S} \)

\( \text{SO}_2 + 2\text{H}_2\text{S} \rightarrow 3\text{S} + 2\text{H}_2\text{O} \)

\( (ii) \text{Sn} + 4\text{HNO}_3 \rightarrow \text{H}_2\text{SnO}_3 + 4\text{NO}_2 + \text{H}_2\text{O} \)

conc. meta stannic acid

\( (iii) \text{Pb}_3\text{O}_4 + 4\text{HNO}_3 \rightarrow 2\text{Pb(NO}_3)_2 + 2\text{H}_2\text{O} + \text{PbO}_2 \)

14. \( (i) \text{HI} < \text{HBr} < \text{HCl} < \text{HF} \)

The strength of H–X bond decreases from HF to HI. The larger is H–X bond length, lower is the bond energy, lesser is the bond strength.

(ii) \( \text{HOCI} < \text{HOCl} < \text{H(ClO}_3) < \text{HClO}_3 \)

As the number of oxygen atoms increase, the -ve charge dispersal becomes more and more from Cl atom due to more electronegativity of oxygen atom and thus lesser is the charge on Cl atom, more will be its stability.

(iii) \( \text{SiO}_2 < \text{CO}_2 < \text{N}_2\text{O}_5 < \text{SO}_3 \)

Among oxides of the non-metals, the acidic strength increases with oxidation state. Hence SO_3 (O.S. of S = +6) is most acidic followed by N_2O_5 (O.S. of N = +5) and CO_2 and SiO_2 (O.S. of C and Si = +4). Further CO_2 is more acidic than SiO_2 because of small size of C-atom.

(iv) Since carbon has no d-orbital, it cannot extend its coordination number beyond four, its halides are not attacked (hydrolysed) by water. On the other hand, silicon have vacant d-orbitals to which water molecules can coordinate and hence their halides are hydrolysed by water.

**NOTE**: Increasing order of extent of hydrolysis

\( \text{CCl}_4 < \text{MgCl}_2 < \text{AlCl}_3 < \text{SiCl}_4 < \text{PCl}_3 \)

15. \( (i) 2\text{FeBr}_3 + 3\text{Cl}_2 \rightarrow 2\text{FeCl}_3 + 2\text{Br}_2 \)

\( (ii) 2\text{SnCl}_2 + 2\text{I}_2 \rightarrow \text{SnCl}_4 + \text{SnI}_4 \)

\( (iii) \text{SO}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{SO}_4 \)

\( \text{H}_2\text{SO}_4 + 2\text{NaCl} \rightarrow \text{Na}_2\text{SO}_4 + 2\text{HCl} \)

16. The two resonating structures of ozone are:

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{O} & \quad \text{O} \\
\end{align*}
\]
17. \( \text{PbS} \xrightarrow{\text{heat in air}} 2\text{PbO} + \text{PbS} \) (A)

\( \xrightarrow{\text{heat in the absence of air (B)}} 3\text{Pb} + \text{SO}_2 \)

18. (i) \( 2\text{P} + 3\text{I}_2 + 6\text{H}_2\text{O} \rightarrow 2\text{H}_2\text{PO}_4 + 6\text{HI} \)

(ii) \( 2\text{KNO}_3 + 10\text{K} \rightarrow 6\text{K}_2\text{O} + \text{N}_2 \)

(iii) \( 2\text{NH}_3 + \text{NaOCl} \rightarrow \text{H}_2\text{N}_2\text{NH}_2 + \text{NaCl} + \text{H}_2\text{O} \)

(iv) \( \text{Sn} + 2\text{KOH} + 4\text{H}_2\text{O} \rightarrow \text{K}_2\text{Sn(OH)}_6 + 2\text{H}_2 \)

19. 

Number of P – O single bonds = 12
Number of P – O double bonds = 4

20. At first (Bi(NO)\(_3\))\(_3\) hydrolyses to give nitric acid which, being an oxidising agent, oxidises potassium iodide liberating free iodine responsible for dark brown precipitate. Iodine dissolves in excess of potassium iodide forming soluble KI\(_3\) imparting yellow colour to solution

\[
\begin{align*}
\text{Bi(NO}_3\text{)}_3 + \text{H}_2\text{O} & \rightarrow [\text{Bi(OH)(NO}_3\text{)}_2]^+ + \text{HNO}_3 \\
\text{NO}_3^- + 4 \text{H}^+ + 3\text{e}^- & \rightarrow \text{NO}_2^- + 2\text{H}_2\text{O} \times 2
\end{align*}
\]

\[
2\text{NO}_3^- + 8\text{H}^+ + 6\text{I}^- \rightarrow 2\text{NO} + 4\text{H}_2\text{O} + 3\text{I}_2 \quad \text{(dark brown ppt)}
\]

KI + I\(_2\) \rightarrow KI\(_3\)

(Yellow solution)

21. (a) \( 2\text{KI} + \text{Cl}_2 \rightarrow 2\text{KCl} + \text{I}_2 \)

Since Cl\(_2\) is more powerful oxidising agent than I\(_2\), Cl\(_2\) is able to displace I\(^-\) to form I\(_2\).

\[
\begin{align*}
2\text{I}^- & \rightarrow \text{I}_2 + 2\text{e}^- \\
\text{E}^0 & = +0.54 \text{V} \quad \text{..(i)}
\end{align*}
\]

\[
\begin{align*}
\text{Cl}_2 + 2\text{e}^- & \rightarrow 2\text{Cl}^- \\
\text{E}^0 & = 1.36 \text{V} \quad \text{..(ii)}
\end{align*}
\]

On subtracting eq. (i) from eq. (ii), we get

\[
\begin{align*}
\text{Cl}_2(g) + 2\text{I}^-_{(aq)} & \rightarrow 2\text{Cl}^-_{(aq)} + I_2(s) \\
\text{E}^0 & = 0.82 \text{V}
\end{align*}
\]

(b) \( 2\text{KClO}_3 + \text{I}_2 \rightarrow 2\text{KClO}_3 + \text{Cl}_2 \)

Here \( \text{ClO}_3^- \) is more powerful oxidising agent than \( \text{I}^- \), so Cl is displaced by I.

\[
\begin{align*}
2\text{I}^-_{(aq)} + 12\text{H}^+ + 10\text{e}^- & \rightarrow \text{I}_2 + 6\text{H}_2\text{O} \quad \text{E}^0 = 1.195 \text{V} \quad \text{..(i)}
\end{align*}
\]

\[
\begin{align*}
2\text{ClO}_3^- + 12\text{H}^+ + 10\text{e}^- & \rightarrow \text{Cl}_2 + 6\text{H}_2\text{O} \quad \text{E}^0 = 1.47 \text{V} \quad \text{..(ii)}
\end{align*}
\]

On subtracting eq. (i) from eq. (ii), we get

\[
\begin{align*}
2\text{ClO}_3^- + \text{I}_2 & \rightarrow 2\text{ClO}_3^- + \text{Cl}_2 \\
\text{E}^0 & = 0.275 \text{V}
\end{align*}
\]

22. The poisonous element M may be As. So on the basis of the given facts,

\[
\begin{align*}
\text{AsCl}_3 + 6\text{H} \xrightarrow{\text{Zn/H}_2\text{SO}_4} & \text{H}_3\text{AsCl}_3 + 3\text{HCl} \\
\text{AsH}_3 \xrightarrow{\Delta} & 2\text{As} + 3\text{H}_2 \uparrow \\
\text{Hence M} & = \text{As; N} = \text{As}_3\text{H}_3
\end{align*}
\]

23. In cyclic \( \text{Si}_3\text{O}_9^{6-} \), three tetrahedra of \( \text{SiO}_3^{2-} \) are joined together sharing two oxygen atoms per tetrahedron.

24. \( \text{SO}_2 + \text{PCl}_3 \rightarrow \text{SOCl}_2 + \text{POCl}_3 \)

Thionyl chloride

\[
\begin{align*}
\text{FeCl}_3 + 6\text{H}_2\text{O} + 6\text{SOCl}_2 & \rightarrow \text{FeCl}_3 + 12\text{HCl} + 6\text{SO}_2 \\
\text{FeCl}_3 + 6\text{H}_2\text{O} + 6\text{CH}_3-\text{C(OCH}_3\text{)}_2-\text{CH}_3 & \rightarrow \text{FeCl}_3 + 12\text{CH}_3\text{OH} + 6\text{CH}_3\text{COCH}_3
\end{align*}
\]

25. \( 7\text{H}_3\text{PO}_4 + \text{Ca}_5\text{(PO}_4\text{)}_3 \text{F} \rightarrow 5\text{Ca}(\text{H}_2\text{PO}_4)_2 + \text{HF} \)

Triple superphosphate

26. The reaction is

\[
\begin{align*}
\text{HNO}_2 + 2\text{H}_2\text{SO}_3 + \text{H}_2\text{O} & \rightarrow \text{NH}_2\text{OH} + 2\text{H}_2\text{SO}_4 \\
\text{(A)} & \quad \text{(B)} \quad \text{(C)} \quad \text{(D)}
\end{align*}
\]

The structures of A, B, C and D are as follows.

\[
\begin{align*}
\text{HO} & \quad \text{O} \quad \text{H} \quad \text{HO} \quad \text{O} \\
\text{N}=\text{O} & \quad \text{OH} \quad \text{S} \quad \text{OH} \quad \text{H} \quad \text{N} \quad \text{OH} \quad \text{HO} \quad \text{S} \quad \text{OH} \\
\text{O} & \quad \text{(A)} \quad \text{(B)} \quad \text{(C)} \quad \text{(D)}
\end{align*}
\]

27. Sulphur trioxide produced in the contact process is absorbed by sulphuric acid forming \( \text{H}_2\text{SO}_3 \). It is not dissolved in water as it gives a dense fog of sulphuric acid particles.

The catalyst used in the contact process is vanadium pentoxide.

28. In such a case

\[
\begin{align*}
\text{A} = \text{Ca(OH)}_2, \text{B} = \text{NH}_4\text{HCO}_3, \text{C} = \text{Na}_2\text{CO}_3, \text{D} = \text{NH}_4\text{Cl} \text{ and E} = \text{CaCl}_2
\end{align*}
\]

\[
\begin{align*}
\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 \quad \text{(A)}
\end{align*}
\]

\[
\begin{align*}
\text{NH}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{NH}_4\text{HCO}_3 \\
\text{Sod. Bicarbonate (B)}
\end{align*}
\]
$\text{NH}_4\text{HCO}_3 + \text{NaCl} \rightarrow \text{NaHCO}_3 + \text{NH}_4\text{Cl}$  
Amm. chloride(D)

$2\text{NaHCO}_3 \xrightarrow{\Delta} \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} + \text{CO}_2$
Sod. carbonate (C)

$\text{Ca(OH)}_2 + 2\text{NH}_4\text{Cl} \rightarrow \text{CaCl}_2 + 2\text{NH}_3 + 2\text{H}_2\text{O}$
(E) can be used again

29. More electronegative halogen displaces lesser electronegative halogen from its halide. Thus,
$\text{Cl}_2 + 2\text{KBr} \text{ (or } 2\text{ KI}) \rightarrow 2\text{KCl} + \text{Br}_2 \text{ (or } 12) \text{)

30. TIPS/Formulæ:
Use the formula
$$H \text{ (hydridisation), } H = \frac{1}{2}(V + M - C + A)$$
where
$V$ = number of electron in valence shell of central atom
$M$ = number of monovalent atoms surrounding the central atom
$C$ = Charge on cation
$A$ = Charge on anion

$\text{XeF}_2 : H = \frac{1}{2}(8 + 2 - 0 + 0) = 5$ Hence hybridisation is $sp^3d$, and thus its structure is linear.

$\text{XeF}_4 : H = \frac{1}{2}(8 + 4 - 0 + 0) = 6$, Hence hybridisation is $sp^3d^2$, and thus its structure is square planar.

$\text{XeO}_2\text{F}_2 : H = \frac{1}{2}(8 + 2 - 0 + 0) = 5$, Hence hybridisation is $sp^3d$, and shape is as seen saw.

31. Elemental nitrogen exists as a diatomic molecule because nitrogen can form $pt - pt$ multiple bonds which is not possible in case of phosphorus due to repulsion between non-bonded electrons of the inner core. There is no such repulsion in case of smaller nitrogen atoms as they have only $1s^2$ electrons in their inner core.

32. Since $\text{B}_2\text{O}_3$ is formed by reaction of $\text{Y}$ with air, $\text{Y}$ therefore should be $\text{B}_2\text{H}_6$ in which % of hydrogen is 21.72. The compound $\text{X}$ on reduction with $\text{LiAlH}_4$ gives $\text{B}_2\text{H}_6$. Thus it is boron trihalide. The reactions are shown as:

$4\text{BX}_3 + 3\text{LiAlH}_4 \rightarrow 2\text{B}_2\text{H}_6 + 3\text{LiX} + 3\text{AlX}_3$  
(X = Cl or Br)

$\text{B}_2\text{H}_6 + 3\text{O}_2 \rightarrow \text{B}_2\text{O}_3 + 3\text{H}_2\text{O} + \text{heat}$  
(Y)

33. Polymerisation continues on both ends to give linear silicone.

(i) $\text{SiCl}_4 + 2\text{Mg} \rightarrow \text{Si} + 2\text{MgCl}_2$

(ii) $\text{SiCl}_4 + 2\text{CH}_3\text{MgCl} \rightarrow (\text{CH}_3)_2\text{SiCl}_2 + 2\text{MgCl}_2$

Thus the diborane molecule has four two-centre-two-electron bonds ($2c - 2e$ bonds) also called usual bonds and two three-centre-two-electron bonds ($3c - 2e$) also called banana bonds. Hydrogen attached to usual and banana bonds are called $H_a$ (terminal $H$) and $H_b$ (bridged $H$) respectively.

34. (i) $\text{Al}_4\text{C}_3 + 12\text{H}_2\text{O} \rightarrow 4\text{Al(OH)}_3 + 3\text{CH}_4$

(ii) $\text{CaCN} + 3\text{H}_2\text{O} \rightarrow \text{CaCO}_3 \downarrow + 2\text{NH}_3$

35. NOTE: When hot concentrated HCl is added to borax ($\text{Na}_2\text{B}_3\text{O}_5$, 10$\text{H}_2\text{O}$) the sparingly soluble $\text{H}_3\text{BO}_3$ is formed which on subsequent heating gives $\text{B}_2\text{O}_3$ which is reduced to boron on heating with Mg, Na or K.
Na₂B₄O₇ (anhydrous) + 2HCl (hot, conc.)

→ 2NaCl + H₂B₄O₇

H₂B₄O₇ + 5H₂O → 4H₃BO₃ ↓

2H₃BO₃ → B₂O₃ + 3H₂O

B₂O₃ + 6K → 2B + 3K₂O or

B₂O₃ + 6Na → 2B + 3Na₂O or

B₂O₃ + 3Mg → 2B + 3MgO

**39.** 6CaO + P₄O₁₀ → 2Ca₃(PO₄)₂

Moles of P₄O₁₀ = \( \frac{852}{284} = 3 \)

Moles of CaO = 3 × 6 = 18; wt. of CaO = 18 × 56 = 1008 g

For structure of P₄O₁₀: See question 20 of this section.

**40.** (CH₃)₃N and (Me₃Si)₃N are not isostructural, the former is pyramidal while the latter is trigonal planar. Silicon has vacant d orbitals which can accommodate lone pair of electrons from N (back bonding) leading to planar shape.

**41.**

A. Conc. H₂SO₄

B. Br₂

C. NO₂⁺

D. O₂N

Reactions involved are

2NaBr + 2H₂SO₄ + MnO₂

[A]

→ Na₂SO₄ + MnSO₄ + Br₂ ↑ + 2H₂O

[B]

Brown fumes and pungent smell

H₂SO₄ + HNO₃ → HSO₄⁻ + NO₂⁺ + H₂O

[C]

F. **Match the Following**

1. (A)-(t), Pb(N₃)₂ is an explosive

(B)-(s), Al₂O₃ is used to prepare artificial gun

(C)-(v), Extraction of copper involves self-reduction process.

(D)-(u), Fe₂O₃ is a magnetic material.

2. (A)-(q), Bi³⁺ hydrolysates to yield BiO⁺ ion

(B)-(s), AlO₂⁻ on dilution yields a white ppt. of Al(OH)₃

(C)-(p), When heated (SiO₃)²⁻ changes to (SiO₂)⁴⁻

(D)-(r), When acidified (B₃O₃)³⁻ gives B(OH)₃ (or H₂BO₃)
3. (A) $\sigma_{1s^2}, \sigma_{ls^2}, \sigma_{2s^2}, \sigma_{2p_z}$

Bond order = 1

Paramagnetic

(B) $\sigma_{ls^2}, \sigma_{ls^2}, \sigma_{2s^2}, \sigma_{2s^2}, \sigma_{2p_x}, \sigma_{2p_y} = \pi_{2p_z}$

Bond order = 5

Diamagnetic

(C) $O_2^-$ $\sigma_{ls^2}, \sigma_{ls^2}, \sigma_{2s^2}, \sigma_{2s^2}, \sigma_{2p_z}, \pi_{2p_y}$

Bond order = 1.5

Paramagnetic

(D) $O_2^+$ $\sigma_{ls^2}, \sigma_{ls^2}, \sigma_{2s^2}, \sigma_{2s^2}, \sigma_{2p_z}, \pi_{2p_y}$

Bond order = 2

Paramagnetic

5. (c) In case of group 15 (nitrogen group), on moving down the group there occurs a decrease in bond angle of metal hydrides. This decrease in bond angle of metal hydrides of this group may be attributed to the increased p-character in the bond pair which results in more s-character in lone pair orbital.

**NOTE:** The directional character is more for sp$^3$ hybrid orbital than as a s-orbital.

Thus, the correct answer is (c).

6. (b) The reaction between NaOH and white phosphorus ($P_4$) can be represented as follows:

$$P_4 + 3NaOH + 3H_2O \rightarrow 3NaH_2PO_4 + PH_3$$

(white Phosphorus)

**NOTE:** In this reaction Phosphorus is oxidised as well as reduced so it is a disproportionation reaction.

7. (a) $Ca(OC_1)Cl \rightarrow Ca^{2+} + OC_1 + Cl^-$

OC1 hypochlorite ion is anion of the acid HOCl which on dehydration gives Cl$_2$O.

$$2HOCl \rightarrow H_2O + Cl_2O$$

8. (c) Number of millimole of hypo = $0.25 \times 48$

$$= 2 \times \text{millimole of Cl}_2$$

:: Number of millimole of Cl$_2$ = $0.25 \times 48 = 6$

millimole of Cl$_2$ = millimole of CaOCl$_2$

Molarity of bleaching solution

$$\frac{\text{Millimoles of CaOCl}_2}{\text{Vol.}(\text{in mL}) \text{of CaOCl}_2} = \frac{6}{25} = 0.24$$

9. (a) $Cl_2 + 2NaOH(dil.) \rightarrow NaClO + NaCl + H_2O$

(P)

$$3Cl_2 + 6NaOH(\text{conc.}) \rightarrow NaClO_3 + 5NaCl + 3H_2O$$

(Q)

(P) and (Q) are salts of HOCl and HClO$_3$ respectively.

10. (a) $SO_2 + Cl_2 \rightarrow \text{Charcoal} \rightarrow SO_2Cl_2$

(Catalyst)

$$10SO_2Cl_2 + P_4 \rightarrow 4PCl_5 + 10SO_2$$

(R)

(PCl$_5$ + 4H$_2$O $\rightarrow H_3PO_4 + 5HCl$)

(T)
1. (b) Nitrogen cannot form pentahalides because it cannot expand its octet due to non-availability of d-orbitals. So E is not correct explanation of S.
2. (c) F has slightly less electron affinity than chlorine because F has very small atomic size (only two shells). Hence there is a tendency of electron-electron repulsion, which results in less loss of energy in the formation of F\(^-\) ion. Assertion is correct but reason incorrect.
3. (a) Both assertion and reason are correct and reason explains assertion.
4. (e) SiCl\(_4\) undergoes hydrolysis due to the presence of empty d orbitals in the valence shell of Si, while C has no vacant d orbitals to accommodate electron pairs donated by water molecules during hydrolysis.
5. (c) Statement-1 is correct but statement-2 incorrect. Orthoboric acid (H\(_3\)BO\(_3\)) is soluble in water and behaves as weak monobasic acid. It does not donate protons like most acids, but rather it accepts OH\(^-\) ions. It is, therefore, Lewis acid, and is better written as B(OH)\(_3\).

\[
\text{B(OH)}_3 + 2\text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + [\text{B(OH)}_4^-], K_a = 9.25
\]
6. (a) Both statements are true. Boron forms only covalent compounds (bonds) because small sized B ion polarizes the corresponding anion largely.
7. (c) NOTE: In group 14 elements, the lower (and not higher) oxidation states are more stable for heavier members of the group due to inert pair effect.
Thus Pb\(^{4+}\) is less stable as compared to Sn\(^{4+}\) (lead is heavier than tin). Therefore Pb\(^{4+}\) acts as a strong oxidising agent than Sn\(^{4+}\). Hence statement 1 is false and statement 2 is true. Thus the correct answer is option (c).

I. Integer Value Correct Type
1. Coordination number of Al is 6. It exists in ccp lattice with 6 coordinate layer structure.
2. Total cationic charge = Total anionic charge
\[
2n + 6 + 24 = 36 \Rightarrow n = 3
\]
3. 5

\[
3\text{Br}_2 + 3\text{Na}_2\text{CO}_3 \rightarrow 5\text{NaBr} + \text{NaBrO}_3 + 3\text{CO}_2
\]
4. 4

\[
\text{PCl}_5 + \text{SO}_2 \rightarrow \text{POCl}_3 + \text{SOCl}_2 \\
\text{PCl}_5 + \text{H}_2\text{O} \rightarrow \text{POCl}_3 + 2\text{HCl} \\
\text{PCl}_5 + \text{H}_2\text{SO}_4 \rightarrow \text{POCl}_3 + 2\text{SO}_2\text{Cl}_2 + 2\text{HCl} \\
6\text{PCl}_5 + \text{P}_4\text{O}_{10} \rightarrow 10\text{POCl}_3
\]
5. (8)

\[
\text{O} = \text{O} = \text{O} \\
\text{N} = \text{N} = \text{N}
\]
Number of lone pairs = 8
6. (6)

\[
3\text{B}_2\text{H}_6 + 18\text{CH}_3\text{OH} \rightarrow 6\text{B(OCH}_3\text{)}_3 + 18\text{H}_2
\]

Section-B

**JEE Main/ AIEEE**

1. (e) Alum furnishes Al\(^{3+}\) ions which bring about coagulation of negatively charged clay particles, bacteria etc.
2. (d) In the formation of XeF\(_2\), sp\(^3\)d\(^3\) hybridisation occurs which gives the molecule a trigonal bipyramidal structure.

\[
\begin{array}{c}
\text{5s} \\
\text{5p} \\
\text{5d}
\end{array}
\]
Ground state configuration

\[
\begin{array}{c}
\text{1} \\
\text{1} \\
\text{1} \\
\text{1} \\
\text{1} \\
\text{1}
\end{array}
\]
Excited state configuration

In the formation of XeF\(_4\), sp\(^3\)d\(^2\) hybridization occurs which gives the molecule an octahedral structure.

\[
\begin{array}{c}
\text{1} \\
\text{1} \\
\text{1} \\
\text{1} \\
\text{1} \\
\text{1}
\end{array}
\]
Excited state config.

In the formation of XeF\(_6\), sp\(^3\)d\(^3\) hybridization occurs which gives the molecule a pentagonal bipyramidal structure.

\[
\begin{array}{c}
\text{F} \\
\text{F} \\
\text{F} \\
\text{F} \\
\text{F} \\
\text{F}
\end{array}
\]

3. (a) \(\gamma\text{N} = 1s^2 2s^2 2p^3\); \(\gamma\text{P} = 1s^2 2s^2 2p^6 3s^2 3p^3\)

**NOTE:** In phosphorus the 3d- orbitals are available. Hence phosphorus can form pentahalides also but nitrogen can not form pentahalide due to absence of d-orbitals.
4. (c)

5. (d)
6. (d) \( \text{CaOCl}_2 \) — or it can also be written as

\[
\text{Ca(OCl)}_\frac{x_1}{x_2} \text{Cl}
\]

hence oxidation no. of Cl in OCl\(^-\) is

\[
-2 + x_2 = -1
\]

\[
x_2 = 2 - 1 = +1
\]

now oxidation no. of another Cl is -1 as it is present as Cl\(^-\).

7. (d) On mixing phosphine with chlorine gas PCl\(_3\) and HCl forms. The mixture cools down.

\[
\text{PH}_3 + 4\text{Cl}_2 \rightarrow \text{PCl}_4 + 3\text{HCl}
\]

8. (a) 4HCl + O\(_2\) \(\rightarrow\) 2Cl\(_2\) + 2H\(_2\)O

9. (c) In graphite, carbon is sp\(^2\) hybridized. Each carbon is thus linked to three other carbon atoms forming hexagonal rings. Since only three electrons of each carbon are used in making hexagonal ring, fourth electron of each carbon is free to move. This makes graphite a good conductor of heat and electricity. Further, graphite has a two dimensional sheet like structure. These various sheets are held together by van der Waal’s force of attraction. Due to these weak forces of attraction, one layer can slip over the other. This makes graphite soft and a good lubricating agent.

10. (a) Glass is a translucent or transparent amorphous supercooled solid solution or we can say super cooled liquid of silicates and borates having general formula R\(_2\)O . MO . 6 SiO\(_2\), where R = Na or K and M = Ca, Ba, Zn or Pb.

11. (b) Among the given compounds, NH\(_3\) is most basic. Hence has highest proton affinity.

12. (d) It is mercury because it exists as liquid at room temperature.

13. (d) The fluorine has low dissociation energy of F-F bond and reaction of atomic fluorine is exothermic in nature.

14. (c) Helium is heavier than hydrogen although it is non-inflammable.

15. (c) The maximum valency of beryllium is +2 while that of aluminium is +3.

16. (b) \( \text{Al}_2\text{Cl}_6 + 12\text{H}_2\text{O} \rightarrow 2[\text{Al(H}_2\text{O})_6]^{3+} + 6\text{Cl}^- \)

17. (b) 4KI + 2CuSO\(_4\) \(\rightarrow\) I\(_2\) + Cu\(_2\)I\(_2\) + 2K\(_2\)SO\(_4\)

18. (c) Hypophosphorous acid H – O – P \(\rightarrow\) O \(\rightarrow\) H

Two H-atoms are attached to P atom.

19. (c) The H–X bond strength decreases from HF to HI i.e. HF > HCl > HBr > HI. Thus HF is most stable while HI is least stable. This is evident from their decomposition reaction. HF and HCl are stable upto 1473K, HBr decreases slightly and HI dissociates considerably at 713K. The decreasing stability of the hydrogen halide is also reflected in the values of dissociation energy of the H–X bond

\[
\begin{align*}
\text{H} & - \text{F} & 135 \text{kcal mol}^{-1} \\
\text{H} & - \text{Cl} & \text{103} \text{kcal mol}^{-1} \\
\text{H} & - \text{Br} & \text{87} \text{kcal mol}^{-1} \\
\text{H} & - \text{I} & \text{71} \text{kcal mol}^{-1}
\end{align*}
\]

20. (b) The solution of aluminium chloride in water is acidic due to hydrolysis.

\[
\text{AlCl}_3 + 3\text{H}_2\text{O} \rightarrow \text{Al(OH)}_3 + 3\text{HCl}
\]

On heating it till dryness Al(OH)\(_3\) is converted into

\[
\text{Al}_2\text{O}_3 \Delta \rightarrow \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O}
\]

21. (d) In Si\(_2\)O\(_4\) (quartz), each of O-atom is shared between two SiO\(_4\) tetrahedra.

22. (d) In diborane structure B\(_2\)H\(_6\) there are two 2c-2e bonds and two 3c-2e bonds (see structure of diborane).

Structure of B\(_2\)H\(_6\):

![Structure of B2H6](image)

23. (b) The HNO\(_3\) is stronger than HNO\(_2\). The more the oxidation state of N, the more is the acid character.

24. (b) The correct order of ionisation enthalpies is F > P > S > B

**NOTE:** On moving along a period ionization enthalpy increases from left to right and decreases from top to bottom in a group. But this trend breaks up in case of atom having fully or half filled stable orbitals.

In this case P has a stable half filled electronic configuration hence its ionisation enthalpy is greater in comparison to S. Hence the correct order is B < S < P < F.

25. (b) During disproportionation same compound undergo simultaneous oxidation and reduction.

\[
\begin{align*}
\text{Oxidation} & \\
\text{Reduction} & \\
3\text{HOCI} & \rightarrow 2\text{HCl} + \text{HClO}_3
\end{align*}
\]

26. (d) Chlorine reacts with excess of ammonia to produce ammonium chloride and nitrogen.

27. (a) \( (\text{NH}_4\text{SO}_4 + 2\text{H}_2\text{O}) \rightarrow 2\text{H}_2\text{SO}_4 + \text{NH}_4\text{OH} \)

H\(_2\)SO\(_4\) is a strong acid and increases the acidity of soil.
28. (c) The correct formula of inorganic benzene is B$_3$N$_3$H$_6$ so (d) is incorrect statement

\[ \text{Boric acid (H}_3\text{BO}_3 \text{ or } \begin{array}{c} \text{B} \\ \text{OH} \end{array}) \text{ is a Lewis acid so (a) is } \begin{array}{c} \text{OH} \end{array} \text{ incorrect statement.} \]

The coordination number exhibited by beryllium is 4 and not 6 so statement (b) is incorrect. Both BeCl$_2$ and AlCl$_3$ exhibit bridged structures in solid state so (c) is correct statement.

29. (d) The products of the concerned reaction react each other forming back the reactants.

\[ \text{XeF}_6 + 3\text{H}_2\text{O} \rightarrow \text{XeO}_3 + 6\text{HF} \]

30. (a) The ease of formation and stability of hydrides decreases rapidly from NH$_3$ to BiH$_3$. This is evident from their dissociation temperature which decreases from NH$_3$ to BiH$_3$. As we go down the group the size of central atom increases and thus metal-hydrogen bond becomes weaker due to decreased overlap between the large central atom and small hydrogen atom.

\[ \text{NH}_3 > \text{PH}_3 > \text{AsH}_3 > \text{SbH}_3 > \text{BiH}_3 \]

(least stable)

31. (d) Oxidation of sulphur varies from +2 to +6 in its various compounds.

32. (a) Boron cannot form BF$_6$ due to non-availability of d-orbitals.

33. (c) All the members form volatile halides of the type AX$_3$. All halides are pyramidal in shape. The bond angle decreases on moving down the group due to decrease in bond pair-bond pair repulsion.

\[ \text{NCl}_3 \quad \text{PCl}_3 \quad \text{AsCl}_3 \\
107^\circ \quad 94^\circ \quad 92^\circ \]

34. (c) Acidic strength increases as the oxidation number of central atom increases. Hence acidic strength order is

\[ (+7) > (+5) > (+3) > (+1) \]

\[ \text{HClO}_4 > \text{HClO}_3 > \text{HClO}_2 > \text{HCl} \]

35. (a) Nitric oxide is paramagnetic in the gaseous state because of the presence of one unpaired electron in its outermost shell.

The electronic configuration of NO is

\[ \pi^1 \sigma^2 \pi^2 \pi^2 \sigma^2 \sigma^2 \sigma^2 \sigma^2 \]

36. (b) CsI$_3$ dissociates as

\[ \text{CsI}_3 \rightarrow \text{Cs}^+ + \text{I}^- \]

37. (b) ICl

Order of reactivity of halogens

\[ \text{Cl}_2 > \text{Br}_2 > \text{I}_2 \]

But, the interhalogen compounds are generally more reactive than halogens (except F$_2$), since the bond between two dissimilar electronegative elements is weaker than the bond between two similar atoms i.e., X–X

38. (c) Nitrogen and oxygen in air do not react to form oxides of nitrogen in atmosphere because the reaction between nitrogen and oxygen requires high temperature.

39. (b) Xe. As we move down the group, the melting and boiling points show a regular increase due to corresponding increase in the magnitude of their van der Waals forces of attraction as the size of the atom increases.

40. (c) Phosphorous acids contain P in +3 oxidation state.

<table>
<thead>
<tr>
<th>Acid</th>
<th>Formula</th>
<th>Oxidation state of Phosphorous</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrophosphorous acid</td>
<td>H$_3$P$_2$O$_5$</td>
<td>+3</td>
</tr>
<tr>
<td>Pyrophosphoric acid</td>
<td>H$_4$P$_2$O$_7$</td>
<td>+5</td>
</tr>
<tr>
<td>Orthophosphorous acid</td>
<td>H$_3$PO$_3$</td>
<td>+3</td>
</tr>
<tr>
<td>Hypophosphorous acid</td>
<td>H$_4$P$_2$O$_6$</td>
<td>+4</td>
</tr>
</tbody>
</table>

41. (c) Reaction of Zn with dil. HNO$_3$

\[ 4\text{Zn} + 10\text{HNO}_3(\text{dil}) \rightarrow 4\text{Zn(NO}_3)_2 + 5\text{H}_2\text{O} + \text{N}_2\text{O} \]

(Zn reacts differently with very dilute HNO$_3$)

Reaction of Zn with conc. HNO$_3$

\[ \text{Zn} + 4\text{HNO}_3(\text{conc.}) \rightarrow \text{Zn(NO}_3)_2 + 2\text{H}_2\text{O} + 2\text{NO}_2 \]
The d- and f-Block Elements and Co-ordination Compounds

Section-A : JEE Advanced/ IIT-JEE

   5. FeSO₄.7H₂O, ZnSO₄.7H₂O  6. paramagnetism  7. hexaminecobalt (III) chloride
   8. zero  9. H₂S


C  1. (a)  2. (d)  3. (b)  4. (b)  5. (b)  6. (c)  7. (d)
   8. (a)  9. (a) 10. (b) 11. (c) 12. (c) 13. (a) 14. (d)
   15. (a)  16. (c) 17. (b) 18. (a) 19. (d) 20. (b) 21. (b)
   22. (c)  23. (c) 24. (a) 25. (b) 26. (a) 27. (a) 28. (b)
   29. (c)  30. (a) 31. (a) 32. (b) 33. (a) 34. (a) 35. (d)
   36. (b)  37. (c) 38. (c) 39. (b) 40. (a) 41. (b) 42. (c)
   43. (b)  44. (c) 45. (d) 46. (a) 47. (c) 48. (b) 49. (b)

D  1. (b,c)  2. (c,d) 3. (b)  4. (b,c) 5. (c)  6. (a,c) 7. (d)
   8. (c,d)  9. (a,d) 10. (b,c,d) 11. (a,c,d) 12. (b,d) 13. (a,b,c) 14. (a,b,c) 15. (a,b)

E  11. sodium zincate, water  12. CO  14. (iii), (iv)
   15. (i) pentammine nitritocobalt (III) chloride,  (ii) potassium hexacyanochromate (III)
   (iii) pentamminecarbonatochromium (III) chloride
   17. (i) [CoCl(NH₃)₂]Cl₂, (ii) LiAlH₄
   20. [Cr(H₂O)₆]Cl₃, [Cr(H₂O)₇Cl]Cl₂, [Cr(H₂O)₆Cl₂]Cl₃, [Cr(H₂O)₆Cl₃](H₂O)Cl
   24. [Cr(NH₃)₆BrCl]Cl : (d²sp³), [Cr(NH₃)₆Cl₂]Br : (d²sp³), 3.87 BM, 3.87 BM
   26. Potassium ammonitetricyanonitrosotetrachromate (I), (d²sp³), octahedral shape.
   27. (b) +2, dsp²; (c) diamagnetic
   28. CuCO₃, Cu(OH)₂, Cu₂S, Cu, CuO, Cu₂I₂, SO₂

A  1. (A - p, q, s); (B - p, r, s); (C - q, s); (D - q, s)
   2. (A - p, s); (B - q, s); (C - r, t); (D - q, t)
   3. (b)

F  1. (A - p, q, s); (B - p, r, s); (C - q, s); (D - q, s)
   2. (A - p, s); (B - q, s); (C - r, t); (D - q, t)
   3. (b)

G  1. (a)  2. (c)  3. (a)  4. (b)  5. (d)  6. (b)  7. (b)  8. (a)  9. (c)

H  1. (c)  2. (b)  3. (b)  4. (a)

I  1. 4  2. 6  3. 3  4. 6  5. 8  6. 7  7. 3  8. 6  9. 4
   10. 6  11. 5

Section-B : JEE Main/ AIEEE

1. (b)  2. (b)  3. (b)  4. (c)  5. (a)  6. (a)  7. (c)  8. (c)  9. (c)
   10. (a)  11. (d)  12. (a)  13. (a)  14. (b)  15. (a)  16. (c)  17. (d)  18. (b)
   19. (a)  20. (c)  21. (d)  22. (c)  23. (a)  24. (d)  25. (c)  26. (d)  27. (d)
   28. (a)  29. (d)  30. (b)  31. (c)  32. (b)  33. (a)  34. (d)  35. (d)  36. (b)
   37. (a)  38. (d)  39. (d)  40. (b)  41. (a)  42. (c)  43. (d)  44. (a)  45. (a)
   46. (a)  47. (d)  48. (b)  49. (a)  50. (c)  51. (c)  52. (a)  53. (a)  54. (b)
   55. (a)  56. (b)  57. (c)  58. (d)  59. (c)  60. (d)  61. (b)  62. (d)  63. (c)
   64. (a)  65. (d)  66. (b)  67. (d)  68. (c)  69. (d)  70. (d)  71. (a)  72. (d)
   73. (c)  74. (d)
Section-A

JEE Advanced/ IIT-JEE

A. Fill in the Blanks

1. K[Ag(CN)2]
2. PbO2
3. Zinc
4. Hydration/solvation: [A substance dissolves when its \( \Delta H_{\text{hydration}} > \) lattice energy].
5. FeSO4·7H2O, ZnSO4·7H2O;
6. Paramagnetism: [Mn(H2O)6]3+ shows paramagnetism because of presence of 5 unpaired electrons in the outer most orbital (3d5) of Mn2+.
7. Hexamine cobalt (III) chloride
8. zero
9. H2S; It is due to formation of sulphide of silver (Ag2S) which is black.

B. True/False

1. False: Copper metal does not reduces Fe2+ in an acidic medium.
2. True: Hydration energy of AgF is appreciably higher than its lattice energy because of smaller F⁻ ion and thus AgF is soluble in water. In rest of the halides, lattice energy is more than hydration energy to make them insoluble.
3. True: Insolubility of AgCl in H2O is due to its high lattice energy on account of strong van der Waals attraction between silver and chloride ions in addition to electrostatic attraction between them. Further AgCl forms a complex with conc. NaCl solution and is therefore soluble.
4. False: Dipoisite zinc exhibits diamagnetism (and not paramagnetism) because it has no unpaired electron.
5. False: Octahedral complexes of Fe(III) like [Fe(CN)6]3− are low spin (d2sp3 hybridization) with one unpaired electron and have magnetic moment of about 1.9 BM. On the other hand, complexes of Fe(II) like [Fe(CN)6]2− are high spin complex (d2sp3) has no unpaired electron and thus diamagnetic.
6. True: Cu⁺ is the intermediate oxidation state between Cu²⁺ and Cu. If the reduction potential from the intermediate oxidation state to the lower one is more positive than from the higher to the intermediate, then the intermediate state will undergo disproportional.
   \[ \text{Cu}^{\text{II}} \xrightarrow{+0.15V} \text{Cu}^{\text{I}} \xrightarrow{+0.52V} \text{Cu} \]

C. MCQs with One Correct Answer

1. (a) Zn + H2SO4 → ZnSO4 + H2
   \[ \text{Zn} + 2\text{NaOH} \rightarrow \text{Na}_2[\text{ZnO}_2] + \text{H}_2 \]
   \[ \therefore \text{Ratio of H}_2 \text{ evolved is 1 : 1.} \]
2. (d) Basicity of hydroxides decreases on moving left to right in a period.
3. (b) German silver is alloy of Cu + Zn + Ni
4. (b) Zn + 2NaOH → Na2[ZnO2] + H2
   \[ \text{Sod. meta zincate(soluble)} \]
5. (b) \[ \text{It has 2 unpaired electrons.} \]
   \[ 3d \text{ orbital of Ni}^{2+} \text{ ion. At No. of Ni = 28.} \]
6. (c) Hypo solution (Na2S2O3) is used in photography to remove the unaffected AgBr in the form of soluble complex.
   \[ \text{AgBr} + 2\text{Na}_2\text{S}_2\text{O}_3 \rightarrow \text{Na}_3[\text{Ag(S}_2\text{O}_3)_2] + \text{NaBr} \]
   \[ \text{Sod. argentothiosulphate} \]
7. (d) Conc. HNO₃ renders iron passive by forming a thin protective film of Fe₃O₄ on its surface.
8. (a) \[ \text{CaCO₃} \xrightarrow{\text{Heat}} \text{CaO} + \text{CO}_2; \]
   \[ \text{CaO} + \text{SiO}_2 \rightarrow \text{CaSiO}_3 \text{(slag).} \]
9. (a) Zinc-copper couple is obtained by mixing zinc dust with copper guaze.
10. (b) Mn²⁺ in Mn(SO₄)·4H₂O has d⁵ configuration (five unpaired electrons); Cu²⁺ in Cu(SO₄)·5H₂O has d⁹ configuration (one unpaired electron); Fe²⁺ in Fe₂(SO₄)·6H₂O has d⁶ configuration (four unpaired electrons); and Ni²⁺ in Ni(SO₄)·6H₂O has d⁸ configuration (two unpaired electron). Thus Cu(SO₄)·5H₂O has lowest degree of paramagnetism.
11. (c) Atom/Ion Complex | Configuration | No. of unpaired electrons | Magnetic nature
    | Ni²⁺ (d⁸) | [NiCl₄]²⁻ | \[ \begin{array}{ccc} 3d & 4s & 4p \\ \uparrow & \uparrow & \\ \uparrow & \uparrow & \end{array} \]
    | Cu²⁺ (d⁹) | \[ \begin{array}{ccc} 3d & 4s & 4p \\ \uparrow & \uparrow & \end{array} \]
    | \[ \begin{array}{ccc} 4s & 4p \\ \uparrow & \uparrow \end{array} \]
    | Reorganisation | 2 | Paramagnetic
    | Paramagnetic
    | Ni²⁺ (d⁵) | \[ \begin{array}{ccc} 3d & 4s & 4p \\ \uparrow & \uparrow & \end{array} \]
    | \[ \begin{array}{ccc} 3d & \uparrow & \uparrow \\ \uparrow & \uparrow \end{array} \]
    | Reorganisation | 2 | Paramagnetic
    | Diamagnetic
12. (c) Solder is an alloy containing Sn – 67% and Pb – 33%.
13. (a) 2KMnO₄ + 16HCl → 2KCl + 2MnCl₂ + 8H₂O + 3Cl₂
14. (d) Cu₂SO₄ + 2KCN → Cu₂(CN)₂ + K₂SO₄
   \[ \text{2Cu₂(CN)₂ → Cu₃(CN)₄}_2 + \text{(Cyanogen)} \]
   \[ \text{Cu₃(CN)₄}_2 + 6\text{ KCN} \rightarrow \text{2K₃[CN(CN)₄]} \]
15. (a) HgS does not dissolved in hot dil. HNO₃
16. (e) **TIPS/FORMLAUE:**
   Chrome alum is K₂SO₄·Cr₂(SO₄)₃·24H₂O
   The filtrate is yellow due to CrO₄²⁻ ion and residue is brown due to Fe(OH)₃.
17. (b) \[ \text{(NH₄)₂Cr₂O₇} \xrightarrow{\Delta} \text{Cr₂O₃ + N₂ + 4H₂O} \]
   \[ \text{(green)} \]
   Hence green coloured powder blown in the air is Cr₂O₃.
18. (a) The reaction of \( \text{MnO}_4^- \) and \( \text{SO}_3^{2-} \) in acidic medium is derived as follows:

\[
\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O} \quad \times 2
\]
\[
\text{SO}_3^{2-} + \text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + 2\text{H}^+ + 2\text{e}^- \]
\[
2\text{MnO}_4^- + 5\text{SO}_3^{2-} + 6\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 5\text{SO}_4^{2-} + 3\text{H}_2\text{O}
\]

Hence, 2 mole \( \text{MnO}_4^- = 5 \text{ mol} \text{ SO}_3^{2-} \)

i.e., \( \frac{2}{5} \text{ mol MnO}_4^- = 1 \text{ mol SO}_3^{2-} \)

19. (d) Organometallic compounds are those compounds in which metal atom is directly bonded with C-atom. \( \text{H}_2\text{C}=\text{Li} \).

20. (b) The electronic configurations of cations in the given salts are

\[ \text{Ag}^+ (4d^{10}), \text{Cu}^{2+} (3d^9), \text{Mg}^{2+} (2s^2, 2p^6), \text{Cu}^+ (3d^{10}) \]

Only \( \text{Cu}^{2+} \) ion has one unpaired electron in 3d orbital and so, its salt is expected to be coloured.

21. (b) The structure of \( \text{C}_{2}\text{O}_4^{2-} \)

\[
\begin{array}{c}
\text{O} \\
\text{Cr} \\
\text{O} \\
\text{Cr} \\
\text{O} \\
\text{Cr} \\
\end{array}
\]

There are six normal \( \text{Cr} - \text{O} \) bonds and two bridged \( \text{Cr} - \text{O} \) bonds.

The six normal \( \text{Cr} - \text{O} \) bonds are expected to be equivalent and different from those of the bridged \( \text{Cr} - \text{O} \) bonds.

22. (c) **NOTE**: In metal carbonyl the metal is in **zero** oxidation state.

In \( \text{Ni(CO)}_4 \), O.N. of Ni = 0

For Ni (Z = 28)

\[
\begin{array}{c}
\uparrow & \uparrow & \uparrow & \uparrow & \uparrow & \uparrow & \uparrow & \uparrow & \uparrow & \uparrow & \uparrow & \uparrow \\
\end{array}
\]

In presence of CO two 4s electrons pair up, thus

\[
\begin{array}{c}
\uparrow & \uparrow & \uparrow & \uparrow & \uparrow & \uparrow & \uparrow & \uparrow & \uparrow & \uparrow & \uparrow & \uparrow \\
\end{array}
\]

In \( \text{Ni(PPh}_3)_2\text{Cl}_2 \), O.N. of Ni = +2

For Ni\(^{2+}\)

\[
\begin{array}{c}
\uparrow & \uparrow & \uparrow & \uparrow & \uparrow & \uparrow & \uparrow & \uparrow & \uparrow & \uparrow & \uparrow & \uparrow \\
\end{array}
\]

PPh\(_3\) and Cl\(^-\) can’t pair up d-electrons, leading to sp\(^3\) hybridization leading to tetrahedral geometry.

23. (c) Haematite ore \( (\text{Fe}_2\text{O}_3) \) is first reduced to cast iron which is then oxidised for removing carbon (impurity) as CO.

24. (a) In \( [\text{MnO}_4]^- \), Mn is in +7 oxidation state.

Electronic configuration of Mn (Z = 25) : [Ar] 3d\(^{5}\)4s\(^{2}\)

Electronic configuration of Mn\(^{7+}\) : [Ar] 3d\(^{0}\)4s\(^{0}\)

Central atom in other ions have definite number of d electrons

No. of electrons

\[
\begin{array}{c}
[\text{Co(NH}_3)_6]^{3+} & \text{in Co}^{3+}=\text{Six} \\
[\text{Fe(CN)}_6]^{3-} & \text{in Fe}^{3+}=\text{Five} \\
[\text{Cr(H}_2\text{O})_6]^{3+} & \text{in Cr}^{3+}=\text{three}
\end{array}
\]

25. (b) \( 2\text{Fe} + 3\text{Cl}_2 \) (dry) \( \rightarrow \) \( 2\text{FeCl}_3 \) (anhydrous)

26. (a) Stable oxidation state of Mn in alkaline medium is +6. So, \( \text{MnO}_2 \) is oxidised to \( \text{K}_2\text{MnO}_4 \) (purple green) by atmospheric oxygen in KOH medium.

\[
2\text{MnO}_2 + 4\text{KOH} + \text{O}_2 \rightarrow 2\text{K}_2\text{MnO}_4 + 2\text{H}_2\text{O} \quad \text{(Purple)}
\]

27. (a) \( 2\text{Au} + 4\text{CN}^- + \text{H}_2\text{O} + \frac{1}{2}\text{O}_2 \rightarrow 2[\text{Au(CN)}_2]^- + 2\text{OH}^- \quad \text{X'}
\]

\[
2[\text{Au(CN)}_2]^- + \text{Zn} \rightarrow [\text{Zn(CN)}_4]^{2-} + 2\text{Au} \quad \text{Y'}
\]

28. (b) The configuration of Ni\(^{2+}\) is 3d\(^8\). For the elements of the first transition series, Cl\(^-\) behaves as a weak field/high spin ligand. Hence Ni in [NiCl\(_4\)]\(^{2-}\) is sp\(^3\) hybridised leading to tetrahedral shape.

\[
\begin{array}{c}
\text{Cl} \\
\text{Ni} \\
\text{Cl} \\
\text{Cl} \\
\end{array}
\]

sp\(^3\), Tetrahedral

29. (c) **TIPS/FORMULAE**:

\[ \mu = \sqrt{n(n+2)} \text{ BM} \quad (\mu = \text{spin magnetic moment}) \]

Here Co is present as Co\(^{2+}\) ion which has 3 unpaired electrons. So the spin magnetic moment will be \( \sqrt{3(3+2)} \), i.e. \( \sqrt{15} \text{ BM} \).

30. (a) \[ 6\text{MnO}_4^- + \text{I}^- + 6\text{OH}^- \rightarrow 6\text{MnO}_4^{2-} + 1\text{O}_3 + 3\text{H}_2\text{O} \]

31. (a) \( \text{NH}_4\text{Cr}_2\text{O}_7 \rightarrow \text{N}_2 + \text{Cr}_2\text{O}_3 + 4\text{H}_2\text{O} \)

\[ \begin{array}{c}
\text{NH}_4\text{NO}_2 \rightarrow \text{N}_2 + 2\text{H}_2\text{O} \quad \text{Same gas i.e., N}_2 \\
\text{NH}_4\text{NO}_3 \rightarrow \text{N}_2\text{O} + 2\text{H}_2\text{O} \\
\text{Mg}_3\text{N}_2 + 3\text{H}_2\text{O} \rightarrow 3\text{Mg(OH)}_2 + 2\text{NH}_3 \\
2\text{NaNO}_3 + \text{H}_2\text{O} \rightarrow \text{Na}_2\text{O}_2 + 2\text{HNO}_2
\end{array} \]

32. (b) Colour of transition metal ion salt is due to d-d transition of unpaired electrons of d-orbital. Metal ion salt having similar number of unpaired electrons in d-orbitals
shows similar colour in aqueous medium.

\[ \text{V}^{2+}: [\text{Ar}]3d^1 \]

\[ \text{Cu}^{2+}: [\text{Ar}]3d^9 \]

Number of unpaired electrons = 1

33. (a) Co(NH}_3\text{)Br}_2\text{Cl} will show both geometrical and ionization isomerism.

\[ \text{[Co(NH}_3\text{)Br}_2\text{]Cl and [Co(NH}_3\text{)BrCl]Br are ionization isomers and geometrical isomers are} \]

\[ \text{cis} \quad \text{trans} \]

34. (a) CuSO}_4 + 2KCN \rightarrow Cu(CN}_2 + K}_2SO}_4

Cu(CN}_2 \rightleftharpoons CuCN + \frac{1}{2}(CN}_2\text{)}_2

CuCN + 3 KCN \rightleftharpoons K}_2[\text{Cu(CN}_4\text{)}_4]^{3-}

colourless

35. (d) An anionic carbonyl complex can delocalise more electron density to antibonding pi-orbital of CO and hence, lowers the bond order.

36. (b) In the presence of oxygen, Ag metal forms a water soluble complex Na[Ag(CN}_2\text{)] with dilute solution of NaCN

4Ag + 8NaCN + 2H}_2O + O}_2 \rightarrow 4Na[Ag(CN}_2\text{)] + 4NaOH

(Soluble)

37. (c) \text{NOTE : Colour is due to d – d transitions. Coloured compounds contain partly filled d-orbital. The oxidation state of copper in various compounds is + 1 and + 2. In CuF}_2\text{, it is in + 2 oxidation state. In + 2 state its configuration is} \]

\[ \text{Cu}^{2+} = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^9 \]

\[ \text{i.e.} \quad \text{It has one unpaired electron due to this it is coloured. The colour is due to d-d transitions.} \]

\text{(NOTE : CuF}_2\text{ possesses blue colour in crystalline form)}

38. (c) The correct IUPAC name of the given compound is tetrarminenickel (II) - tetrachloronickelate (II) thus (c) is the correct answer.

39. (b) \text{NOTE : O. of metal is zero} \n
In [Ni(CO}_4\text{)], the oxidation state of nickel is zero. Its configuration in Ni(CO}_4\text{) is}

\[ \text{[Ni(CO}_4\text{)]:} \]

\[ \text{3d} \quad \text{4s} \quad \text{4p} \]

sp\textsuperscript{3} hybridisation

In [Ni(CN)}_4\text{] the oxidation state of Ni is 2+ and its configuration is

\[ \text{[Ni(CN)}_4\text{]^{2-}:} \]

\[ \text{3d} \quad \text{4s} \quad \text{4p} \]

dsp\textsuperscript{2} hybridisation

Thus the hybridisations of nickel in these compounds are sp\textsuperscript{3} and dsp\textsuperscript{2} respectively. Hence (b) is the correct answer.

40. (a) Chromium in Cr(CO}_6\text{) is in zero oxidation state and has [Ar]\textsuperscript{18} 3d\textsuperscript{2}4s\textsuperscript{1} as the electronic configuration. However, CrO could be a strong ligand, hence pairing up of electrons takes place leading to following configuration in Cr(CO}_6\text{)

\[ \text{3d} \quad 4s \quad 4p \]

\text{3d\textsuperscript{2}4s\textsuperscript{1} Hybridisation}

Since the complex has no unpaired electron, its magnetic moment is zero.

41. (b) Ionisation isomer of [Cr(H}_2O)_4Cl(NO}_2\text{)]Cl is [Cr(H}_2O)_4Cl}_2NO}_2.

42. (c) The correct structure of EDTA is

\text{HOOC–H}_2C\text{–N–CH}_2–CH}_2–N\text{–CH}_2\text{–COOH}

\text{HOOC–H}_2C\text{–N–CH}_2–CH}_2–N\text{–CH}_2\text{–COOH}

43. (b) [NiCl}_4\text{]^{2-} O.S. of Ni = +2

\text{Ni(28) = 3d\textsuperscript{8} 4s\textsuperscript{2}}

\[ \text{3d} \quad \text{4s} \quad \text{4p} \]

\text{Cl being weak ligand it cannot pair up the two electrons present in 3d orbital}

\[ \text{3d} \quad \text{4s} \quad \text{4p} \]

sp\textsuperscript{3}

No. of unpaired electrons = 2

Magnetic moment, \(\mu = 2.82\) BM.
The d- and f-Block Elements and Co-ordination Compounds

44. (c) Complex | No. of electrons in outer d orbital | No. of unpaired electron (s)
---|---|---
[Fe(CN)₆]³⁻ | 3d⁵ | 1 (CN⁻ causes pairing of electrons)
[Co(NH₃)₆]³⁺ | 3d⁶ | –
[Co(octal)₃]²⁻ | 3d⁶ | –
[Ni(H₂O)₆]²⁺ | 3d⁸ | 2
[Pt(CN)₅]³⁻ | 5d⁸ | D (CN⁻ causes pairing of electrons)
[Zn(H₂O)₆]²⁺ | 3d¹⁰ | –

45. (d) [Co(H₂O)₆(NH₃)₃]Cl₃ = Diammineteraqua cobalt (III) chloride.

46. (a) CuSO₄ will be absorbing orange-red colour and hence will be of blue colour.

47. (c) In both states (paramagnetic and diamagnetic) of the given complex, Ni exists as Ni²⁺ whose electronic configuration is [Ar] 3d⁸4s⁰.

\[ 3d \quad 4s \quad 4p \]

Thus L, M, O and P are diamagnetic.

48. (b) The electronic configuration of central metal ion in complex ions P, Q and R are

\[ P = \text{[FeF₆]}^{3-}, \text{Fe}^{3+} \]

\[ Q = [V(H₂O)₆]^{2+}, V^{2+} \]

\[ R = [Fe(H₂O)₆]^{2+}, Fe^{2+} \]

Higher the no. of unpaired electron(s), higher will be magnetic moment.
Thus the correct order of spin only magnetic moment is Q < R < P

49. (b) Compound/Ion | Magnetic nature of compound
---|---
1. [Ni(CO)₄] | Diamagnetic
2. [NiCl₄]²⁻ | Paramagnetic
3. [Co(NH₃)₆Cl₂]Cl | Diamagnetic
4. Na₃[CoF₆] | Paramagnetic
5. Na₂O₂ | Diamagnetic
6. CsO₂ | Paramagnetic

So total number of paramagnetic compounds is 3.

D. MCQs with One or More Than One Correct

1. (b, c) \(2\text{MnO}_2 + 4\text{KOH} + \text{O}_2 \xrightarrow{\text{heat}} 2\text{K}_2\text{MnO}_4 + 2\text{H}_2\text{O}; 2\text{KOH} + \text{HCHO} + 2\text{K}_2\text{MnO}_4 \xrightarrow{\text{K}_2\text{MnO}_4 + \text{H}_2\text{O} + \text{HCOOH}} \)

2. (c, d) Aqueous solution of Co(NO₃)₂ and CrCl₃ in which Co²⁺ (d⁷) and Cr³⁺ (d⁶) contains incompletely filled d-orbitals are coloured.

3. (b) Highest paramagnetic character will be shown by the ion having maximum number of unpaired electrons in their d-subshells.

25 Cr³⁺ has 3 unpaired electrons.
26 Fe²⁺ has 4 unpaired electrons
29 Cu²⁺ has 1 unpaired electron
30 Zn²⁺ has no unpaired electrons

So (a), (b) & (c) show paramagnetism. Out of which (b) has the highest paramagnetism.

4. (b, c) Brass : Cu (60-80%), Zn (40-20%), Gun Metal : Cu (87%), Sn (10%), Zn (3%).

5. (c) The magnetic moment (\(\mu\)) of a species is related to its number of unpaired electrons (n) in form of following expressions.

\[ \mu = \sqrt{n(n+2)} \text{ B.M} \]

The number of unpaired electrons in the given pairs are as follows:

\[ \text{Fe}^{2+} = 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^6 \]

\[ \text{Fe}^{3+} = 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^5 \]

Thus here \(n = 4\).

Thus here \(n = 5\)

\[ \text{N}^+ \text{ or } \text{N}^{+} \text{O} : n = 0; \text{NO} \text{ or } \text{N}^{++} \text{O} : n = 1 \]

The given combinations differ in the number of unpaired electrons. Hence these can be differentiated by the measurement on the solid state magnetic moment of nitroprusside ion.

6. (a, c) Mn makes steel harder and increases its elasticity and tensile strength. Further Mn acts as deoxidiser. MnO reacts with S present in cast iron, gets oxidised and then combine to form slag.
7. (d) The metal to ligand bonding creates a synergic effect which strengthens the bond between CO and the metal (Fe) leading to contraction of bond between C and O of CO.

8. (c,d) In acidic medium

\[ \text{MnO}_2 \rightarrow \text{Mn}^{2+} \]
Change in oxidation state of Mn = 7 – 2 = 5
Thus electrons lost = 5
In neutral medium

\[ \text{MnO}_4^- \rightarrow \text{MnO}_2 \]
Change in oxidation state of Mn = 7 – 4 = 3
Electrons lost = 3

9. (a,d) In acidic medium

CuSO_4 \rightarrow Cu^{2+} \quad \text{Cu}^{2+} + 4\text{SCN}^- \rightarrow \text{Cu}([\text{SCN}]_4)^{2-} \quad \text{Cu}^{2+} + \text{CuCl}_2 \rightarrow 2\text{CuCl} \quad \text{CuCl}_2 + \text{Cu} \rightarrow 2\text{CuCl} \quad \downarrow

10. (b,c,d) Cu^{2+} ions will react with CN^- and SCN^- forming [Cu(CN)_4]^{3-} and [Cu(SCN)_4]^{3-} leading the reaction in the backward direction.

Cu^{2+} + 2\text{CN}^- \rightarrow \text{Cu(CN)}_2^-
2\text{Cu(CN)}_2 \rightarrow 2\text{CuCN} + \text{CN}^-
\text{CuCN} + 3\text{CN}^- \rightarrow [\text{Cu(CN)}_4]^{3-}
\text{Cu}^{2+} + 4\text{SCN}^- \rightarrow [\text{Cu(SCN)}_4]^{3-}
\text{Cu}^{2+} also combines with CuCl_2 which reacts with Cu to produce CuCl pushing the reaction in the backward direction.

CuCl_2 + Cu \rightarrow 2\text{CuCl} \quad \downarrow

11. (a,c,d)

KI(aq) + K_{3}[Fe(CN)_6](aq) \rightarrow KI_3(aq) + K_{4}[Fe(CN)_6](aq)
Brownish-yellow
ZnSO_4(aq)

K_2Zn_2[Fe(CN)_6]_2 or K_2Zn[Fe(CN)_6]_3 \uparrow + KI_3(aq)
white ppt

K_2Zn[Fe(CN)_6] + NaOH \rightarrow white ppt
[Zn(OH)_4]^{2-} + [Fe(CN)_6]^{4-} \quad \text{aq}

12. (b,d) The pair of complex ions [Cu(NH_3)_4]^{2+} and [Pt(NH_3)_2(H_2O)]^{2+} show geometrical isomerism. The pair of complexes [Pt(NH_3)_2(NO_2)]Cl and [Pt(NH_3)_2Cl]Br show ionisation isomerism. The other pairs given do not have same type of isomerism.

13. (a,b,c) Na \rightarrow NH_4 \quad \text{(excess)} \rightarrow \text{Dilute solution of Na in liq. NH}_3 \rightarrow \text{Paramagnetic}
K + O_2 \rightarrow K\text{O}_2 \quad \text{(O}_2^- \text{is paramagnetic)}
Cu + HNO_3 \rightarrow Cu(NO_3)_2 + NO
(NO is paramagnetic)
2-Ethylanthraquinol + O_2 \rightarrow 2-Ethylanthraquinone + H_2O
(H_2O is diamagnetic)

14. (a,b,c) Cr^{3+} is a reducing agent and Mn^{3+} is an oxidizing agent and both have electronic configuration d^3.

\[ E^{\circ}_{\text{Cr}^{3+}/\text{Cr}^{2+}} = -0.41\text{V} \quad E^{\circ}_{\text{Mn}^{3+}/\text{Mn}^{2+}} = 1.51\text{V} \]
Above \( E^{\circ} \) values explains reducing nature of Cr^{2+} and oxidizing behaviour of Mn^{3+}.

15. (a,b)

E. Subj ective Problems

1. (i) Since the compound (A) on strong heating gives two oxides of sulphur (C and D) which might be SO_2 and SO_3, it must be a sulphate.

(ii) The reaction of compound (E) with thiocyanate to give blood red coloured compound (H) indicates that (E) must have Fe^{3+} ion. Thus the compound (A) must be Fe(II) sulphate, FeSO_4.7H_2O, which explains all given reactions as below (Fe^{3+} ion of FeSO_4 is changed to Fe^{2+} during heating).

FeSO_4 \cdot 7\text{H}_2\text{O} \xrightarrow{\text{heat}} \text{FeSO}_4 \cdot 7\text{H}_2\text{O}^\uparrow
\text{Ferrous sulphate} \quad \text{Ferrous sulphate}
(A) \quad \text{(A)}

2\text{FeSO}_4 \xrightarrow{\text{heat}} \text{Fe}_2\text{O}_3 \cdot \text{SO}_3 + \text{SO}_3 \quad \text{(C)}
\text{(D)}
\text{Ferrous oxide, (Blackish brown powder)}
\text{Ferric oxide, (Yellow solution, E)}

2\text{FeCl}_3 + \text{H}_2\text{S} \xrightarrow{\text{heat}} 2\text{FeCl}_2 + 2\text{HCl} + \text{S}
\text{Apple green (G) with white turbidity (F)}

\text{FeCl}_3 + 3\text{NH}_3\text{CNS} \rightarrow \text{Fe(CNS)}_3 + 3\text{NH}_4\text{Cl}
\text{Ferric thiocyanate (blood red colour)}

2. (i) ZnCO_3 \xrightarrow{\Delta} \text{ZnO} + \text{CO}_2
\text{(A)} \quad \text{(B)}

(ii) ZnO + 2\text{HCl} \rightarrow \text{H}_2\text{O} + \text{ZnCl}_2 \quad \text{(C)}
\text{(solubile)}

(iii) 2\text{ZnCl}_2 + K_4[\text{Fe(CN)}_6] \rightarrow 4\text{KCl} + \text{Zn}_2[\text{Fe(CN)}_6] \downarrow \quad \text{(white ppt)}
\text{(solubile)}

(iv) ZnCO_3 + \text{HCl} \rightarrow \text{CO}_2 + \text{ZnCl}_2
\text{(A)} \quad \text{(B)}
\text{(solubile)}

(v) \text{CO}_2 + \text{Ca(OH)}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}
\text{(Milkly)}

(vi) \text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{Ca(HCO}_3\text{)}_2
\text{(soluble)}
The d- and f-Block Elements and Co-ordination Compounds

(vii) ZnCl₂ + H₂S ⇌ NH₄OH → 2HCl + ZnS ↓
    (white)
(viii) ZnCl₂ + 2NaOH → 2NaCl + Zn(OH)₂↓
     (white) E
(ix) Zn(OH)₂ + 2NaOH → Na₃ZnO₂ + H₂
     sod. zincate (soluble)

3. (i) 2Ag + 2H₂SO₄ → Ag₂SO₄ + SO₂ + H₂O
     (white)
(ii) (NH₄)₂Cr₂O₇ → Cr₂O₃ + N₂ + 4H₂O
     (green)
(iii) 2KMnO₄ + 3H₂SO₄ + 5H₂O →
     K₂SO₄ + 2MnSO₄ + 5SO₂ + 8H₂O
     (turbidity)

4. On standing FeCl₃ is hydrolysed and produces colloidal solution of Fe(OH)₃ which is in form of brown precipitate.

FeCl₃ + 3H₂O → Fe(OH)₃ ↓ + 3HCl
     Brown ppt

5. SO₂ + MnO₄⁻ + H⁺ → SO₄²⁻ + Mn²⁺ + H₂O

6. (i) 2CuSO₄ + SO₂ + 2H₂O + 2KCNS
     → 2CuCNS ↓ + K₂SO₄ + 2H₂SO₄
     Cuprous thiocyanate
     (white)
(ii) Fe₂(SO₃)₃ + 2KI → 2FeSO₄ + K₂SO₄ + I₂
(iii) 2MnO₄⁻ + 4H⁺ → MnO₂ + MnO₂⁺ + H₂O
(iv) 2K₂CrO₇ + H₂SO₄ → K₂CrO₃ + K₂SO₄ + H₂O
     (yellow)
     (orange red)
(v) 2KMnO₄ + 4KOH + MnO₂ → 3K₂MnO₄ + 2H₂O
     or 2KMnO₄ + H₂O → 2MnO₂ + 2KOH + 3[O]
(vi) K₃[Fe(CN)₆] + 6H₂SO₄ + 6H₂O
     → 2K₂SO₄ + FeSO₄ + 3(NH₄)₂SO₄ + 6CO
(vii) 3HCl + HNO₃ → NOCl + 2H₂O + 2(Cl)
     (aqua regia)
Au + 2[Cl] → HCl → AuCl₃ → HCl → HAuCl₄
     Aurochloric acid
(viii) Ag₂S + 4NaCN → 2Na[Ag(CN)₂] + Na₂S
     (silver glance)
4NaS + SO₂ + 2H₂O → 2Na₂SO₄ + 4NaOH + 2S
[NOTE : Na₂S is converted into Na₂SO₄ to avoid reversibility of first reaction]
2NaAg(CN)₂ + Zn → Na₂[Zn(CN)₄]₂ + 2Ag
     (sod. zincocyanide)
(ix) AgCl + 2NaCN ⇌ NaCl + Na[Ag(CN)₂]
     2Na[Ag(CN)₂] + Zn → Na₂[Zn(CN)₄]₂ + 2Ag↓
     (soluble)

(x) CoCl₂ + 2KNO₂ → Co(NO₃)₂ + 2KCl
    KNO₃ + H₂C₂O₄ → CH₂COOK + HNO₂
    Co(NO₃)₂ + 3KNO₂ + 2H₂O
    → K₃[Fe(NO₃)₆]↓ + NO + H₂O
    Pot. cobaltinitrite
    (yellow ppt.)

(xi) 2CuFeS₂ + O₂ → Cu₂S + 2FeS + SO₂
     (copper pyrites)
    2Cu₂S + 3O₂ → 2Cu₂O + 2SO₂
    2FeS + 3O₂ → 2FeO + 2SO₂
    Smelting
    with coke
    and sand
    Bessmerization

(xii) K₂Cr₂O₇ + 4NaCl + 6H₂SO₄
     → 2CrO₂Cl₂↑ + 4NaHSO₄ + 2KHSO₄ + 3H₂O
     chromyl chloride
     (orange)
(xiii) 4Fe + 10HNO₃ → 4Fe(NO₃)₂ + NH₄NO₃ + 3H₂O
(xiv) 2KMnO₄ + 3MnSO₄ + 2H₂O
     → 5MnO₂ + K₂SO₄ + 2H₂SO₄
     This is known as Volhard method for estimation of manganese.

(xv) The individual reactions are
3Cu + 8HNO₃ (dil.) → 2NO + 3Cu(NO₃)₂ + 4H₂O
Cu + 4HNO₃ (dil.) → Cu(NO₃)₂ + 2NO + 2H₂O
For the molar ratio of 2 : 1 of NO and NO₂, we will have
7Cu + 20HNO₃ → 7Cu(NO₃)₂ + 4NO + 2NO₂ + 10H₂O
(xvi) 2CuSO₄ + 2Na₂CO₃ + H₂O
     → CuCO₃·Cu(OH)₂ + 2Na₂SO₄ + CO₂
(xvii) K₂Cr₂O₇ + 14HCl → heat
     2KCl + 2CrCl₃ + 7H₂O + 3Cl₂
(xviii) AgBr + 2Na₂S₂O₃ → Na₃[Ag₂(S₂O₃)₂] + NaBr
     (sod. argentothiosulphate)
(xix) (NH₄)₂S₂O₃ + 2H₂O + MnSO₄
     → MnO₂ + 2H₂SO₄ + (NH₄)₂SO₄
(xx) 3[NO₄]²⁻ + 4H⁺ → MnO₂ + 2H₂SO₄ + (NH₄)₂SO₄
(xxı) 3SO₄²⁻ + Cr₂O₇²⁻ + 2H⁺ → 2Cr³⁺ + 3SO₄²⁻ + H₂O

(xxii) Ag₂S + 2KCNS → [Ag(CN)₂]₂+ + K₂S
     (argentite)
     Potassium argentocyanide
(xxiii) [Zn + 2HNO₃ (dil.) → Zn(NO₃)₂ + 2[H]⁺] × 4
     2HNO₃ + 8[H]⁺ → N₂O₂ + 5H₂O
     4Zn + 10HNO₃ → 4Zn(NO₃)₂ + N₂O₂ + 5H₂O

7. Equations for extraction of silver from its sulphide ore.

Cyanide Process:

Ag₂S + 2NaCN → Na₂S + 2AgCN
(sulphide ore)
AgCN + NaCN → Na[Ag(CN)₂]

Sodium argentocyanide (soluble)

2Na[Ag(CN)₂] + Zn → Na₂[Zn(CN)₂] + 2Ag

[NOTE: Zn is more electropositive than Ag.]

8. (i) It is because silver bromide, being sensitive to light, reduces into metallic silver grains when light fall on it.

(ii) The transition metals form coloured compounds and coloured complexes. They have vacant d-orbitals. Electrons take up energy from the visible region and move to higher energy levels. The visible colour of the substance is the complementary colour of the absorbed light.

[NOTE: The colour is due to d-d transitions]

(iii) Zinc is cheaper and stronger reducing agent than copper and zinc is volatile

(iv) Mercurocyanic chloride changes from white to black when treated with ammonia due to the formation of finely divided mercury.

(v) Cu²⁺ is reduced to Cu⁺ by I⁻, hence cupric iodide is converted into cuprous iodide so [CuI]²⁻ does not exist, Cl⁻ cannot effect this change and thus [CuCl₄]²⁻ exists.

(vi) CrO₄ is acid anhydride of H₂CrO₄ (Chromic acid)

[Anhydride are formed by loss of water from acid]

H₂CrO₄ → Dehydration → CrO₄²⁻ + H₂O

In H₂CrO₄, Cr is present in +6 oxidation state.

9. 2Mn(OH)₂ + 5NaIO₃ + 18H⁺ → 2MnO₂ + 5Bi³⁺ + 5Na⁺ + 11H₂O

10. (i) CuSO₄ + 4NH₃OH → [Cu(NH₃)₄]SO₄ + 4H₂O

or CuSO₄ + 2NH₃OH → Cu(OH)₂ + (NH₃)₂SO₄

Cu(OH)₂ + 2(NH₃)₂SO₄ → [Cu(NH₃)₄]SO₄ + 2H₂O + H₂SO₄

deep blue complex

(ii) H₂O₂ → H₂O + [O] → 2CrCl₃ + 3NaOH → (Cr(OH)₃)₃↓ + 3NaCl

2Cr(OH)₃ + 4NaOH + 3[O] → 2Na₂CrO₄ + 5H₂O

2CrO₃ + 10NaOH + 3H₂O₂ → 2Na₂CrO₄ + 6NaCl + 8H₂O

yellow

11. ZnO + 2NaOH → Na₂ZnO₂ + H₂O

Sod. Zincate

12. Carbon monoxide is the actual reducing agent of haematite in blast furnace.

13. 3[Fe(H₂O)₅]²⁺ + NO₃⁻ + 4H⁺ → NO + 3[Fe(H₂O)₅]³⁺ + 2H₂O

[Fe(H₂O)₅]³⁺ + NO → [Fe(H₂O)₅]NO²⁺ + H₂O

For the explanation of colouration of complexes, first of all find out the number of unpaired electrons present in outer available d-orbitals

(i) [Ti(NO₃)₄]₂⁻; 22Ti⁺⁺: [Ar] 3d⁰ 4s⁰

(ii) [Cu(NC CH₃)₄]²⁻ BF₄⁻; 29Cu⁺: [Ar] 3d¹⁰ 4s⁰

14. (iii) [Cr(NH₃)₆]³⁺ 3Cl⁻; 29Cr³⁺: [Ar] 3d² 4s⁰

(iv) K₃[VFe₆]₃₂⁻ V⁺³: [Ar] 3d² 4s⁰

Due to the presence of unpaired electrons in d-orbitals, two complexes i.e., [Cr(NH₃)₆]³⁺ 3Cl⁻ and K₃[VFe₆]₃₂⁻ are coloured.

Others having all paired electrons are colourless

15. (i) Pentammineruthenocobalt (III) chloride

(ii) Potassium hexacyanochromate (III)

(iii) Pentamminecobaltocobalt (III) chloride.

16. 2₉Cu = 1s² 2s² 2p⁶ 3s² 3p⁶ 3d¹⁰ 4s¹

2₉Zn = 1s² 2s² 2p⁶ 3s² 3p⁶ 3d¹⁰ 4s²

On the basis of configuration of Cu and Zn, first ionisation potential of Zn is greater than that of copper because in zinc the electron is removed from 4s² configuration while in copper it is removed from 4s¹ configuration. So more amount of energy is required for the removal of electron of 4s² (completely filled orbital) than that of 4s¹ while the second ionisation potential of Cu is higher than that of zinc because Cu⁺ has 3d¹⁰ (stable configuration) in comparison to Zn⁺ (4s¹ configuration).

17. (i) [CoCl(NH₃)₆]Cl²⁻ Formula of pentamminechlorocobalt (III)

(ii) LiAlH₄ Formula of lithium tetrahydroaluminate (III)

18. Haematite(Fe₂O₃) on burning with coke and lime at 2000°C results in the following reactions.

C + O₂ → CO₂

CO₂ + O → 2CO

3CO + Fe₂O₃ → 2Fe + 3CO₂ (Reduction of Fe₂O₃ to form steel)

(Steel)

SiO₂ + CaO → CaSiO₃ (Slag, CaSiO₃ is used as building material)

(Lime) (Slag)

19. 2Cu + H₂O + CO₂ + O₂ → CuCO₃ + Cu(OH)₂

Green basic copper carbonate

20. The complex A does not react with concentrated H₂SO₄ implying that all water molecules are coordinated with Cr³⁺ ion. Hence, its structure would be [Cr(H₂O)₆]Cl₃.

The compound B loses 6.75% of its original mass when treated with concentrated H₂SO₄. This loss is due to the removal of water molecules which is not directly coordinated to Cr³⁺ ion.

The mass of water molecules removed per mole of the complex

\[ \frac{6.75}{100} \times \text{molar mass of the complex} = \frac{6.75}{100} \times 266.5 \text{ g} = 17.98 \text{ g} \]

This corresponds to one mole of water. Hence, the structure of the compound B will be [Cr(H₂O)₆]Cl₃[H₂O]Cl₂

NOTE: The compound C loses 13.5% of its mass when treated with concentrated H₂SO₄ which is twice of the mass lost by the compound B. Hence, the structure of the compound C will be [Cr(H₂O)₆][H₂O]Cl₂.

21. NaNO₃ + H₂SO₄ → NaHSO₄ + HNO₃

6FeSO₄ + 2HNO₃ + 3H₂SO₄ → 3Fe₂(SO₄)₃ + 4H₂O + 2NO

[Fe(H₂O)₆]SO₄ + H₂O + NO → [Fe(H₂O)₆]NO₃SO₄ + 2H₂O

brown ring
22. \[ \text{[Co(NH}_3\text{)}_6]^{3+} \]

\[ \text{Co}^{3+} \hspace{1cm} 3d \hspace{1cm} \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \hspace{1cm} 4s \hspace{1cm} 4p \]

\[ \Rightarrow \hspace{1cm} \uparrow \downarrow \uparrow \uparrow \uparrow \uparrow \downarrow \hspace{1cm} \text{Octahedral complex, } d^2sp^3 \text{ hybridisation} \]

\[ \text{[Ni(CN)}_4\text{]}^{2-} \]

\[ \text{Ni}^{2+} \hspace{1cm} 3d \hspace{1cm} \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \hspace{1cm} 4s \hspace{1cm} 4p \]

\[ \text{Ni}^{2+} \text{ (after rearrangement)} \hspace{1cm} \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \hspace{1cm} \text{Pairing due to CN}^- \hspace{1cm} \text{dsp}^2 \]

\[ \text{[Ni(CO)}_4\text{]}^{-2} \]

\[ \text{Ni} \hspace{1cm} \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \hspace{1cm} 3d \hspace{1cm} 4s \hspace{1cm} 4p \]

\[ \text{Ni} \text{ (after rearrangement)} \hspace{1cm} \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \hspace{1cm} \text{Pairing due to CO} \hspace{1cm} \text{sp}^3 \]

\[ \text{Tetrahedral (} sp^3 \text{ hybridisation)} \]

23. (i) Argentite is \( \text{Ag}_2\text{S} \). Silver is extracted from its ore argentite (silver glance, \( \text{Ag}_2\text{S} \)) as follows:

1. Silver glance is concentrated by froth flotation.
2. Leaching: The concentrated ore is ground to fine powder and dissolved in dilute solution of sodium cyanide.

\[ \text{Ag}_2\text{S} + 4\text{NaCN} \rightarrow 2\text{NaAg(CN)}_2 + \text{Na}_2\text{S} \]

Oxygen of air converts \( \text{Na}_2\text{S} \) to \( \text{Na}_2\text{SO}_4 \) thereby preventing reaction to take place in the reversible direction.


Silver is precipitated out by adding electropositive metal, Zn.

\[ 2\text{Na[Ag(CN)}_2\text{]} + \text{Zn} \rightarrow \text{Na}_2\text{[Zn(CN)}_4\text{]} + 2\text{Ag} \]

(ii) For development, activated grains are preferentially reduced by mild reducing agents like hydroquinone

\[ \text{HO} \hspace{1cm} \text{OH} \rightarrow \text{O} \hspace{1cm} \text{O} \hspace{1cm} 2e^- + 2\text{H}^+ \]

Hydroquinone

Quinone

\[ \text{AgBr(s)} + e^- \rightarrow \text{Ag(s)} + \text{Br}^- \]

Reduction of activated AgBr to elemental silver.

The photographic film is permanently fixed by immediately washing out any non activated AgBr grains in hypo emulsion.

\[ \text{AgBr(s)} + 2\text{Na}_2\text{S}_2\text{O}_3 \rightarrow \text{Na}_3\text{Ag(S}_2\text{O}_3)_2 + \text{NaBr} \]

hypo soluble

24. Compound (A) on treatment with AgNO\(_3\) gives white precipitate of AgCl, which is readily soluble in dil aq. NH\(_3\). Therefore, it has at least one Cl\(^-\) ion in the ionization sphere furthermore chromium has coordination number equal to 6. So its formula is \([\text{Cr(NH}_3\text{)}_4\text{BrCl}]\). Compound (B) on treatment with AgNO\(_3\) gives pale yellow precipitate of AgBr soluble in conc. NH\(_3\). Therefore, it has Br\(^-\) in the ionization sphere. So its formula is \([\text{Cr(NH}_3\text{)}_4\text{Cl}_2]\)Br.

\[ \text{Cr}^{3+} (Z = 24) \hspace{1cm} \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \hspace{1cm} 3d \hspace{1cm} 4s \hspace{1cm} 4p \]

State of hybridization of chromium in both (A) and (B) is \( d^2sp^3 \).

Spin magnetic moment of (A) or (B),

\[ \mu_{\text{sp}} = \sqrt{n(n+2)} = \sqrt{3(3+2)} = \sqrt{15} = 3.87 \text{ BM} \]

25. Cl\(^-\) is a weak ligand which is unable to pair the electrons of Ni\(^{2+}\). Therefore, here hybridisation is \( sp^3 \) and shape will be tetrahedral.

Electronic configuration of Ni\(^{2+}\) (No. of electrons = 26) in presence of Cl\(^-\) ion, a weak ligand.

\[ \text{3d} \hspace{1cm} \uparrow \uparrow \uparrow \uparrow \uparrow \hspace{1cm} 4s \hspace{1cm} 4p \]

\[ \text{sp}^3 \text{ hybridisation} \]

Magnetic moment of \([\text{NiCl}_4]^{2-}\) = \( \sqrt{2(2+2)} = 2.82 \text{ BM} \)

On the other hand, CN\(^-\) is a strong ligand which pairs up the
electrons of Ni^{2+}. Therefore, here hybridisation is \( d^{sp^2} \) and shape will be square planar.

Electronic configuration of Ni^{2+} in presence of CN\(^-\) ion, a strong ligand.

\[ \begin{array}{c}
\uparrow & \uparrow & \uparrow & \uparrow \\
\uparrow & \uparrow & \uparrow & \uparrow \\
\end{array} \]

\( d^{sp^2} \) Hybridisation

For structure of [Ni(CN)]\(_2\)\(^2-\), refer question 24 in Section (E).

Magnetic moment of [Ni(CN)]\(_2\)\(^2-\) = \( \sqrt{0(0+2)} = 0.0 \) BM

26. The spin magnetic moment, \( \mu \) of the complex is 1.73 BM.

\[ \mu = \sqrt{n(n+2)} = 1.73 \Rightarrow n = 1 \]

It means that nucleus of the complex, chromium ion has one unpaired electron. So the ligand NO is unit positively charged.

IUPAC name:

Potassium amminetetracyanonitrosorhodinate (I).

(a) Electronic configuration of Cr\(^{3+}\):

\( 3d \quad 4s \quad 4p \)

(b) Electronic configuration of Cr\(^{3+}\) under the influence of strong field ligand CN\(^-\):

\[ \text{Cr}^{3+} \begin{array}{c}
\uparrow \uparrow \uparrow \uparrow \uparrow \\
\uparrow \uparrow \uparrow \uparrow \uparrow \\
\end{array} \]

\( d^{sp^3} \)

29. Fe\(^{3+}\) + SCN\(^-\) (excess) \( \rightarrow \) [Fe(SCN)(H\(_2\)O)\(_3\)]\(^{3+}\) (blood red)

\( [\text{FeSCN}(\text{H}_2\text{O})_5]^{3+} + 6\text{F}^- \rightarrow [\text{FeF}_6]^{3-} + \text{SCN}^- \) (B)

IUPAC name of A is pentaaquaquathiocyanatoferrate (III) ion

IUPAC name of B is hexafluoroferrate (III)

In \([\text{FeF}_6]^{3-}\) coordination no. of Fe = 6

In \([\text{FeF}_6]^{3-}\) oxidation state of Fe = +3

It has 5 unpaired electrons, \( n = 5 \), Fe\(^{3+}\) is \( 3d^5 \)

Magnetic moment (\( \mu \)) = \( \sqrt{n(n+2)} \) (B.M.)

\( \sqrt{5(5+2)} = \sqrt{35} = 5.92 \) B.M.

30. Reaction involved in developing of a black and white photographic film.

\[ \text{Hydroquinone} \quad (\text{developer}) \]

\[ \text{AgBr} + 2\text{Na}_2\text{S}_2\text{O}_3 \rightarrow \text{Na}_3[\text{Ag}(\text{S}_2\text{O}_3)_2] + \text{NaBr} \]

\( \text{unexposed portion} \)

\[ \text{Na}_2\text{S}_2\text{O}_3 + 2\text{H}^+ \rightarrow 2\text{Na}^+ + \text{H}_2\text{SO}_3 + \text{S} \downarrow \text{colloidal sulphur} \]

31. \( [\text{A}] = [\text{Ti(H}_2\text{O})_6]\text{Cl}_3 \) \( [\text{B}] = \text{HCl} \)

\[ \text{TiCl}_4 \quad \text{Zn} \quad \text{heat} \rightarrow \text{TiCl}_3 \quad \text{H}_2\text{O} \rightarrow [\text{Ti(H}_2\text{O})_6]\text{Cl}_3 \quad \text{purple} \quad [\text{A}] \]

\[ \text{TiCl}_4 + (n + 2) \text{H}_2\text{O} \rightarrow \text{TiO}_2\text{(H}_2\text{O})_n + 4 \text{HCl} \uparrow \quad \text{white} \quad \text{fumes} \quad [\text{B}] \]
The d- and f-Block Elements and Co-ordination Compounds

Ti^{4+} = [Ar] 3d^0, Ti^{3+} = [Ar] 3d^1
TiCl₄ is colourless since Ti^{4+} has no d electrons, hence d-d transition is impossible. On the other hand, Ti^{3+} is coloured due to d-d transition. Ti^{2+} absorbs greenish yellow compound of white light, hence its aqueous solution is purple which is complementary colour of greenish yellow in white light.

**F. Match the Following**

1. **(A): (p), (q) and (s)**
   In [Co(NH₃)₆(H₂O)]²⁺, Co is in + 2 state having 3d⁷ configuration, which makes it paramagnetic due to odd electrons. Moreover, it is an octahedral complex showing cis-trans isomerism w.r.t., H₂O.
   \[
   \begin{align*}
   \text{Co}^{2+} & = 3d^7 \text{ (Paramagnetic)} \\
   \text{cis} & = \begin{bmatrix}
   \text{H}_3\text{N} & \text{NH}_3 \\
   \text{H}_3\text{N} & \text{OH}_2
   \end{bmatrix} \\
   \text{trans} & = \begin{bmatrix}
   \text{H}_3\text{N} & \text{OH}_2 \\
   \text{H}_3\text{N} & \text{NH}_3
   \end{bmatrix}
   \end{align*}
   \]

2. **(B): (p), (r) and (s)**
   In [Pt(NH₃)₂Cl₂], Pt is in + 2 state with configuration 5d⁶. Since NH₃ is a strong field ligand, it will pair all the electrons making the complex diamagnetic. Moreover, it is a square planar complex showing cis-trans isomerism.
   \[
   \begin{align*}
   \text{cis} & = \begin{bmatrix}
   \text{H}_3\text{N} & \text{Cl} \\
   \text{H}_3\text{N} & \text{Pt}
   \end{bmatrix} \\
   \text{trans} & = \begin{bmatrix}
   \text{H}_3\text{N} & \text{Pt} \\
   \text{H}_3\text{N} & \text{Cl}
   \end{bmatrix}
   \end{align*}
   \]

3. **(C): (q) and (s)**
   In [Co(H₂O)₆Cl]Cl, Co is in + 2 state with 3d⁷ configuration making it paramagnetic.

4. **(D): (q) and (s)**
   In [Ni(H₂O)₆Cl₂], Ni is in + 2 state with 3d⁸ configuration. It is attached with weak field ligands, therefore it is paramagnetic.

**G. Comprehension Based Questions**

1. (a) \( \text{Ni}^{2+} \underset{\text{KCN excess}}{\rightarrow} K_2[\text{Ni(},\text{CN)}_4] \); \( \text{Ni}^{2+} \underset{\text{KCl excess}}{\rightarrow} K_2[\text{NiCl}_4] \)

2. (c) For [Ni(CN)₄]²⁻, \( \text{Ni} = [\text{Ar}] 3d^{8}4s^{2} \); \( \text{Ni}^{2+} = [\text{Ar}] 3d^{8} \)
   \[ \text{Ni}^{2+} \begin{array}{ccc}
   3d & 4s & 4p \\
   \times & \times & \times \times
   \end{array} \]
   However, \( \text{CN}^{-} \) is a strong field ligand so it forces the 3d electrons to pair up and hence the effective configuration in this case will be \( \text{Ni}^{2+} \) in presence of \( \text{CN}^{-} \)

3. (a) Discussed above.
4. (b) \( \text{2CuFeS}_{2} + \text{O}_{2} \rightarrow \text{Cu}_{2}\text{S} + \text{SO}_{2} \uparrow + \text{2FeS} \)
   \( \text{2FeS} + \text{3O}_{2} \rightarrow \text{2FeO} + \text{2SO}_{2} \uparrow \)
   \( \text{2Cu}_{2}\text{S} + \text{3O}_{2} \rightarrow \text{2Cu}_{2}\text{O} + \text{2SO}_{2} \uparrow \)
5. (d) \( \text{FeO} + \text{SiO}_{2} \rightarrow \text{FeSiO}_{3} \)
6. (b) \( \text{Cu}_{2}\text{S} + \text{2CuO} \rightarrow \text{6Cu} + \text{SO}_{2} \)
   The reducing species is the one which gets oxidised. So, it is \( \text{S}^{2-} \) ion getting oxidised to \( \text{S}^{4+} \).
7. (b) 8. (a)
9. (c) \( \text{Cu} + \text{2AgNO}_{3} \rightarrow \text{Cu(NO)}_{3} \text{2} + \text{2Ag} \)
   (M) (N) Blue
NaCl + AgNO₃ → AgCl ↓ + NaNO₃  
(remaining) (O)

2AgCl + 2NH₃(aq) → [Ag(NH₃)₂]⁺  
(Soluble)

Cu(NO₃)₂ + 4NH₃(aq) → [Cu(NH₃)₄](NO₃)₂  
(remaining) (Deep blue colour)

**H. Assertion & Reason Type Questions**

1. (c) The statement is correct.  
2Na₂CrO₄ + H₂SO₄ → Na₂Cr₂O₇ + Na₂SO₄ + H₂O  
(remaining) (yellow) (orange)  
Oxidation state of Cr in Na₂CrO₄ and Na₂Cr₂O₇ is +6, i.e. no change in O.S. So explanation is wrong.

2. (b) 3d  
4s

Zn

Zn²⁺  

Zn²⁺ is diamagnetic because of absence of unpaired electrons.

3. (b) The geometrical isomers of [M(NH₃)₄Cl₂] can be represented as follows:-

H₃N

M

Cl

H₃N

M

Cl

(trans-form)  
cis - form

These isomers are optically inactive and they possess axis of symmetry.

Both the statements are thus true. Out of two possible answers i.e. option (a) and (b) option (b) is correct as the statement 2 is not a correct explanation of statement 1.

For a molecule to be optically active it should not possess alternate axis of symmetry.

4. (a) In [Fe(H₂O)₆]NO₃, Let the oxidation state of Fe be x. Then for [Fe(H₂O)₆]NO₃²⁻,  
x + 1 = +2  
x = +2 - 1 = +1  
Hence in this complex the oxidation state of Fe is +1  
Electronic configuration of Fe⁺ can be represented as  
Fe⁺ = 1s²2s²2p⁶3s²3p⁶3d⁷. This unexpected configuration is due to strong ligand field.  
Due to which 1 electron from 4s¹ gets shifted to 3d- orbitals.  
The 3d⁷ electrons in five 3d- orbitals can be shown as  

3d

\[ \uparrow \uparrow \uparrow \uparrow \uparrow \]

In it we find 3 unpaired electrons.  
Because of the presence of unpaired electrons the complex is paramagnetic i.e. statement 1 is true.

**I. Integer Value Correct Type**

1. The number of water molecules directly bonded to the metal centre in CuSO₄·5H₂O is 4.

2. 2MnO₂ + 4KOH + O₂ → 2K₂MnO₄ + 2H₂O  
Oxidation number of Mn in K₂MnO₄ is 6  
K₂MnO₄ ,  2 + x = 8 = 0  
x = 6

3. The number of geometrical isomers is 3:

4. m moles of [Cr(H₂O)₅Cl]Cl₂ = 0.01 × 30 = 0.3  
m moles of Cl⁻ = 0.3 × 2 = 0.6  
[1 mol of complex gives 2 Cl⁻ ions]  
m moles of Ag⁺ = m moles of Cl⁻  
0.1 × V = 0.6  
V = 6 mL

5. (8)

6. (7)  
K₂Cr₂O₇ + KI + H₂SO₄ → K₂SO₄ + Cr₂(SO₄)₃  
+ I₂ + H₂O  
2CuSO₄ + KI → 2CuI + I₂ + 2K₂SO₄  
H₂O₂ + 2KI → 2KOH + I₂  
Cl₂ + 2KI → 2KCl + I₂
The d- and f-Block Elements and Co-ordination Compounds

\[ \text{O}_3 + \text{H}_2\text{O} + 2\text{KI} \rightarrow 2\text{KOH} + \text{O}_2 + \text{I}_2 \]
\[ \text{FeCl}_3 + 2\text{KI} \rightarrow 2\text{KCl} + \text{FeCl}_2 + \text{I}_2 \]
\[ \text{HNO}_3 + \text{KI} \rightarrow \text{KNO}_3 + \text{I}_2 + \text{NO} \]

7. (3) \[ \text{CH}_3^- \rightarrow \text{Fe}^2+ \rightarrow \text{Br}^- \]

8. (6) All the complexes given show cis-trans isomerism

\[ [\text{Co(NH}_3_2^- \text{CH}_2^- \text{CH}_2^- \text{NH}_2_2^- \text{Cl}_2]^- \quad [\text{CrCl}_2(\text{C}_2\text{O}_4)_3]^3^- \]

\[ [\text{Fe(H}_2\text{O})_4(\text{OH})]^3^- \]

\[ [\text{Fe(NH}_3)_4(\text{CN})]^3^- \]

\[ [\text{Co(NH}_3_2^- \text{CH}_2^- \text{CH}_2^- \text{NH}_2_2^- \text{Cl}]^- \]

\[ [\text{Co(NH}_3)_4(\text{H}_2\text{O})]^2^- \]

9. (4) \[ \text{Fe(26)} \rightarrow [\text{Ar}]_{18} 3d^6 4s^2 \]
\[ \text{Fe}^{3+} \rightarrow [\text{Ar}]_{18} 3d^5 4s^0 \]
SCN⁻ is weak field ligand hence pairing will not occur.
\[ \therefore \text{Fe}^{3+} \rightarrow [\text{Ar}]_{18} 3d^5 4s^0 \]

### Section-B

1. (b) A square planar complex is formed by hybridisation of \( s, p_x, p_y \) and \( d_x^2 - y^2 \) atomic orbitals

2. (b) The chemical formula of nitropentamine chromium (III) chloride is

\[ [\text{Cr(NH}_3)_5\text{NO}_2]\text{Cl}_2 \]

It can exist in following two structures

\[ [\text{Cr(NH}_3)_5\text{NO}_2]\text{Cl}_2 \] and

\[ [\text{Cr(NH}_3)_5\text{ONO}]\text{Cl}_2 \]

Nitropentamine chromium (III) chloride

Therefore the type of isomerism found in this compound is linkage isomerism as nitro group is linked through N as −NO₂ or through O as −ONO.

3. (b) Compounds that contain at least one carbon metal bond are known as organometallic compounds. In \( \text{CH}_3\text{-Mg-Br} \) (Grignard's reagent) a bond is present between carbon and Mg (Metal) hence it is an organometallic compound.

4. (c) Common oxidation states of Ce (Cerium) are +3 and +4

5. (a) In lanthanides there is a regular decrease in the atomic radii as well as ionic radii of trivalent ions as the atomic number increases from Ce to Lu. This decrease in size of atoms and ions is known as lanthanide contraction.

Although the atomic radii do show some irregularities but ionic radii decreases from La to Lu. Thus the correct order is:

\[ \text{Yb}^{3+} < \text{Pm}^{3+} < \text{Ce}^{3+} < \text{La}^{3+} \]

86.8 pm 97 pm 102.2 pm 103.4 pm

6. (a) Mn⁴⁺ – 5 unpaired electrons

\( \text{Fe}^{3+} - 4 \) unpaired electrons

\( \text{Ti}^{4+} - 2 \) unpaired electrons

\( \text{Cr}^{3+} - 4 \) unpaired electrons

Hence maximum no. of unpaired electron is present in Mn⁴⁺.
NOTE: Magnetic moment \( \propto \) number of unpaired electrons

7. (c) The cyano and hydroxo complexes are far more stable than those formed by halide ion. This is due to the fact that CN\(^-\) and OH\(^-\) are strong lewis bases (nucleophiles). Further [Fe(OH)\(_5\)]\(^{3-}\) is not formed. hence most stable ion is [Fe(CN)\(_5\)]\(^{3-}\).

8. (c) 
\[
\begin{align*}
\text{Mn}_2\text{O}_5 & \xrightarrow{4\text{e}^-} [\text{KMnO}_4] \xrightarrow{\text{7e}^-} [\text{MnO}_4]^{2-} \\
& \xrightarrow{-5\text{e}^-} \text{Mn}^{2+} \\
& \xrightarrow{-3\text{e}^-} [\text{MnO}_4]^{2-}
\end{align*}
\]

9. (c) Ionic radii \( \propto \frac{1}{z} \)

Thus, \( \frac{Z_2}{Z_1} \Rightarrow \frac{1.06}{(\text{Ionic radii of Lu}^{3+})} = \frac{71}{57} \Rightarrow \text{Ionic radii of Lu}^{3+} = 0.85 \text{ Å} \)

10. (a) \( \text{NH}_3 + \text{H}^+ \) (acid medium) \( \Rightarrow \) \( \text{NH}_4^+ \)

11. (d) \( \text{Co(NH}_3)_5\text{Cl}_3 \rightleftharpoons [\text{Co(NH}_3)_5\text{Cl}]^2^+ + 2\text{Cl}^- \)
   \( \therefore \) Structure is \( [\text{Co(NH}_3)_5\text{Cl}]\text{Cl}_2 \).
   Now \( [\text{Co(NH}_3)_5\text{Cl}]\text{Cl}_2 + 2\text{AgNO}_3 \)
   \( \Rightarrow [\text{Co(NH}_3)_5\text{Cl}]\text{(NO}_3)_2 + 2\text{AgCl} \)

12. (a) Let the O. No of Ni in \( K_4[\text{Fe(CN)}_6] \) be \( x \) then
   \( 4 + x + (-1) \times 4 = 0 \Rightarrow 4 + x - 4 = 0 \)
   \( x = 0 \)

13. (a) When KI is added to mercuric iodide it dissolves in it and form complex.
   \( \text{HgI}_2 + \text{KI} \rightarrow \text{K}_2[\text{HgI}_4] \).
   
   On heating \( \text{HgI}_2 \) decomposes as
   \( \text{HgI}_2 \rightarrow \text{Hg} + \text{I}_2 \)
   (violet vapours)

14. (b) 'block elements show a regular decrease in atomic size due to lanthanide/actinide contraction.

15. (a) When a solution of potassium chromate is treated with an excess of dilute nitric acid. Potassium dichromate and \( \text{H}_2\text{O} \) are formed.
   \( 2\text{K}_2\text{CrO}_4 + 2\text{HNO}_3 \rightarrow 2\text{K}_2\text{Cr}_2\text{O}_7 + 2\text{KNO}_3 + \text{H}_2\text{O} \)
   Hence \( \text{Cr}_2\text{O}_7^{2-} \) and \( \text{H}_2\text{O} \) are formed.

16. (c) \( \text{AgNO}_3 \) on heating till red hot decomposes as follows:
   \( \text{AgNO}_3 \rightarrow \text{Ag} + \text{NO}_2 + \frac{1}{2}\text{O}_2 \)

17. (d) \((n-1)\text{d}^5\text{ns}^2\) attains the maximum O.S. of +7

18. (b) Grey tin \( \text{grey tin} \) 
   Grey tin is brittle and crumbles down to powder in very cold climate
   The conversion of grey tin to white tin is accompanied by increase in volume, This is known as tin plaque or tin disease.

19. (a) \( \text{CN}^- \) ion acts good complexing as well as reducing agent.

20. (c) The coordination number of central metal atom in a complex is equal to number of monovalent ligands, twice the number of bidentate ligands and so on, around the metal ion bonded by coordinate bonds. Hence coordination number = no. of \( \sigma \) bonds formed by metals with ligands

21. (d) Hybridization
   \( \text{[Fe(CN)}_6]^{4-}, \text{[Mn(CN)}_6]^{4-}, \text{d}^2\text{sp}^3 \)
   \( \text{[Co(NH}_3)_6]^{3+}, \text{[Ni(NH}_3)_6]^{2+} \text{d}^2\text{sp}^3 \text{d}^2 \)
   Hence \( \text{[Ni(NH}_3)_6]^{2+} \) is outer orbital complex.

22. (c) The chlorophyll molecule plays an important role in photosynthesis, contain porphyrin ring and the metal Mg not Ca.

23. (a) The \(+4\) oxidation state of cerium is also known in solution.

24. (d) Isomers
   \( \text{[Ru(NH}_3)_4\text{Cl}_2]^+, \text{[Co(NH}_3)_5\text{Cl}]^{2+}, \text{cis and trans} \text{none} \)
   \( \text{[Ir(PR}_3)_2\text{H(CO)}]^{2+}, \text{[Co(en)}_2\text{Cl}_2]^+, \text{cis and trans and optical isomers} \)

25. (c) \( \text{[Fe(CN)}_6]^{4-} \rightarrow \text{[Fe(CN)}_6]^{4-} \), \( \text{[Co(en)}_2\text{Cl}_2]^+ \)
   \( \text{no of unpaired electron} = 0 \)
   \( \text{[MnCl}_4]^{2-} \rightarrow \text{[MnCl}_4]^{2-} \), \( \text{[Fe(CN)}_6]^{4-} \)
   \( \text{no of unpaired electron} = 5 \)
   \( \text{[CoCl}_4]^{2-} \rightarrow \text{[CoCl}_4]^{2-} \), \( \text{[Fe(CN)}_6]^{4-} \)
   \( \text{no of unpaired electron} = 3 \)

26. (d) Oxidation state of Cr in \( \text{[Cr(NH}_3)_4\text{Cl}_2]^+ \).
   Let it be \( x \), \( 1 \times x + 4 \times 0 + 2 \times (-1) = 1 \) Therefore \( x = 3 \).

27. (d) \( 2\text{Cu}_2\text{O} + \text{Cu}_2\text{S} \rightarrow 6\text{Cu} + \text{SO}_2 \)
   Self reduction.

28. (a) \( \text{Cr}_2\text{O}_7^{2-} + 6\text{I}^- + 14\text{H}^+ \rightarrow 3\text{I}_2 + 7\text{H}_2\text{O} + 2\text{Cr}^{3+} \)
   Oxidation state of Cr is 3+.

29. (d) \( \text{Hg}_2\text{Cl}_2 + 2\text{NH}_4\text{OH} \rightarrow \text{Hg}_2\text{NH}_2\text{Cl} + \text{NH}_4\text{Cl} + 2\text{H}_2\text{O} \)

30. (b) NOTE: In vertical columns of transition elements, there is an increase in size from first member to second member as expected but from second member to third member, there is very small chang in size and some times sizes are same. This is due to lanthanide contraction this is the reason for Zr and Hf to have same radius.
31. (c) $K_3[Fe(CN)_6]$ is potassium hexacyano ferrate (III).

32. (b) [Image of non-superimposable mirror images]

Non-superimposable mirror images, hence optical isomers.

33. (a) No. of unpaired electron
   a) Co$^{3+}$
   b) Fe$^{3+}$
   c) Mn$^{3+}$
   d) Cr$^{3+}$
   
   The effective magnetic moment is given by the number of unpaired electrons in a substance, the lesser the number of unpaired electrons lower is its magnetic moment in Bohr – Magnetron and lower shall be its paramagnetism

34. (d) $d^5$ — strong ligand field

   $t_{2g}$
   $e_g$
   $\mu = n\sqrt{n+2} = \sqrt{3} = 1.73$ BM

   $d^3$ — in weak as well as in strong field

35. (d) In lanthanides, there is poorer shielding of $5d$ electrons by $4f$ electrons resulting in greater attraction of the nucleus over $5d$ electrons and contraction of the atomic radii.

36. (b) [Co(NO)$_3$(NH$_3$)$_2$]Cl$_2$
pentaammine nitrito-N-cobalt (III) chloride

37. (a) Metal atom in the lower oxidation state forms the ionic bond and in the higher oxidation state the covalent bond. Because higher oxidation state means small size and great polarizing power and hence greater the covalent character. Hence MCI$_2$ is more ionic than MC$_4$.

38. (d) $[Ni^2+]^{2+}$, the electronic configuration of Ni$^{2+}$ is

   [Image of electron configuration]

   It contains two unpaired electrons and the hybridisation is sp$^3$ (tetrahedral).

39. (d) Due to some backbonding by sideways overlapping of between d-orbitals of metal and p-orbital of carbon, the Fe–C bond in Fe(CO)$_5$ has both $\sigma$ and $\pi$ character.

40. (b) The configuration of Lanthanides show that the additional electron enters the 4f subshell. The shielding of one 4f electron by another is very little or imperfect. The imperfect shielding of 4f electrons is due to the shape of f orbitals which is very much diffused. Thus as the atomic number increases, the nuclear charge increases by unity at each step. While no comparable increase in the mutual shielding effect of 4f occurs. This causes a contraction in the size of the 4f subshell. As a result atomic and ionic radii decreases gradually from La to Lu.

41. (a) EDTA has hexadentate four donor O atoms and 2 donor N atoms and for the formation of octahedral complex one molecule is required.

42. (c) The number of unpaired electrons in Ni$^{2+}$(aq) = 2; Water is weak ligand hence no pairing will take place spin magnetic moment = $\sqrt{2(n+2)} = 2(2+2)$

43. (d) Reluctance of valence shell electrons to participate in bonding is called inert pair effect. The stability of lower oxidation state (+2 for group 14 element) increases on going down the group. So the correct order is SiX$_2$ < GeX$_2$ < SnX$_2$ < PbX$_2$.

44. (a) 4f orbital is nearer to nucleus as compared to 5f orbital therefore, shielding of 4f is more than 5f.

45. (a) Complexes with $dp^3$ hybridisation are square planar. So $[PtCl_4]^{2-}$ is square planar in shape.

46. (a) NOTE: More the distance between nucleus and outer orbitals, lesser will be force of attraction on them. Distance between nucleus and 5f orbitals is more as compared to distance between 4f orbital and nucleus. So actinoids exhibit more number of oxidation states in general than the lanthanoids.

47. (d) In the given complex we have two bidentate ligands (i.e en and $C_2O_4$), so coordination number of E is 6

   $2(2 + 1 \times 2) = 6$

   Let the oxidation state of E in complex be x, then

   $x + (–2) = 1$ or $x = 3$

   or $x = + 3$, so its oxidation state is +3

   Thus option (d) is correct.

48. (b) NOTE: The main reason for exhibiting larger number of oxidation states by actinoids as compared to lanthanoids is lesser energy difference between 5f and 6d orbitals as compared to that between 4f and 5d orbitals.
In case of actinoids we can remove electrons from 5f as also from 6d and due to this actinoids exhibit larger number of oxidation state than lanthanoids. Thus the correct answer is option (b).

49. (a) In octahedral complex the magnitude of $\Delta_0$ will be highest in a complex having strongest ligand. Of the given ligands $CN^-$ is strongest so $\Delta_0$ will be highest for $(Co(CN)_6)^3-$. Thus option (a) is correct.

50. (c) The titration of oxalic acid with $KMnO_4$ in presence of HCl gives unsatisfactory result because of the fact that $KMnO_4$ can also oxidise HCl along with oxalic acid. HCl on oxidation gives $Cl_2$ and HCl reduces $KMnO_4$ to $Mn^{2+}$ thus the correct answer is (c).

51. (c) Enantiomers of $cis-[Co(en)_2(NH_3)_2]^3+$

52. (a) Lower oxidation state of an element forms more basic oxide and hydroxide, while the higher oxidation state will form more acidic oxide/hydroxide. For example,

$$\begin{align*}
\text{basic} & : \text{MnO}^2+ & \text{Mn}_2\text{O}_3 & = 7 \\
\text{acidic} & : \text{Mn}_2\text{O}_7 & & = 4 + 3
\end{align*}$$

53. (a) The SCN$^-$ ion can coordinate through S or N atom giving rise to linkage isomerism

54. (b) Most of the Ln$^{3+}$ compounds except $La^{3+}$ and $Lu^{3+}$ are coloured due to the presence of f-electrons.

55. (a) $CoCl_3.6NH_3 \rightarrow xCl^- \text{ 2.675g}$

$$\begin{align*}
xCl^- + AgNO_3 \rightarrow x AgCl \downarrow \\
4.78g
\end{align*}$$

Number of moles of the complex $= \frac{2.675}{267.5} = 0.01$ moles

Number of moles of $AgCl$ obtained $= \frac{4.78}{143.5} = 0.03$ moles

$\therefore$ No. of moles of $AgCl$ obtained $= 3 \times$ No. of moles of complex

$\therefore n = \frac{0.03}{0.01} = 3$

56. (b) For a substance to be optical isomer following conditions should be fulfilled

(a) A coordination compound which can rotate the plane of polarised light is said to be optically active.

(b) When the coordination compounds have same formula but differ in their abilities to rotate directions of the plane of polarised light are said to exhibit optical isomerism and the molecules are optical isomers.

57. (c) Optical isomers are pair of molecules which are non-superimposable mirror images of each other.

(c) This is due to the absence of elements of symmetry in the complex.

(d) Optical isomerism is expected in tetrahedral complexes of the type $Mabcd$.

Based on this only option (2) shows optical isomerism $[Co(en)_3]^3+$

58. (d) Complexes of $Zn^{2+}$ cannot show optical isomerism as they are tetrahedral complexes with plane of symmetry.

$[Co(H_2O)_4(en)]^{3+}$ have two planes of symmetry hence it is also optically inactive.

Hence the formula of the complex is $[Co(NH_3)_6]Cl_3$

$[Cr(NH_3)_6]Cl_3$ is an inner orbital complex, because in this complex d-orbital used is of lower quantum number i.e $n - 1$. It results from $d^2 sp^3$ (inner orbital) hybridization.

59. (c) $[NiCl_4]^{2-}$

$$\begin{array}{c}
\text{sp}^3 \text{ hybridisation} \\
\text{i.e the number of unpaired electrons in } [NiCl_4]^{2-} \text{ is } 2. \\
n = \sqrt{n(n+2)} = \sqrt{2(4)} = 2\sqrt{2} = 2 \times 1.41 \\
= 2.82 \text{ BM}
\end{array}$$

60. (d) The configuration of Gd is $4f^7 5d^1 6s^2$

61. (b) $[Cr(en)_2Br_2]Br$

dibromodimethyldiamine chromium (III) Bromide.

62. (d) $Fe^{3+}$ is easily hydrolysed than $Fe^{2+}$ due to more positive charge.

63. (c) Octahedral coordination entities of the type $Ma_{2}b_{3}$ exhibit Geometrical isomerism. The compound exists both as facial and meridional isomers.
64. (a) 

(1) V = 3d^3 4s^2 \quad V^{2+} = 3d^3 \quad = \quad 3\text{ unpaired electron}
Cr = 3d^5 4s^1 \quad Cr^{2+} = 3d^4 \quad = \quad 4\text{ unpaired electron}
Mn = 3d^5 4s^2 \quad Mn^{2+} = 3d^5 \quad = \quad 5\text{ unpaired electron}
Fe = 3d^6 4s^2 \quad Fe^{2+} = 3d^6 \quad = \quad 4\text{ unpaired electron}

hence the correct order of paramagnetic behaviour

\( \text{V}^{2+} < \text{Cr}^{2+} < \text{Fe}^{2+} < \text{Mn}^{2+} \)

(2) For the same oxidation state, the ionic radii generally decrease as the atomic number increases in a particular transition series. hence the order is

\( \text{Mn}^{2+} > \text{Fe}^{2+} > \text{Co}^{2+} > \text{Ni}^{2+} \)

(3) In solution, the stability of the compounds depends upon electrode potentials, SEP of the transitions metal ions are given as

\( \text{Co}^{3+} / \text{Co} = +1.97, \text{Fe}^{3+} / \text{Fe} = +0.77; \)

\( \text{Cr}^{3+} / \text{Cr}^{2+} = -0.41, \text{Sc}^{3+} \) is highly stable as it does not show +2 O.S.

(4) Sc = (+2), (+3)
Ti = (+2), (+3), (+4)
Cr = (+1), (+2), (+3), (+4), (+5), (+6)
Mn = (+2), (+3), (+4), (+5), (+6), (+7)
i.e. Sc < Ti < Cr = Mn

\( E_a = 53598.6 \text{ J/mol} = 53.6 \text{ kJ/mol} \)

65. (d) 

\( E^{0}_{\text{Cr}^{3+} / \text{Cr}^{2+}} = -0.41 \text{ V} \)

\( E^{0}_{\text{Fe}^{3+} / \text{Fe}^{2+}} = +0.77 \text{ V} \)

\( E^{0}_{\text{Mn}^{3+} / \text{Mn}^{2+}} = +1.57 \text{ V} \)

\( E^{0}_{\text{Co}^{3+} / \text{Co}^{2+}} = +1.97 \text{ V} \)

66. (b) 

For a given metal ion, weak field ligands create a complex with smaller \( \Delta \), which will absorb light of longer \( \lambda \) and thus lower frequency. Conservatively, stronger field ligands create a larger \( \Delta \), absorb light of shorter \( \lambda \) and thus higher \( \nu \) i.e. higher energy.

Red < Yellow < Green < Blue

\( \lambda = 650 \text{ nm} \quad 570 \text{ nm} \quad 490 \text{ nm} \quad 450 \text{ nm} \)

So order of ligand strength is

\( L_1 < L_2 < L_3 < L_4 \)

67. (d) In equation (i) \( \text{Fe}_2(\text{SO}_4)_3 \) and in equation (ii) \( \text{Fe}_2(\text{SO}_4)_3 \) on decomposing will form oxide instead of Fe.

The correct sequence of reactions is

\[ \text{Fe} \overset{\text{O}_2, \text{heat}}{\longrightarrow} \text{Fe}_2\text{O}_3 \overset{\text{Co}, 600^\circ C}{\longrightarrow} \text{Fe}_2(\text{SO}_4)_3 \overset{\Delta}{\longrightarrow} \text{Fe} \]

68. (c) 

69. (d) (A) - (ii), (B) - (i), (C) - (iv), (D) - (iii)

70. (d) Square planar complexes of type \( \text{M}[\text{ABCD}] \) form three isomers. Their position may be obtained by fixing the position of one ligand and placing at the \( \text{trans} \) position any one of the remaining three ligands one by one.

\[ \text{HO}_2\text{N} \quad \text{Cl} \quad \text{HO}_2\text{N} \quad \text{Cl} \]

\[ \text{py} \quad \text{NH}_3 \quad \text{py} \quad \text{NH}_3 \]

\[ \text{Pt} \quad \text{trans} \quad \text{NH}_3 \quad \text{Cl} \]

\[ \text{Pt} \quad \text{cis} \quad \text{NH}_3 \quad \text{Cl} \]

\[ \text{HO}_2\text{N} \quad \text{Cl} \quad \text{HO}_2\text{N} \quad \text{Cl} \]

\[ \text{py} \quad \text{NH}_3 \quad \text{py} \quad \text{NH}_3 \]

\[ \text{Pt} \quad \text{cis} \quad \text{NH}_3 \quad \text{Cl} \]

\[ \text{Pt} \quad \text{trans} \quad \text{NH}_3 \quad \text{Cl} \]

71. (a) L \( \rightarrow \) M charge transfer spectra. \( \text{KMnO}_4 \) is colored because it absorbs light in the visible range of electromagnetic radiation. The permanganate ion is the source of color, as a ligand to metal, \( (L \rightarrow M) \) charge transfer takes place between oxygen's \( p \) orbitals and the empty \( d \)-orbitals on the metal. This charge transfer takes place when a photon of light is absorbed, which leads to the purple color of the compound.

72. (d) Out of all the four given metallic oxides \( \text{Cr}_2O_2 \) is attracted by magnetic field very strongly. The effect persists even when the magnetic field is removed. Thus \( \text{Cr}_2O_2 \) is metallic and ferromagnetic in nature.

73. (c) Optical isomerism occurs when a molecule is non-superimposable with its mirror image hence the complex \( \text{cis-[Co(en)_2Cl_2]} \) is optically active.

74. (d) 

<table>
<thead>
<tr>
<th>Complex</th>
<th>Metal ion</th>
<th>Configuration</th>
<th>Magnetic moment ( \mu = \sqrt{n(n+2)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) [ \text{Cr(H}_2\text{O})_6\text{]}^{2+} ]</td>
<td>Cr ( ^{2+} )</td>
<td>( d^4 )</td>
<td>( \sqrt{24} )</td>
</tr>
<tr>
<td>(b) [ \text{Fe(H}_2\text{O})_6\text{]}^{2+} ]</td>
<td>Fe ( ^{2+} )</td>
<td>( d^6 )</td>
<td>( \sqrt{24} )</td>
</tr>
<tr>
<td>(c) [ \text{CoCl}_4\text{]}^{2-} ]</td>
<td>Co ( ^{2+} )</td>
<td>( d^7 )</td>
<td>( \sqrt{15} )</td>
</tr>
<tr>
<td>(d) [ \text{Mn(H}_2\text{O})_6\text{]}^{2+} ]</td>
<td>Mn ( ^{2+} )</td>
<td>( d^5 )</td>
<td>( \sqrt{35} )</td>
</tr>
</tbody>
</table>

Since (a) and (b), each has 4 unpaired electrons, they will have same magnetic moment.
Haloalkanes and Haloarenes

Section-A : JEE Advanced/ IIT-JEE

1. chlorine
2. Grignard
3. Thioalcohol
4. polyvinyl chloride

1. F
2. F
3. (d)
4. (d)
5. (b)
6. (a)
7. (b)
8. (b)
9. (a)
10. (d)
11. (b)
12. (d)
13. (d)
14. (a)

15. (b)
16. (a)

8. \( \text{CH}_2\text{Cl}; \ Y: \text{CH}_2\text{Cl}\text{CH}_2\text{Cl}; \ Z: \text{CH}_3\text{CHCl}_2 \)

9. \[
\begin{align*}
\text{H} & \quad \text{OH;} \\
\text{CH}_3 & \\
\end{align*}
\]

10. \[
\begin{align*}
\text{CH}_3 & \quad \text{C} & & \text{CH}_2 = \text{C} & & \text{CH} - \text{CH}_3; & & \text{CH}_3 - \text{C} & & = \text{C} - \text{CH}_3 \\
\end{align*}
\]

12. [A] \quad [B]

Section-B : JEE Main/ AIEEE

1. (d)
2. (b)
3. (b)
4. (b)
5. (c)
6. (d)
7. (d)
8. (a)
9. (b)
10. (c)
11. (d)
12. (a)
13. (c)
14. (d)
15. (d)
16. (b)
17. (c)
18. (b)

Section-A : JEE Advanced/ IIT-JEE

A. Fill in the Blanks

1. Chlorine: because rate of formation of \( \cdot \text{CH}_3 \) (one of the propagating steps) is high when \( \text{X}^* \) is Cl.
   \[ \text{CH}_4 + \text{X}^* \rightarrow \text{CH}_3 + \text{H} - \text{X} \]

2. Grignard (RMgX)

3. Thioalcohol

4. polyvinyl chloride.

B. True/False

1. False: \( m \)-Chlorobromobenzene and \( m \)-bromochlorobenzene is one and the same compound.

2. False: \( \text{CH}_2 = \text{CHCl} + \text{H}_2 \rightarrow \text{CH}_3\text{CHCl}(\text{i}) \) vinyl chloride 1- chloro-1-iodoethane

This is an example of Markownikoff's rule as \( \text{I}^- \) is added at the \( \text{C} \) with less number of H-atoms.

NOTE: anti-Markonikov's rule is applicable only to HBr, but not to HI and HCl.

C. MCQs with One Correct Answer

1. (d) \( \text{C}_6\text{H}_5\text{NH}_2 \xrightarrow{\text{HONO}} \text{C}_6\text{H}_5\text{N}_2\text{Cl} \xrightarrow{\text{CuCl}} \text{C}_6\text{H}_5\text{Cl} \)

2. (d) TIPS/Formulæ:
   The given reaction is an example of electrophilic substitution. Further, \( \text{CH}_3 \) group in toluene is \( o, p \)-directing.

3. (a) Chlorination beyond monochlorination during the preparation of alkyl halides in presence of UV light can be suppressed by taking alkane in excess.
NOTE: For isomeric alkanes the one having largest straight chain has highest b.p. because of large surface area.

4. (b) \[ \text{CH}_3 \text{C} - \text{CH}_2 - \text{CH}_2 \text{Br} \xrightarrow{\text{ethanolic KOH}} \text{CH}_3 - \text{CH} = \text{CH}_2 \] 
   Further dehydrohalogenation of \( \text{CH}_3\text{CH} = \text{CH}_2 \) can be done only by strong base like \( \text{NaNH}_2 \).

5. (b) Addition of \( \text{HBr} \) of 2-pentyne gives two structural isomers (I) and (II)
   \[ \text{CH}_3 - \text{C} \equiv \text{C} - \text{CH}_2\text{CH}_3 \xrightarrow{\text{HBr}} \]
   \[ \text{CH}_3\text{C}(\text{Br}) = \text{CHCH}_2\text{CH}_3 + \text{CH}_3\text{CH} = \text{C}(\text{Br})\text{CH}_2\text{CH}_3 \] 
   (I) (II)
   Each one of these will exist as a pair of geometrical isomers. Thus, there are two structural and four configurational isomers.

6. (a) \[ \text{H}_3\text{C} - \text{H}_2\text{C} - \text{H}_2\text{C} - \text{CH}_2\text{Cl} \xrightarrow{\text{alc. KOH}} \text{CH}_3 - \text{CH}_2\text{CH} = \text{CH}_2 \] 
   (Elimination reaction)
   1-butene
   NOTE: Alkyl halides give alcohols with \( \text{aq. KOH} \), which is a substitution reaction.

7. (b) TIPS/Formulae:
   The reaction proceeds via free radical mechanism.
   As \( 2^\circ \) free radical is more stable than \( 1^\circ \), so \( \text{CH}_3\text{CH}_2\text{CH}(\text{Br})\text{CH}_3 \) would be formed.

8. (b) \[ (\text{CH}_3)_2\text{CHCH}_2\text{MgBr} \xrightarrow{\text{C}_2\text{H}_5\text{OH}} (\text{CH}_3)_2\text{CHCH}_3 \]

9. (a) \[ (\text{CH}_3)_2\text{C} - \text{MgCl} + \text{D}_2\text{O} \rightarrow (\text{CH}_3)_2\text{C} - \text{D} + \text{Mg(OH)}\text{Cl} \]

10. (d) Occurrence of racemization points towards the formation of carbocation as intermediate, which being planar can be attacked from either side.

11. (b) Dehydrobromination by strong base (alc. NaOH) followed by Markownikoff addition of HBr.

12. (d) \[ \text{CH}_3 \xrightarrow{\text{H}^+} \text{CH}_3\text{CH}_2\text{CH} = \text{CH}_2 + \text{CH}_3\text{CH} = \text{CHCH}_3 \]
   (Butene-1) (Butene-2)
   \[ \text{CH}_3\text{CH}_2\text{CH} = \text{CH}_2 \xrightarrow{\text{Br}_2} \text{CH}_3\text{CH}_2 \text{CHCH}_2\text{Br} \]
   (cis- and trans)
   (+) + and (-) enantiomer

13. (d) TIPS/Formulae:
   It is an example of intramolecular Wurtz reaction.
   \[ \text{Cl} \xrightarrow{\text{Na} \text{ ether}} \xrightarrow{\text{Cl}} + \text{NaCl} \]
   NOTE: \( \text{Br}^- \) is a better leaving group than chloride. In this reaction alkali metal (Na) is electron donor.

14. (a) Grignard reagents react with compounds containing active hydrogen to form hydrocarbons corresponding to alkyl (or aryl) part of the Grignard reagent.
   \[ \text{C}_6\text{H}_5\text{MgBr} + \text{Me}_3\text{COH} \rightarrow \text{C}_6\text{H}_6 + \text{Me}_3\text{COMgBr} \]

15. (b) \[ \text{BrCH}_2 - \text{CH}_2\text{Br} \xrightarrow{\text{Alc KOH}} \text{CH}_2 = \text{CHBr} \]
   \[ \xrightarrow{\text{NaNH}_2} \text{CH} = \text{CH} \]
   NOTE: Elimination of HBr from \( \text{CH}_2 = \text{CHBr} \) requires a stronger base because here, Br acquires partial double bond character due to resonance.

16. (a) The product (a) will be formed.
   Nucleophilic substitution of an alkyl halide is easier as compared to that of an aryl halide.
   PhS\(^{-}\) is a strong nucleophile and dimethyl formamide \[ \overset{\text{O}}{\text{H}} - \text{C} - \overset{\|}{\text{NMe}_2} \] is a highly polar aprotic solvent.
   These reagent favour \( S_N^2 \) reactions at 2\(^\circ\) benzyllic carbon.
   NOTE: In a \( S_N^2 \) reaction, the major product formed is inversion product.
D. MCQs with One or More Than One Correct

1. (b, e) **TIPS/Formulate:**
   Aryl halides are stable due to resonance stabilization.
   The resonating structures

   ![Resonating Structures](image)

   stabilise the aryl halide. These structures include a double bond between C and Cl which is shorter and thus stronger than the usual C—Cl single bond. The \(sp^2\) hybridised carbon, being electronegative, makes the C—Cl bond shorter and stronger.

2. (e) Chlorination of toluene to form benzyl chloride is a free radical substitution reaction; only Cl\(_2\) can give Cl in presence of light.

E. Subjective Problems

1. (a)
   (i) \(\text{CaC}_2 + 2\text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 + \text{C}_2\text{H}_2\text{O}\)
   \(\text{C}_2\text{H}_2\text{O} \xrightarrow{\text{H}_2/\text{Ni}} \text{C}_6\text{H}_6 \xrightarrow{\text{Cl}_2(\text{excess})/\text{UV}} \text{CCl}_3 - \text{CCl}_3\)

   (ii) \(\text{CS}_2 + 3\text{Cl}_2 \rightarrow \text{CCl}_4 + \text{S}_2\text{Cl}_2\)
   \(\text{CCl}_4 + 2\text{[H]} \xrightarrow{\text{Fe/H}_2\text{O}} \text{CHCl}_3 + \text{HCl}\)

   (b) Carbylamine test.
   \(\text{CHCl}_3 + \text{aq KOH} + \text{aniline (i.e. primary amine)} \rightarrow \text{bad smelling isocyanide}\)
   \(\text{C}_2\text{H}_3\text{OH} + \text{aq KOH} + \text{aniline} \rightarrow \text{No reaction}\)

2. (i) \(\text{C}_6\text{H}_5\text{NH}_2 + \text{CHCl}_3 \xrightarrow{\text{alkali KOH}} \text{C}_6\text{H}_5 - \text{N} \equiv \text{C}\)
   Phenyl isocyanide

   (ii) \(\text{C}_2\text{H}_4\text{O} \xrightarrow{} \text{C} = \text{O}\)
   Diethyl carbonate

   (iii) \((\text{CH}_3)_2\text{C} - \text{CH}_2\text{CH}_3 \xrightarrow{\text{alkaline KOH}} (\text{CH}_3)_2\text{C} = \text{CHCH}_3\)

   (iv) \(\text{CH}_3\text{CH}_2\text{CHCl}_2 \xrightarrow{\text{boil alkali}} \text{CH}_3\text{CH}_2\text{CH(OH)}_2\)
   \((-\text{H}_2\text{O}) \rightarrow \text{CH}_3\text{CH}_2\text{CHO}\)

   (v) \(\text{C}_6\text{H}_5\text{CH}_2 - \text{CH} - \text{CH}_3 \xrightarrow{\text{alkaline KOH}} \text{C}_6\text{H}_5\text{CH} = \text{CH} - \text{CH}_3\)
   (Saytzeff product)

   \(\text{HBr} \rightarrow \text{C}_6\text{H}_5 - \text{C} - \text{CH}_2\text{CH}_3\)

   [NOTE: \(\text{C}_6\text{H}_5\text{CH}_2\text{CH} = \text{CHCH}_3\) and \(\text{C}_6\text{H}_5\text{CH} = \text{CHCH}_2\text{CH}_3\) carbenium ions are formed on addition of HBr on \(\text{C}_6\text{H}_5\text{CH} = \text{CHCH}_3\), the latter being benzylic carbenium ion, is stabilised due to resonance and hence Br\(^{-}\) adds on it forming \(\text{C}_6\text{H}_5\text{CHBrCH}_2\text{CH}_3\) as the final product.]

   (vi) \(\text{2Me} \xrightarrow{\text{Heat}} \text{Me} \xrightarrow{\text{Cu}} \text{Me}\)

   (vii) \(\text{C}_6\text{H}_5 - \text{CH}_2 - \text{CH} - \text{C}_6\text{H}_5\)

   \(\text{KOH (alcoholic)} \xrightarrow{\Delta} \text{C}_6\text{H}_5\text{H}_2\text{C} = \text{CH}_2\text{C}_6\text{H}_5\text{H}_2\)
   (cis and trans - Styrene (trans is major))

   (viii) \(\text{CH}_3 \xrightarrow{\text{C} = \text{CHBr}} \text{C} \xrightarrow{\text{C}_6\text{H}_4\text{OH (S_{aq}) reaction}} \text{CH}_2\text{C} = \text{CHOC}_6\text{H}_5\)

3. (i) **TIPS/Formulate:**
   7-Bromo-1,3,5-cycloheptatriene is aromatic whereas 5-Bromo-1,3-Cycloheptadiene is non-aromatic.

   ![Diagram of 7-Bromo-1,3,5-cycloheptatriene](image)
   Its corresponding cation is \(\text{Br}^-\)

   ![Diagram of 5-Bromo-1,3-cyclohexadiene](image)
   Its corresponding cation is \(\text{Br}^-\)

   (ii) **NOTE:** The former halide is a 3° halide, hence it undergoes \(S_{n1}\) reaction forming HBr, as one of the products, which make solution acidic.

   \(\text{C}_6\text{H}_5 - \text{C} - \text{Br} \xrightarrow{\text{C}_6\text{H}_5\text{OH(aq) (S_{n1})}} \text{CH}_3\)
   A 3° bromide

   \(\text{C}_6\text{H}_5\text{H}_2\text{C} = \text{CHOC}_6\text{H}_5\text{H}_2 + \text{HBr}\)
   (acidic)

   ![Diagram of 2-Bromo-1,3-dichloroethane](image)
   2-Bromo-1,3-dichloroethane (acidic)

   \(\text{Br} - \text{CH(CH}_3)_2\) is an aryl halide so it does not undergo nucleophilic substitution reactions. Hence the solution will remain neutral.
4. (i) \(4 \text{C}_2\text{H}_5\text{Br} + 4(\text{Na} + \text{Pb}) \xrightarrow{\text{dry ether}} \text{Pb} (\text{C}_2\text{H}_5)_4 + 4\text{NaBr} + 3\text{Pb}\)

(ii) \(\text{Al}_4\text{C}_3 \xrightarrow{\text{H}_2\text{O}} \text{CH}_4 \xrightarrow{\text{Cl}_2 } \xrightarrow{\text{sun light}} \text{CH}_3\text{Cl}\)

5. Dichloroethene exists in three isomeric forms.

\[
\begin{align*}
\text{Cl} - & \text{C} - \text{Cl} \\
\text{H} - & \text{C} - \text{H} \\
\text{H} - & \text{C} - \text{Cl} \\
\text{Cl} & - \text{C} - \text{H}
\end{align*}
\]

\(\text{(cis)}-1, 2\text{-dichloroethene}\)

\(\text{(trans)}-1, 2\text{-dichloroethene}\)

\(\text{trans}-1, 2\text{-Dichloroethene has zero dipole moment.}\)

\[
\begin{align*}
\text{Cl} - & \text{C} - \text{H} \\
\text{H} - & \text{C} - \text{Cl}
\end{align*}
\]

\[\text{NOTE} : \text{ Dipole moment is a vector quantity}\]

6. \(\text{C}_6\text{H}_5\text{CH}_3 \xrightarrow{\text{Cl}_2 } \xrightarrow{\text{UV Light}} \text{C}_6\text{H}_5\text{CH}_2\text{Cl}\)

\(\xrightarrow{\text{Cl}_2 } \text{C}_6\text{H}_5\text{CH}_2\text{Cl} \xrightarrow{\text{Cl}_2 } \text{C}_6\text{H}_5\text{CCl}_3\)

Benzotrichloride

\[\text{NOTE} : \text{This follows free radical mechanism.}\]

7. **TIPS/Formulae** :

Resonance decreases the dipole moment of vinyl chloride (\(\text{CH}_2\text{=CHCl}\)).

The positive charge on Cl and a negative charge on C (developed by resonance) oppose each other and hence diminish the electronegativity of Cl and thus polarity (and dipole moment) of the bond. The dipole moments of vinyl chloride and chlorobenzene are 1.4D and 1.7D respectively, while the dipole moment of alkyl halides is 2-2.2D.

8. \% of Cl in X = \(\frac{35.5 \times 2.9}{143.5} \times 100 = 71.72\%\)

**Empirical formula of (X)**

<table>
<thead>
<tr>
<th>Element</th>
<th>%</th>
<th>Relative no. of atoms</th>
<th>Simplest ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>24.24</td>
<td>2.02</td>
<td>1</td>
</tr>
<tr>
<td>H</td>
<td>4.04</td>
<td>4.04</td>
<td>2</td>
</tr>
<tr>
<td>Cl</td>
<td>71.72</td>
<td>2.02</td>
<td>1</td>
</tr>
</tbody>
</table>

\(\therefore\) **Empirical formula of (X) is \text{CH}_2\text{Cl}\)**

Since X has two isomers Y and Z; both react with KOH(aq).

\[Y \xrightarrow{\text{KOH(aq)}} \text{dihydroxy compound i.e. 2Cl atoms on adjacent carbon}\]

\[Z \xrightarrow{\text{KOH(aq)}} \text{CH}_3\text{CHO i.e. Z should have 2Cl atoms on one C atom}\]

Thus Z should be \(\text{CH}_3\text{CHCl}_2\) (1, 1-dichloethane) and Y should \(\text{CH}_2\text{CICHCl}_2\) (1, 2-dichloroethane)

9. **S_N_2 reaction leads to inversion in configuration.**

\[\text{Br} \xrightarrow{\text{NaOH S_N_2}} \text{H} \xrightarrow{\text{OH}} \text{C}_2\text{H}_5\]

10. **Summary of the given facts**

\[\text{C}_6\text{H}_5\text{Cl} \xrightarrow{\text{(CH}_3\text{)_2CO}} \text{Two isomeric alkenes}\]

\(\text{X} \text{ and } \text{Y}\)

\[\begin{align*}
\text{CH}_3 & \text{ CH}_3 \\
\text{CH}_3 & \text{ CH}_3 \\
\text{H}_2 & \text{CH}_3 - \text{ CH} - \text{ CH} - \text{CH}_3 \\
\end{align*}\]

2,3-Dimethylbutane

The two isomeric precursors (Y and Z) of 2, 3-dimethylbutane are

\[\begin{align*}
\text{CH}_3 & \text{ CH}_3 \\
\text{CH}_3 & \text{ CH}_3 \\
\text{CH}_3 - & \text{C} = \text{CH} - \text{CH}_3 \\
\text{CH}_3 - & \text{C} = \text{C} - \text{CH} - \text{CH}_3
\end{align*}\]

Hence the precursor of Y & Z should have following structure which explains all the given facts

\[\begin{align*}
\text{CH}_3 & \text{ CH}_3 \\
\text{CH}_3 & \text{ CH}_3 \\
\text{CH}_3 - & \text{CH} - \text{CH}_3 + \text{CH}_3 - \text{C} = \text{C} - \text{CH}_3
\end{align*}\]

\[\begin{align*}
\text{CH}_3 & \text{ CH}_3 \\
\text{CH}_3 & \text{ CH}_3 \\
\text{CH}_3 - & \text{CH} - \text{CH}_3 \\
\end{align*}\]

2, 3 - Dimethylbutane

11. **Diagram**
H. Assertion & Reason Type Questions

1. (c) When halogen is present directly on the benzene nucleus it produces two opposing effects namely + M (activating effect) and −I (deactivating).

However, + M > −I hence halogens are said to be α, ω-directing (due to + M effect) but deactivating group (due to −I effect) groups giving mainly ω-substituted product.

Section-B

JEE Main/ AIEEE

1. (d) \( \text{C}_6\text{H}_5\text{I} \xrightarrow{\text{NaOH}} \text{C}_6\text{H}_5\text{ONa} \xrightarrow{\text{HNO}_3/\text{H}^+} \)

\( \text{C}_6\text{H}_5\text{OH} \xrightarrow{\text{AgNO}_3} \text{No yellow ppt.} \)

\( \text{C}_6\text{H}_5\text{CH}_2\text{I} \xrightarrow{\text{NaOH}} \text{C}_6\text{H}_5\text{CH}_2\text{ONa} \xrightarrow{\text{HNO}_3/\text{H}^+} \)

\( \text{C}_6\text{H}_5\text{CH}_2\text{OH} \xrightarrow{\text{AgNO}_3} \text{yellow ppt.} \)

Since benzyl iodide gives yellow ppt. hence this is compound B and A was phenyl iodide (\( \text{C}_6\text{H}_5\text{I} \)).

2. (b) DDT is prepared by heating chlorobenzene and chloral with concentrated sulphuric acid
Haloalkanes and Haloarenes

**NOTE:** $S_N2$ reaction is shown to maximum extent by primary halides. The only primary halides given is $\text{CH}_2\text{Cl}$ so the correct answer is (d).

12. (a) 

13. (c) 

14. (d) 

15. (d) 

16. (b) 

17. (c) 

18. (b) 

---

3. (b) Due to steric hindrance tertiary alkyl halide do not react by $S_N2$ mechanism they react by $S_N1$ mechanism. $S_N2$ mechanism is followed in case of primary and secondary alkyl halides. The order is $\text{CH}_2\text{X} < \text{CH}_3\text{CH}_2\text{X} < (\text{CH}_3)_2\text{CH}\text{X} < (\text{CH}_3)_3\text{C}\text{X}$

4. (b) In Corey-House synthesis of alkanes alkyl halide react with lithium dialkyl cuprate $\text{R}^+\text{X} + \text{LiR_2Cu} \rightarrow \text{R}^-\text{+} + \text{RCu + LiX}$

5. (c) $\text{CH}_3 - \text{CH} = \text{CH}_2 \rightarrow \text{CH}_3 + \text{HBr}$

6. (d) $\text{CH}_3\text{OH} + \text{C}_6\text{H}_5\text{MgBr} \rightarrow \text{CH}_3\text{O.MgBr} + \text{C}_6\text{H}_6$

7. (d) 

8. (a) The reaction is dehydrohalogenation

9. (b) 

10. (c) In $S_N2$ mechanism transition state is pentavalent. For bulky alkyl group it will have steric hindrance and smaller alkyl group will favour the $S_N2$ mechanism. So the decreasing order of reactivity of alkyl halides is $\text{RCH}_2\text{X} > \text{R}_2\text{CH}\text{X} > \text{R}_3\text{C}\text{X}$

11. (d) $S_N2$ reaction is favoured by small groups on the carbon atom attached to halogen. So, the order of reactivity is $\text{CH}_3\text{Cl} > (\text{CH}_3)_2\text{CHCl} > (\text{CH}_3)_2\text{CCl} > (\text{C}_2\text{H}_5)_2\text{CHCl}$

Since $S_N1$ reactions involve the formation of carbocation as intermediate in the rate determining step, more is the stability of carbocation higher will be reactivity of alkyl halides towards $S_N1$ route. Now we know that stability of carbocations follows the order : $3^\circ > 2^\circ > 1^\circ$, so $S_N1$ reactivity should also follow the same order. $3^\circ > 2^\circ > 1^\circ > \text{Methyl (}S_N1\text{ reactivity)}$

Four monochloro derivatives are chiral.

DDT is a non-biodegradable pollutant.

Steric congestion around the carbon atom undergoing the inversion process will slow down the $S_n2$ reaction, hence less congestion faster will the reaction. So, the order is $\text{CH}_3\text{Cl} > (\text{CH}_3)_2\text{CHCl} > (\text{CH}_3)_2\text{CHCl} > (\text{CH}_3)_3\text{CCl}$

Alkyl fluorides are more conveniently prepared by heating suitable chloro-base bromo-alkanes with organic fluorides such as $\text{AsF}_3$, $\text{SbF}_3$, $\text{CoF}_2$, $\text{AgF}$, $\text{Hg}_2\text{F}_2$ etc. This reaction is called Swarts reaction. $\text{CH}_3\text{Br} + \text{AgF} \rightarrow \text{CH}_3\text{F} + \text{AgBr}$ $2\text{CH}_3\text{CH}_2\text{Cl} + \text{Hg}_2\text{F}_2 \rightarrow 2\text{CH}_3\text{CH}_2\text{F} + \text{Hg}_2\text{Cl}_2$
Alcohols, Phenols and Ethers

Section-A : JEE Advanced/ IIT-JEE

A 1. aldol (β-hydroxybutanal) 2. resonance stabilization 3. nucleophilic 4. phenoxide ion
5. peroxides 6. secondary

B 1. F

C 1. (c) 2. (a) 3. (d) 4. (b) 5. (c) 6. (a) 7. (d)
8. (a) 9. (c) 10. (b) 11. (d) 12. (d) 13. (a) 14. (c)
15. (b) 16. (c) 17. (b) 18. (d) 19. (d) 20. (d) 21. (c)

D 1. (b) 2. (a, d) 3. (a, c) 4. (b) 5. (a, c, d) 6. (a, b, c) 7. (b)

E 1. A is C_2H_5OH and B is C_2H_4
2. C_2H_5OC_2H_5, C_2H_5I, C_2H_5OH
3. X Y Z A
4. m-cresol
5. HC = C.H_2.CH_2.CH_2OH
6. n-butanol, MnO_2
7. C_6H_5CH(OH)CH_3, C_6H_5COOH
8. D E
9. CH_3
10. CH=C-CH=CH-(CH_2)_8CH_2OH (Bombykol)

11. CH=C-CH=CH-(CH_2)_8CH_2OH (Bombykol)

14. C_6H_5CH(OH)CH_3, C_6H_5COOH

15. CH=C-CH=CH-(CH_2)_8CH_2OH

16. CH=C-CH=CH-(CH_2)_8CH_2OH

Section-B : JEE Main/ AIEEE

F 1. (a)

G 1. (c) 2. (c) 3. (b) 4. (b) 5. (a) 6. (d)

H 1. (c)

I 1. 9 2. 4

1. (d) 2. (a) 3. (a) 4. (c) 5. (b) 6. (b)
7. (c) 8. (d) 9. (d) 10. (b) 11. (b) 12. (b)
13. (a) 14. (d) 15. (c) 16. (b) 17. (a) 18. (a)
19. (d) 20. (a)
Section-A

A. Fill in the Blanks

1. **aldol** (β-hydroxybutanal);
   \[ \text{CH}_3\text{CH}_2\text{OH} \xrightarrow{\text{Cu, heat}} \text{CH}_3\text{CHO} \xrightarrow{\text{OH}^-} \text{CH}_3\text{CH(OH)CH}_2\text{CHO} \]

2. **resonance stabilization**

3. **nucleophilic**

4. **phenoxyion**

5. **peroxides**. On standing in contact with air, ethers are converted into unstable peroxides (R₂O → O) which are highly explosive even in low concentrations. Hence ether is always purified before distillation. Purification (removal of peroxides) can be done by washing ether with a solution of ferrous salt (which reduces peroxides to alcohols) or by distillation with conc. H₂SO₄ (which oxidises peroxides)

6. **Secondary.**

B. True / False

1. False: Ethanol is not acidic enough to react with aq. NaOH. Thus sod. ethoxide (C₂H₅ONa) is prepared by the reaction of Na metal with ethyl alcohol.
   \[ 2 \text{C}_2\text{H}_5\text{OH} + 2\text{Na} \rightarrow 2 \text{C}_2\text{H}_5\text{ONa} + \text{H}_2 \uparrow \]

C. MCQs with ONE Correct Answer

1. (c) \[ 2\text{C}_2\text{H}_5\text{OH} \xrightarrow{\Delta, \text{H}_2\text{SO}_4} \text{C}_2\text{H}_4 + \text{H}_2\text{O} \]

2. (a)

3. (d) **TIPS/Formulae**:
   The order of reactivity of alcohol with Lucas reagent is tert. > sec. > pri.
   **Lucas test** is based on the difference in the three types of alcohols (having 6 or less carbon) towards Lucas reagent (a mixture of conc. hydrochloric acid and anhydrous zinc chloride) at room temperature.
   \[ \text{ROH} + \text{HCl} \xrightarrow{\text{ZnCl}_2} \text{RCI} + \text{H}_2\text{O} \]
   The tertiary alcohols produce turbidity immediately, the secondary alcohols give turbidity within 5 – 10 minutes, and the primary alcohols do not give turbidity at all, at room temperature. Hence 2-methylpropan-2-ol (a 3° alcohol) reacts fastest.

4. (b) **TIPS/Formulae**:
   Compounds having \( -\text{C} - \text{CH}_3 \) groups show positive iodoform test.
   Hence, CH₃ – CH₂ – CH₂ – C – CH₃
   \( \text{(pentanone-2)} \) gives this test.

5. (c) \[ \text{C}_2\text{H}_5\text{OC}_2\text{H}_5 + 2\text{HI} \xrightarrow{\Delta} 2 \text{C}_2\text{H}_3\text{I} + \text{H}_2\text{O} \]

6. (a) \[ \text{CO} + \text{H}_2 + \text{H}_2 \xrightarrow{\text{Cr}_2\text{O}_3 - \text{ZnO}} \xrightarrow{300\degree\text{C}} \text{CH}_3\text{OH} \quad \text{Methanol} \]

7. (d) \[ \begin{array}{c}
\text{OH} \\
\text{Br} \\
\text{Br}
\end{array} \quad \xrightarrow{3\text{Br}_2 (\text{aq.})} \quad \begin{array}{c}
\text{OH} \\
\text{Br} \\
\text{Br}
\end{array} \\
\text{2, 4,6-Tribromophenol}
\]

NOTE:
The –OH group in phenol, being activating group, facilitates substitution in the o- and p-positions.

8. (a) Reactions involving cleavage of carbon-oxygen bond, (C – OH) follows the following order:
   Tertiary > Secondary > Primary

9. (c) **TIPS/Formulae**:
   Secondary alcohols oxidise to produce ketone.
   \[ \text{CH}_3\text{CHOHCH}_2\text{CH}_3 \xrightarrow{\text{oxid}} \text{CH}_3\text{COCH}_2\text{CH}_3 \]
   Ethyl methyl ketone

10. (b) \[ \begin{array}{c}
\text{OH} \\
\text{Br} \\
\text{Br}
\end{array} \quad \xrightarrow{\text{Br}_2, \text{in CS}_2, 0\degree\text{C}} \quad \begin{array}{c}
\text{OH} \\
\text{Br}
\end{array} \\
\text{+}
\]

NOTE: In absence of CS₂, polyhalogenation in o- and p-positions takes place.

11. (d) \[ \text{C}_6\text{H}_5\text{CH}_3 + \text{Cl}_2 (\text{exc.}) \xrightarrow{\text{light heat}} \text{C}_6\text{H}_5\text{CCl}_3 \]

12. (d) **TIPS/Formulae**:
   Riemer-Tiemann reaction involves electrophilic substitution on the highly reactive phenoxy ring.
   \[ \text{HCCl}_3 + \text{OH}^- \rightarrow \text{H}_2\text{O} + :\text{CCl}_3 \]
   \[ :\text{CCl}_3 \xrightarrow{\text{HCl}} \text{Cl}^- + :\text{CCl}_2 \]
   Note the C has only a sextet of electrons

\[ \begin{array}{c}
\text{O} \\
\text{C}\text{Cl}
\end{array} \quad \xrightarrow{\text{CCl}_2} \quad \begin{array}{c}
\text{O} \\
\text{C}\text{Cl}
\end{array} \\
\text{A benzal chloride}
\]

\[ \begin{array}{c}
\text{O} \\
\text{C}\text{Cl}
\end{array} \quad \xrightarrow{\text{OH}^-} \quad \begin{array}{c}
\text{O} \\
\text{C}\text{Cl}
\end{array} \\
\text{A benzal chloride}
\]
13. (a) TIPS/Formulae:
Compound \((\text{CH}_3)_2\text{N}^+\text{I}^-\) is most reactive due to (i) better leaving group, I\(^{-}\) and (ii) due to the fact that the methyl group, with positive N, is more electron deficient. Hence this group is more reactive towards nucleophile, \(\text{OH}^-\).

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_3 & \quad \text{N}^+\text{I}^- \\
\text{CH}_3 & \quad \text{OH} \\
\end{align*}
\]

\(\rightarrow\) \(\text{CH}_3\text{OH} + (\text{CH}_3)_2\text{N}^+\text{I}^-\)

14. (c) NOTE:
Fehling solution is a weak oxidising agent which can oxidise aldehyde but not ketone. Primary alcohols undergoes oxidation with alkaline KMnO\(_4\), acidic dichromate and conc. H\(_2\)SO\(_4\) to give acids, whereas with Cu they give aldehydes.

\[
\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \xrightarrow{\text{Cu, heat}} \text{CH}_3\text{CH}_2\text{CHO}
\]
Propenal-1 (responds Fehling solution)

\[
\text{CH}_3\text{CHOHCH}_3 \rightarrow \text{CH}_3\text{COCH}_3
\]
Propenal-2 (negative to Fehling solution)

15. (b) NOTE: This reaction is an example of Williamson's synthesis.
C\(_2\)H\(_4\)O\(^-\) will abstract proton from phenol converting the latter into phenoxide ion. This would then make nucleophilic attack on the methylene carbon of alkyl iodide forming C\(_2\)H\(_5\)OC\(_2\)H\(_5\). But if C\(_2\)H\(_4\)O\(^-\) is in excess, C\(_2\)H\(_5\)OC\(_2\)H\(_5\) will be formed C\(_2\)H\(_3\)I\(^-\) is a better nucleophile than C\(_2\)H\(_4\)O\(^-\) (phenoxide) ion because in the former the negative charge is localised over oxygen, while in the latter it is delocalised over the whole molecular framework. So, it is C\(_2\)H\(_3\)I\(^-\) that would make nucleophilic attack at ethyl iodide to give diethyl ether (Williamson's synthesis).

16. (c) NOTE: Addition of water to 2-phenylpropene follows Markownikov's rule.

\[
\begin{align*}
\text{Ph} & \quad \text{CH} = \text{CH}_2 \\
\text{H}_2\text{O}^+ & \rightarrow \text{CH}_3 - \text{CH} \\
\text{OH} & \quad \text{Ph}
\end{align*}
\]

17. (b) TIPS/Formulae:
Conc. HCl, HBr and conc. HCl + ZnCl\(_2\) all are nucleophiles, thus convert alcohols to alkyl halides. However, conc. H\(_3\)PO\(_4\) is a good dehydrating agent which converts an alcohol to an alkene.

18. (d) Among the given compounds, hydroxybenzene (IV) has least molar mass and therefore possess least boiling point. Among the three isomeric dihydroxybenzenes, 1,2-dihydroxybenzene (I) forms intramolecular H-bonding with the result it will not form intermolecular H-bonding leading to lowest boiling point. On the other hand 1,3-dihydroxybenzene (II) and 1,4-dihydroxybenzene (III) do not undergo chelation, hence they will involve extensive intermolecular H-bonding leading to higher boiling point. Further intermolecular hydrogen bonding is stronger in the \(p\)-isomer than the m-isomer hence former has highest b.p. Thus the decreasing order of boiling points is III > II > I > IV.

19. (d) In dye test, phenolic — OH group is converted to \(—\text{O}^-\) which activates the ring towards electrophilic aromatic substitution.

20. (d) Ph\(_3\)C\(^-\)O — R \xrightarrow{\text{H}^+} \text{Ph}_3\text{C}^+ \xrightarrow{\text{H}^-} \text{Ph}_3\text{C}^- + \text{ROH}

Thus, higher the stability of the carbocation, greater will be reactivity. Presence of electron releasing group (e.g., \(-\text{OCH}_3\)) in \(p\)-position of the phenyl group will disperse the positive charge of the carbocation by +M effect, hence stabilizes the carbocation.

D. MCQs with ONE or More Than One Correct

1. (b) The mechanism of this reaction is represented as follows.

\[
\begin{align*}
\text{CH}_3 - \text{C} = \text{CH}_2 & \xrightarrow{\text{H}^+} \text{Ph} \quad \text{CH}_3 - \text{CH}_2 + \text{H}^+ \\
\text{CH}_3 - \text{CH}_2 & \xrightarrow{\text{H}^+} \text{Ph}_3\text{C}^+ \quad \text{Ph}_3\text{C}^- + \text{ROH}
\end{align*}
\]

Benzyl carbonium ion (stable)

2. (a,d) TIPS/Formulae:
The aromatic ethers are cleaved to give phenol as one of the products.
3. (a, c)  
   \[ \text{OH} \quad \xrightarrow{\text{NaOH, } -\text{H}_2\text{O}} \quad \text{O}^\ominus \quad \xrightarrow{\text{Br}_2} \quad \text{Br}^\ominus \quad \xrightarrow{\text{Br}_2} \quad \text{Br}^\ominus \]
   (I)  
   (II)  
   (III)  
   (IV)  

Product of reaction of phenol with NaOH/Br2 is sodium salt of 2,4,6-tribromophenol. Hence, species (I), (II), (III) are formed as intermediate.

4. (b)  
   \[ \text{OH} \quad \xrightarrow{\text{Br}_2\text{(3.0 equivalents)}} \quad \text{Br}\text{SO}_3\text{H} \]

5. (a, c, d) Isomeric alcohols with molecular formula C4H10O are
   - n-Butanol (Butan-1-ol)
   - Butan-2-ol
   - Isobutyl alcohol (2-methylpropan-1-ol)
   - tert-Butanol (2-methylpropan-2-ol)

6. (a, b, c) —OH group is strongly activating and α, p-directing due to +M effect. Thus positions a, b and c are the sites for attack by an electrophile. However, sites b and c are not preferred by bulky electrophile due to steric crowding. Thus more bulky electrophile (like I2) can attack only site a, which is least sterically hindered, a bit smaller electrophile (Br2) can attack at sites a and also b (relatively less sterically hindered site) and the smallest electrophile (Cl2) can attack all the three sites.

7. (b)  
   High Pressure, heat
   Radial, initiator, O2
   Cumene hydroperoxide, U

E. Subjective Problems

1. ‘A’ is C2H5OH and ‘B’ is C2H4
   \[ \text{C}_2\text{H}_5\text{OH} \xrightarrow{\text{Conc. H}_2\text{SO}_4 - \text{H}_2\text{O}} \text{C}_2\text{H}_4 \]  
   (A) (ethyl alcohol)  
   (B) (ethene)

2. TIPS/Formulae:
   The unreactivity of the compound (X) towards sodium indicates that it is neither an acid nor an alcohol, further its unreactivity towards Schiff’s base indicates that it is not an aldehyde. The reaction of compound (X) with excess of HI to form only one product indicates that it should be an ether.
   Hence its other reactions are sketched as below:
   \[ \text{R} - \text{O} - \text{R} \xrightarrow{\text{Reflux with excess of HI}} 2\text{RI} \xrightarrow{\text{hydrolysis}} 2\text{ROH} \]
   
   Since the carboxylic acid has equivalent weight of 60, it must be acetic acid (CH3COOH), hence Z must be ethyl alcohol, (Y) ethyl iodide and (X) diethyl ether.

3. (i) \[ \text{CH}_3\text{CH(OH)CH}_3 \xrightarrow{\text{Conc. } \text{H}_2\text{SO}_4 - \text{H}_2\text{O}} \text{CH}_3\text{CH} = \text{CH}_2 \]  
   2-propanol
6. The given problem can be sketched as below:

Alcohol $\xrightarrow{(A)}$ Alkene $\rightarrow$ (i) $\text{Br}_2$ (ii) excess of $\text{NaH}_2\text{SO}_4$ (−$\text{HBr}$) $\rightarrow$ New compound $\rightarrow$ Oxidation $\rightarrow$ D $\rightarrow$ Acetic acid

\[
\text{CH}_3\text{CH}_2\text{OH} \xrightarrow{(A)} \text{CH}_2=\text{CH}_2 \xrightarrow{(B)} \text{CH}_3\text{CHO} \xrightarrow{(C)} \text{CH}_3\text{COOH} \xrightarrow{(D)} \text{CH}_2=\text{CH}_2 \xrightarrow{(E)} \text{CH}_3\text{OH} \xrightarrow{(F)} \text{CH}_3\text{COOH}
\]

**NOTE THIS STEP:** From the problem it appears that the compound C is an alkyne, hence D must be an aldehyde or ketone. Further since D can be obtained from acetic acid through its calcium salt it may be either acetaldehyde or acetone. Hence going back, A may be either ethyl alcohol or $\text{t}-\text{propanol}$ both of which explains the given set of reactions.

\[
\text{CH}_3\text{CHOHCH}_2\overset{\text{conc. H}_2\text{SO}_4}{\rightarrow} \text{CH}_2=\text{CH}_2 \overset{\text{Br}_2}{\rightarrow} \text{CH}_3\text{Br} \rightarrow \text{CH}_3\text{Br}
\]

\[
\begin{align*}
\text{CH}_3\text{CHO} + \text{H}_2\text{SO}_4 & \rightarrow \text{CH}_2=\text{CH}_2 + \text{H}_2\text{SO}_4 \\
\text{CH}_3\text{CHO} + \text{H}_2\text{SO}_4 & \rightarrow \text{CH}_2=\text{CH}_2 + \text{H}_2\text{SO}_4 \\
\text{CH}_3\text{CHO} + \text{H}_2\text{SO}_4 & \rightarrow \text{CH}_2=\text{CH}_2 + \text{H}_2\text{SO}_4
\end{align*}
\]

Hence

A is ethyl alcohol, $\text{CH}_3\text{CH}_2\text{OH}$
B is ethylene, $\text{CH}_2=\text{CH}_2$
C is acetylene, $\text{CH}_2=\text{CH}_2$
D is acetaldehyde, $\text{CH}_3\text{CHO}$

7. (i) The compound ($C_7H_8O$) is soluble in aq. NaOH but insoluble in NaHCO₃, indicating it to have a phenolic group.
(ii) The compound, on treatment with $\text{Br}_2$, water, gives $C_6H_5\text{OBr}_3$. Taking into account of molecular formulae of the two compounds, the parent compound seems to be cresol.

\[
\text{C}_6\text{H}_4\overset{\text{CH}_3}{\longrightarrow} \text{OH} \overset{\text{OH}}{\longrightarrow} \text{C}_6\text{H}_4\text{OH}
\]

(iii) Bromination of the compound reveals that it is $m$-cresol as it forms tribromo derivative.
(iv) The reactions are

\[
\begin{align*}
\text{NaHCO}_3 & \rightarrow \text{CH}_3\text{OH} \rightarrow \text{NaOH (aq)} \\
\text{m-Cresol} & \rightarrow \text{CH}_3\text{OH} \rightarrow \text{NaOH (aq)}
\end{align*}
\]

5. (i) Ethanol (due to the presence of active hydrogen atom, $C_2H_5 - O - H$) reacts with sodium metal, while ether and benzene have no such hydrogen atom and hence do not react with sodium and thus can be dried by metallic sodium.

(ii) Phenol (a weaker acid) reacts with $\text{NaHCO}_3$ (a weaker base) to form phenoxyde ion (a stronger base) and carbonic acid (a stronger acid).

\[
\begin{align*}
\text{C}_6\text{H}_5\text{OH} + \text{NaHCO}_3 & \rightarrow \text{C}_6\text{H}_5\text{ONa} + \text{H}_2\text{CO}_3 \\
\text{Weaker acid} & \text{Weaker base} & \text{Stronger base} & \text{Stronger acid}
\end{align*}
\]

Since acid-base equilibria lie towards the weaker acid and weaker base, phenol does not decompose $\text{NaHCO}_3$ (difference from carboxylic acids).

\[
\begin{align*}
\text{RCOOH} + \text{NaHCO}_3 & \rightarrow \text{RCOONa} + \text{H}_2\text{CO}_3 \\
\text{Stronger acid} & \text{Stronger base} & \text{Weaker base} & \text{Weaker acid}
\end{align*}
\]

(iii) Since $3^\circ$ carbocation (formed in case of $t$-butanol) is more stable than $1^\circ$ (formed in $n$-butanol), the dehydration in the former proceeds faster than in the latter.
8. **TIPS/Formulae:**
Iodoform test is used to distinguish methanol and ethanol. Ethanol gives iodoform test while methanol does not respond.

\[
C_2H_5OH + 4I_2 + 6NaOH \rightarrow CH_3 \downarrow + 5NaI + HCOONa + 5H_2O
\]

9. (i) 
\[
\text{SO}_3^+ \quad \text{SO}_3^+ 
\]

(ii) 
\[
\text{SO}_3^+ \quad \text{SO}_3^+ 
\]

(iii) 
\[
\text{SO}_3^+ \quad \text{SO}_3^+ 
\]

10. (i) Since the compound X (C₂H₄O) does not react appreciably with Lucas reagent, it indicates that the compound has a primary alcoholic group (–CH₂OH).

(ii) Reaction of the compound X with ammonical silver nitrate to give a precipitate indicates that it has an acetylenic hydrogen atom, i.e., \(=C - H\) grouping is present.

(iii) Treatment of X with H₂/Pt followed by boiling with excess of HI gives \(n\)-pentane. It indicates that the compound does not have any branch.

On the basis of the above points, compound X (C₂H₄O) may be assigned following structure.

\(HC = C - CH_2 - CH_2 - CH_2OH\)

(X) 4-Pentyn-1-ol (Mol. wt. 84, Eq. wt. = 42)

The above structure for the compound X is in accordance with its equivalent weight obtained from the given data.

224 ml. of CH₄ at STP is obtained from 0.42 g

\[
22400 \text{ ml. of CH}_4 \text{ at STP} = \frac{0.42}{224} \times 22400 = 42 \text{ g}
\]

\(\therefore\) Eq. wt. of the compound X = 42

11. \(n\)-Butanol gives the following reaction in which the purple colour of KMnO₄ changes to brown. *tert*-Alcohols are not oxidisable easily, hence purple colour of KMnO₄ remains same.

\[
\begin{align*}
CH_3CH_2CH_2CH_2OH + KMnO_4 & \rightarrow CH_3CH_2CH_2COOK + MnO_2 \downarrow + KOH \\
& \text{soluble in H}_2O \\
& \text{Brown}
\end{align*}
\]

The brown precipitate is of MnO₂.

12. (i, iv) **TIPS/Formulae:**
The reaction involves electrophilic substitution on the highly reactive phenoxide ion.

Here the electrophile is dichlorocarbene formed by the action of strong alkali on chloroform.

\[
\begin{align*}
\text{CHCl}_3 + \text{OH}^- & \rightleftharpoons \text{CCl}_4^- + \text{H}_2\text{O} \\
: \text{CCl}_3^- & \rightleftharpoons : \text{CCl}_2^- + \text{Cl}^- \\
\quad \text{Dichlorocarbene}
\end{align*}
\]

13. The steps involved in the suggested mechanism are as follows.

(a) The protonation of hydroxyl group.

\[
\begin{align*}
\text{H}_3\text{C} - \text{C} - \text{CH}_3 + \text{OH}^- & \rightarrow \text{H}_3\text{C} - \text{C} - \text{CH}_3 + \text{H}_3\text{O}^+ \\
\text{3,3-Dimethylbutan-2-ol}
\end{align*}
\]

(b) The removal of H₂O to form a secondary (2°) carbonion ion

\[
\begin{align*}
\text{CH}_3 & \rightarrow \text{CH}_3^- \\
\text{H}_3\text{C} - \text{C} - \text{CH}_3 + \text{H}_2\text{O} & \rightarrow \text{H}_3\text{C} - \text{C} - \text{CH}_3^- + \text{H}_3\text{O}^+ \\
\text{3,3-Dimethylbutan-2-ol}
\end{align*}
\]

(c) The conversion of 2° carbonion to the more stable 3° carbonion ion by the shift of CH₃ group

\[
\begin{align*}
\text{CH}_3 & \rightarrow \text{CH}_3^- \\
\text{H}_3\text{C} - \text{C} - \text{CH}_3 + \text{H}_2\text{O} & \rightarrow \text{H}_3\text{C} - \text{C} - \text{CH}_3^- + \text{H}_3\text{O}^+ \\
\text{3,3-Dimethylbutan-2-ol}
\end{align*}
\]
14. **NOTE:**

The reaction of D (C₆H₆O) with alkaline solution of iodine is an iodoform reaction. This reaction is possible if the compound D has –C=–CH₃ or –CH=–CH₃ group.

The high carbon content in D indicates that D is an aromatic compound containing a benzene ring. To account for the given formula, the compound D may be C₆H₆CH(OH)CH₃.

15. **TIPS/Formulæ:**

(a) Since (B) is resistant to oxidation, it must be tert-alcohol.

(b) Since (B) is optically inactive, it must have at least two alkyl groups similar.

C₆H₁₀O → 2H₂ → C₆H₁₄O

Thus the five carbon atoms can be adjusted into three alkyl groups (of which two are similar) either as –CH₃, –CH₂, and –C≡H, or as –C₃H₇, –C₂H₅, and –CH₃.

Thus the possible structure of alcohol (B) is either

CH₃CH₂CH₂CH₂ or CH₃CH₂CH₃

Hence the corresponding compound (A) is either

CH₂CH₃CH₂CH₂ or CH₃CH₂CH₂CH₂

16. **TIPS/Formulæ:**

\[
\text{CH₃CH₂O} \xrightarrow{\text{(1) AlCl₃}} \xrightarrow{\text{(2) H₂O}} \text{COOH}
\]

\[
\text{CH₃CH₂O} \xrightarrow{\text{(1) AlCl₃}} \xrightarrow{\text{(2) H₂O}} \text{COOH}
\]

17. **TIPS/Formulæ:**

The oxirane ring is cleaved via Sₘ₂ mechanism.

H₃C \xrightarrow{\text{H₂O}} \xrightarrow{\text{H₂O}} H₃C

Thus the five carbon atoms can be adjusted into three alkyl groups (of which two are similar) either as –CH₃, –CH₂, and –C≡H, or as –C₃H₇, –C₂H₅, and –CH₃.

Thus the possible structure of alcohol (B) is either

CH₃CH₂CH₂ or CH₃CH₂CH₃

Hence the corresponding compound (A) is either

CH₂CH₃CH₂ or CH₃CH₂CH₂CH₂

18. The method given in (ii) is the correct method for the formation of ether because method (i) leads alkene as the main product.

**NOTE:**

3° alkyl halides are easily dehydrohalogenated by base.

(i) (CH₃)₃CBr \xrightarrow{\text{CH₃ONa}} (CH₃)₂C = CH₂

alkene

(ii) CH₂Br + NaOC(CH₃)₃ \xrightarrow{\text{CH₃-O-C(CH₃)₃}} CH₃OH
21. **TIPS/Formulae**:

Let us summarise the given facts.

- **C₁₀H₁₆O** → **C₁₆H₃₄O** (A) → **(CH₃CO₂)₂O** → Ester
  - **Hydrogenation**
  - **Oxidative ozonolysis**

**CH₃CH₂CH₂COOH + COOH**

- Butanoic acid
- Oxalic acid
- 10 - Acetoxydecanoic acid

(i) Hydrogenation of bombykol (**C₁₆H₃₄O**) to **C₁₀H₁₆O** (A) indicates the presence of two double bonds in bombykol.

(ii) Reaction of A with acetic anhydride to form ester indicates the presence of an alcoholic group in A and hence also in bombykol.

(iii) Products of oxidative ozonolysis of bombykol ester suggests the structure of bombykol.

**CH₃CH₂CH₂COOH + HOOC. COOH + HOOC.(CH₃)₉. CH₂OAc**

- Butanoic acid
- Oxalic acid
- 10 - Acetoxydecanoic acid

The structure of the bombykol ester suggests that bombykol has the following structure:

\[ CH₃CH₂CH = CH - CH = CH(CH₃)₉CH₂OH \] (Bombykol)

and the structure of A is

\[ CH₃CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₂OH \] or \[ C₁₆H₃₄O \].

Four geometrical isomers are possible for the above bombykol structure (as it has two double bonds).

**NOTE:**

In the intermediate carbocation, a carbon bearing positive charge has CH₃ group which decreases the positive charge and hence prevents cyclisation of the compound.
22. (i) Molecular formula of P, C₅H₁₀O indicates 1° of unsaturation. So it should have double bond.

(ii) Acidic hydrolysis of P to Q and R, both of which responds iodoform test, indicates that Q and R should have following structure.

CH₃CH₂OH, (CH₃)₂CHOH, CH₃CHO or CH₃COR

The only possible linkage that can explain such hydrolysis is ether. Hence P should have following type of structure.
C₂ – Component – O – C₃ – Component

Further either the C₂ – or the C₃ – component should have double bond, thus the possible structure for P should be either of the following two structures which explains all the given reactions.

\[ CH₂ = CH - O - CH(CH₃)₂ \]  

\[ CH₃CHO \leftrightarrow CH₂ = CHOHI + HOCH(CH₃)₂ \]

(Q and R), Both responds iodoform test

or

\[ CH₃CH₂ - O - C - CH₂ \]

\[ CH₃CH₂OH + HO - C = CH₂ \rightarrow O = C - CH₃ \]

(Q and R), Both responds iodoform test

Extra reactivity of P toward dil. H₂SO₄ than ethylene is due to formation of highly stable carbocation.

\[ H_3C \xrightarrow{\text{CH}-O-CH(CH₃)₂ \text{ or } CH₃CH₂-O-C-CH₃} \]

\[ \text{2° carbocation} \]

\[ \text{3° carbocation} \]

CH₂ = CH₂ \rightarrow CH₃CH₂⁺ \[ \text{1° carbocation} \]

Extra reactivity of P toward dil. H₂SO₄ than ethylene is due to formation of highly stable carbocation.

H₃C – CH – O – CH(CH₃)₂ or CH₃CH₂ – O – C – CH₃

2° carbocation

3° carbocation

23. OH

\[ \text{H}^+ \text{, heat} \rightarrow \text{H₂O} \]

\[ \text{1° carbocation (5 membered ring)} \]

\[ \text{CH}_3 \]

\[ \text{CH}_3 \]

\[ \text{3° carbocation (6 membered ring)} \]

\[ \text{CH}_3 \]

\[ \text{NaOH intramolecular aldol condensation} \]

\[ \text{O} \]

\[ \text{H}^+ \text{, heat} \rightarrow \text{H₂O} \]

\[ \text{CH}_3 \]

\[ \text{O} \]

\[ \text{Zn, CH₃COOH} \]

\[ \text{[Y]} \]

\[ \text{O} \]

\[ \text{NaOH intramolecular aldol condensation} \]

\[ \text{O} \]

\[ \text{H}^+ \text{, heat} \rightarrow \text{H₂O} \]

\[ \text{OH} \]

G. Comprehension Based Questions

1. (c) Reagents for Reimer – Tiemann reaction are aq. NaOH + CHCl₃.

2. (c) OH⁻ + CHCl₃ \[ \text{\rightleftharpoons} \text{Cl⁻} + \text{CHCl₂ (Dichlorocarbene)} \]

3. (b) \[ \text{Cl⁻} \]

For 4-6. Before answering these question let us complete the sequence of reactions given in data.

The given compound (M) i.e.

\[ \text{H₃C} \xrightarrow{\text{H₃C}} \text{O} \xrightarrow{\text{Ph}} \text{H} \]

is the only product formed by the action of KOH on compound K.

The compound K is \[ \text{Ph} - \text{C} = \text{O} \]

\[ \text{CH₃} \]

2Ph – C = O \[ \text{KOH (Aldol condem.)} \rightarrow \text{Ph} - \text{C} = \text{CH} - \text{C} - \text{Ph} \]

\[ \text{CH₃} \]

\[ \text{CH₃} \]

Compound K (i.e. Ph – C = O) is one of the products

\[ \text{CH₃} \]
of ozonolysis of compound I. Therefore the compound I may be

\[
\begin{align*}
\text{Ph} & \quad \text{Ph} \\
\text{CH}_3 & \quad \text{CH}_3 \\
\text{C} = \text{C} & \xrightarrow{\text{Ozonolysis}} \text{C} = \text{O} \\
& \quad (\text{I}) \quad (\text{J}) \quad (\text{K}) \\
\end{align*}
\]

\[
\begin{align*}
\text{C} = \text{O} & \xrightarrow{\text{KOH}} \text{Ph} - \text{CH}_2 - \text{OH} \\
& \quad (\text{J}) \\
\end{align*}
\]

Thus J seems to be C₆H₅CHO and hence I is

\[
\begin{align*}
\text{PhCH} & \equiv \text{C} - \text{Ph} \\
& \quad \text{CH}_3 \\
\text{CH}_3 & \quad (\text{I}) \\
\end{align*}
\]

Now we will try to answer the questions.

4. (b) As can be seen from above reaction sequence compound (I) is Ph - CH = C - Ph and it is formed by catalytic dehydration (acid catalysed) of a tertiary alcohol (compound H). Therefore compound H is

\[
\begin{align*}
\text{Ph} - \text{CH}_2 & \equiv \text{C} - \text{Ph} \\
& \quad \text{CH}_3 \\
\text{OH} & \quad (\text{H}) \\
\end{align*}
\]

\[
\begin{align*}
\text{Ph} - \text{CH}_2 & \equiv \text{C} - \text{Ph} \\
& \quad \text{CH}_3 \\
\text{OH} & \quad (\text{I}) \\
\end{align*}
\]

(H) can be formed by the action of with PhCH₂MgBr as follows

\[
\begin{align*}
\text{PhCH}_2 & \equiv \text{MgBr} + \text{PhCH}_2 & \equiv \text{C} - \text{Ph} \\
& \quad \text{CH}_3 & \quad \text{CH}_3 \\
\text{H} & \equiv \text{H}_2\text{O} & \text{OH} \\
\text{PhCH} & \equiv \text{C} - \text{Ph} + \text{MgBr} & \text{OH} \\
& \quad \text{CH}_3 & \quad \text{CH}_3 \\
\end{align*}
\]

Therefore the correct answer is option (b).

5. (a) As can be seen from the above sequence of reactions the structure of compound (I) is

\[
\begin{align*}
\text{Ph} & \quad \text{CH}_3 \\
& \quad (\text{I}) \\
\end{align*}
\]

Therefore the correct answer is option (a).

6. (d) As can be seen from the above sequence of reactions the structures of compounds J, K and L respectively are

\[
\begin{align*}
\text{Ph} & \equiv \text{CHO}, \text{Ph} - \text{C} = \text{O} \text{and PhCOO}^+ \text{K}^+ \\
& \quad (\text{J}) \quad (\text{L}) \quad (\text{K}) \\
\end{align*}
\]

Thus the correct answer is option (d).

H. Assertion & Reason Type Questions

1. (c) The solubility of alcohols in water can be explained due to the formation of hydrogen bond between the highly polarised –OH groups present both in alcohol and water. However, in higher alcohols the hydrocarbon character (alkyl chain) of the molecule increases and thus alcohols tend to resemble hydrocarbon (which are insoluble in water) and hence the solubility in water decreases. When the ratio of C to OH is more than 4, alcohols have little solubility in water. So statement is correct but explanation is not.

I. Integer Value Correct Type

1. (9)

2. (4)

2. (4)

aq dilute KMnO₄ excess
1. (d) The dehydration of alcohol to form alkene occurs in following three step. Step (1) is initiation step.

**Step (1)** Formation of protonated alcohol.

\[ \text{CH}_3\text{CH}_2\text{O}^- + \text{H}^+ \rightarrow \text{CH}_3\text{CH}_2\text{H}^+ \]

(protonated ethanol)

**Step (2)** Formation of carboxylation

\[ \text{CH}_3\text{CH}_2\text{H}^+ \rightarrow \text{CH}_3\text{CH}_2\text{H}_2 \]

(Ethyl carboxylation)

**Step (3)** Elimination of a proton to form ethene

\[ \text{H}^- + \text{CH}_3\text{CH}_2\text{H}^+ \rightarrow \text{CH}_3\text{CH}_2\text{H}_2 \]

2. (a) 3-methyl pentanol-3 will be dehydrated most readily since it produces tertiary carbonium ion as intermediate.

\[ \text{CH}_3\text{CH}_2\text{C}^- \text{CH}_2\text{-CH}_2\text{-CH}_3 \]

3. (a) \( \text{CH}_3\text{CH}^-\text{CH} = \text{CH}^-\text{CH}_3 \rightarrow \text{CH}_3\text{CH}^-\text{CH}^-\text{CH}\text{CH}_3 \)

Pyridinium chloro-chromate (PCC) is specific for the conversion.

4. (c) Methyl vinyl ether under anhydrous condition at room temperature undergoes addition reaction.

\[ \text{CH}_2\text{CH} = \text{CH}_2 + \text{HBr} \rightarrow \text{CH}_3\text{CH} = \text{CH}_2 \]

5. (b) Methyl vinyl ether under anhydrous condition at room temperature undergoes addition reaction.

\[ \text{CH}_2\text{CH} = \text{CH}_2 + \text{HBr} \rightarrow \text{CH}_3\text{CH} = \text{CH}_2 \]

6. (b) Only those alcohols which contain \(-\text{CHOHCH}_3\) group undergo haloform reaction. Among the given options only (b) contain this group, hence undergo haloform reaction.

7. (c) **NOTE**: OH group activates the benzene nucleus and

\[ \text{Bz} + \text{Br}_2\text{H}_2\text{O} \rightarrow \text{Bz} \text{Br}_2 \]

8. (d) **NOTE**: This is Riemer-Tiemann reaction and the electrophile is dichlorocarbene.

\[ \text{H}^- \rightarrow \text{Cl} \text{CH} \text{NaOH} \rightarrow \text{Cl}^- \text{C}^- \text{Cl} + \text{NaCl} + \text{H}_2\text{O} \]

\text{dichlorocarbene}

\[ \rightarrow \text{Cl}^- \text{C}^- \text{Cl} + \text{NaCl} + \text{H}_2\text{O} \]

\[ \text{α-elimination} \]

9. (d) \( \text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{CH}_2\text{I} \)

\[ \text{Mg} \rightarrow \text{CH}_3\text{CH}_2\text{MgI} \]

\[ \text{HCHO} \rightarrow \text{H-C-O-MgI} \]

\[ \text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{H}^- \text{C-OH} \]

\[ \text{H} \text{H} \text{D} \]

\[ \text{n-propyl alcohol} \]

10. (b) Phenol on reaction with conc. \( \text{H}_2\text{SO}_4 \) gives a mixture of \text{o-} and \text{p-} products (i.e., \(-\text{SO}_3\text{H}\) group, occupies \text{o-}, \text{p-} position). At room temperature \text{o-} product is more stable, which on treatment with conc. \( \text{HNO}_3 \) will yield \text{o-nitrophenol}.

\[ \text{OH} \rightarrow \text{OH} \rightarrow \text{OH} \]

\[ \rightarrow \text{OH} \rightarrow \text{OH} \]

\[ \text{C} \rightarrow \text{C} \rightarrow \text{C} \]

\[ \text{H} \rightarrow \text{H} \rightarrow \text{H} \]

\[ \text{D} \rightarrow \text{D} \rightarrow \text{D} \]

\[ \text{n-propyl alcohol} \]

11. (b)

12. (b) Tertiary alcohols react fastest with conc. \( \text{HCl} \) and anhydrous \( \text{ZnCl}_2 \) (lucas reagent) as its mechanism proceeds through the formation of stable tertiary carbocation.

**Mechanism**

\[ \text{CH}_3 \]

Step 1: \( \text{CH}_3 \rightarrow \text{C} \rightarrow \text{OH} + \text{H}^- + \text{Cl} \)

\[ \text{CH}_3 \quad \text{2 Methyl Propan-2-ol} \]
Alcohols, Phenols and Ethers

Step 2: \((\text{CH}_3)_3\text{C}^+ + \text{OH}_2 \rightarrow (\text{CH}_3)_3\text{C}^- + \text{H}_2\text{O}\)

Step 3: \((\text{CH}_3)_3\text{C}^+ + \text{Cl}^- \rightarrow (\text{CH}_3)_3\text{C}^- + \text{Cl}\)

13. (a) Whenever dehydration can produce two different alkenes, major product is formed according to Saytzeff rule i.e., more substituted alkene (alkene having lesser number of hydrogen atoms on the two doubly bonded carbon atoms) is the major product. Such reactions which can produce two or more structural isomers but one of them in greater amounts than the other are called regioselective; in case a reaction is 100% regioselective, it is termed as regiospecific.

In addition to being regioselective, alcohol dehydrations are stereoselective (a reaction in which a single starting material can yield two or more stereoisomeric products, but gives one of them in greater amount than any other).

\[\text{C}_6\text{H}_5 - \text{CH}_2 - \text{CH} - \text{CH}_3 \rightarrow \text{Conc. H}_2\text{SO}_4 \rightarrow\]

\[\text{H} \quad \text{OH} \quad \text{CH}_3\]

\[\text{C}_6\text{H}_5 \quad \text{cis} \quad \text{trans}\]

(minor) (major)

14. (d) \(5\text{KBr} + \text{KBrO}_3 + 3\text{H}_2\text{O} \rightarrow 3\text{Br}_2 + 6\text{KOH}\)

15. (e) Electron withdrawing substituents like \(-\text{NO}_2\), \(-\text{Cl}\) increase the acidity of phenol while electron releasing substituents like \(-\text{CH}_3\), \(-\text{OCH}_3\) decreases acidity. Hence the correct order of acidity will be

\[\text{OH} > \text{NO}_2 > \text{Cl} > \text{CH}_3 > \text{OCH}_3\]

16. (b) Tertiary alcohols react fastest with Lucas reagent as the rate of reaction is directly proportional to the stability of carboxylation formed in the reaction. Since most stable \(3^\circ\) carboxylation is formed in the reaction hence it will react fastest further tertiary alcohols appears to react by S_N1 mechanism.

Step 1. \((\text{CH}_3)_3\text{C} \rightarrow \text{OH}_2 \rightarrow (\text{CH}_3)_3\text{C}^+ + \text{H}_2\text{O}\)

Step 2. \((\text{CH}_3)_3\text{C}^+ + \text{OH}_2 \rightarrow (\text{CH}_3)_3\text{C}^- + \text{Cl}\)

17. (a) Sodium Phenoxide

\[\text{OH} \quad \text{COONa}\]

\[\text{H}_2\text{SO}_4 \rightarrow \text{COOH}\]

\[\text{O} \quad \text{CH}_3\]

\[\text{COOH} + \text{CH}_3\text{COOH}\]

Aspirin (Acetyl Salicylate)

18. (a) Among 20 naturally occurring amino acids "Cysteine" has \(-\text{SH}\) or thiol functional group.

\[\text{R} - \text{CH} - \text{COOH}\]

\[\text{NH}_2\]

\[\Rightarrow \text{Value of } R = -\text{CH}_2\text{SH} \text{ in Cysteine.}\]

19. (d) \(N\)-bromosuccinimide results into bromination at allylic and benzylic positions

20. (a) When tert alkyl halides are used in Williamson synthesis elimination occurs rather than substitution resulting into formation of alkene. Here alkoxide ion abstract one of the \(\beta\)-hydrogen atom along with acting as a nucleophile.

\[\text{CH}_3 \rightarrow \text{CH}_2 \rightarrow \text{CH} \rightarrow \text{CH}_3 + \text{Na}^+\text{OCH}_3 \rightarrow \text{CH}_3\text{OH}\]

2-Chloro-2-methylpentane

\[\text{H} \quad \text{CH}_3\]

\[\text{CH}_3\text{CH}_2 \rightarrow \text{C} \rightarrow \text{CH}_3 + \text{CH}_3\text{OH} + \text{NaBr}\]

2-Methyl-pent-2-ene
Aldehydes, Ketones and Carboxylic Acids

Section-A : JEE Advanced/ IIT-JEE

A  1. CO  2. sodium potassium tartrate  3. C₆H₅CH(OCOCH₃)₂  4. \( \text{CH}_3 - \text{C} = \text{CH} - \text{C} - \text{CH}_3 \)


C  1. (b)  2. (c)  3. (a, d)  4. (c)  5. (d)  6. (a)  7. (d)
   8. (b)  9. (a)  10. (a)  11. (b)  12. (d)  13. (b)  14. (a)
   15. (c)  16. (b)  17. (a)  18. (c)  19. (b)  20. (a)  21. (a)
   22. (c)  23. (c)  24. (c)  25. (a)  26. (c)  27. (a)  28. (c)
   29. (c)  30. (b)  31. (d)  32. (a)  33. (b)  34. (d)  35. (d)
   36. (a)  37. (a)

D  1. (a, c)  2. (a, b)  3. (a, b, d)  4. (b, d)  5. (a, b)  6. (b, d)  7. (b)
   8. (a, b, d)  9. (d)  10. (c)  11. (b)  12. (b, d)  13. (a, c, d)
   14. (b, d)  15. (c)  16. (a)  17. (a, b, c)  18. (b, c)  19. (c, d)

E  5. \((\text{CH}_3)_2\text{CHCH} = \text{C}(\text{CH}_3)_2\) \(\cdot\) \((\text{CH}_3)_2\text{CHCOOH} \cdot\) \((\text{CH}_3)_2\text{C(Br)COOH} \cdot\) \((\text{CH}_3)_2\text{C(OH)COOH}

A  B  C  D

7. \text{CH}_3\text{CH}_2\text{OH}, \text{CH}_2 = \text{CH}, \text{CH}_3\text{CHO}
   A  B  C  D

11. \text{CH}_3\text{CONH}_2 < \text{CH}_3\text{COOC}_2\text{H}_5 < (\text{CH}_3\text{CO})_2\text{O} < \text{CH}_3\text{COCl}

12. \text{C}_2\text{H}_5\text{CH(Cl)}\cdot\text{CH(CH}_3)_2\cdot\text{CH}_2\text{CH}=\text{CHCH(CH}_3)_2\cdot\text{C}_2\text{H}_5\text{CH}=\text{C(CH}_3)_2
   A  B  C

13. \text{C}_2\text{H}_5\text{C} = \text{OC}_3\text{H}_7, \text{C}_2\text{H}_5\text{COOH}, \text{n-C}_3\text{H}_7\text{OH}
   15. \text{C}_3\text{H}_7\text{COCH}_3\text{or} (\text{CH}_3)_2\text{CHCOCH}_3

16. \text{CH}_3\text{OH}, \text{CH}_2\text{COOH}, \text{HCHO}, \text{HCOOH}, \text{HCONH}_2
   A  B  C  D  E

18. \((\text{CH}_3)_2\text{CHCH} = \text{CH}_2, (\text{CH}_3)_2\text{CHCH(Br)CH}_3, (\text{CH}_3)_2\text{CHCH(OH)CH}_3, (\text{CH}_3)_2\text{CHCCCH}_3
   A  B  C  D

19. \text{CH}_3 - \text{C} - \text{C}_2\text{H}_5, \text{CH}_3 - \text{CH} - \text{C}_2\text{H}_5, \text{CH}_3\text{CH} = \text{CHCH}_3
   A  B  C

20. \text{HCOOH}, \text{CO}_2, (\text{COOH})_2

21. \text{C}_3\text{H}_7\text{COOC}_2\text{H}_5, \text{C}_2\text{H}_5\text{OH}, \text{C}_4\text{H}_9\text{OH}, \text{CH}_3\text{CHO}
   A  B  C

22. \begin{align*}
   &\text{OCH}_3 \quad \text{OH} \quad \text{CH}_3 \\
   &\text{Anisole (A)} \quad \text{m-Cresol, (B)} \quad \text{(C)} \quad \text{(D)} \quad \text{(E), C}_7\text{H}_5\text{OBr}_3
\end{align*}
Aldehydes, Ketones and Carboxylic Acids

24. $\text{C}_2\text{H}_5\text{COCl}, \text{C}_2\text{H}_5\text{CONH}_2, \text{C}_2\text{H}_5\text{NH}_2$

25. $\text{CH}_3\text{CO} \cdot \text{O} \cdot \text{COCH}_3, \text{CH}_3\text{COOH}, \text{CH}_3\text{COOC}_2\text{H}_5, \text{C}_2\text{H}_5\text{OH}, \text{CH}_3\text{COCH}_3$

26. $\text{CH}_2\text{CHO} < \text{CH}_3\text{COCH}_3 < \text{CH}_3\text{COCH}_2\text{CHO} < \text{CH}_3\text{COCH}_2\text{COCH}_3$

27. $\text{SOCl}_2, \text{POCl}_3, \text{CH}_2\text{COCl}, \text{CH}_2\text{COCH}_3$

28. $\text{O}_3, \text{KO}_2, \text{O}_2$

29. $\text{C}_6\text{H}_5\text{C}=\text{CH}, \text{C}_6\text{H}_5\text{COCH}_3, \text{C}_6\text{H}_5\text{COOH}, \text{CH}_3$

30. (i)

32. $\text{HCOOC}_2\text{H}_7, (\text{CH}_3)_2\text{CHOH}$

33. $\text{C}_6\text{H}_5\text{CH}=\text{CHCH}=\text{CCHO}, \text{CHO}\text{COOH}$

41. $\text{CO}_2, \text{CH}_2=\text{CHCOOH}, \text{CH}_2=\text{CH}\text{C}_2\text{H}_5\text{OH}$

42. 

43. 

46. $\text{H}_2\text{C}=(\text{CH}_3)\text{CH}=$

F 1. (A) - r, s; (B) - p, q; (C) - p, q, r; (D) - p, s 2. (a)

G 1. (d) 2. (a) 3. (c) 4. (b) 5. (a) 6. (b) 7. (b) 8. (a) 9. (d) 10. (c) 11. (a)

H 1. (d) 2. (c) 3. (a) 4. (d)

I 1. 1 2. 4 3. 2 4. 5 5. 4

Section-B: JEE Main/ AIEEE

1. (c) 2. (b) 3. (c) 4. (a) 5. (c) 6. (a) 7. (d)

8. (b) 9. (c) 10. (c) 11. (a) 12. (a) 13. (c) 14. (c)

15. (a) 16. (d) 17. (a) 18. (c) 19. (d) 20. (a, c) 21. (d)

22. (a) 23. (d) 24. (c) 25. (b)
## Section-A

### JEE Advanced/ IIT-JEE

#### A. Fill in the Blanks

1. CO; HCOOH $\xrightarrow{\text{Conc. H}_2\text{SO}_4, \text{heat}}$ CO + H$_2$O

2. Sodium potassium tartarate.

3. C$_6$H$_5$CH(OCOCH$_3$)$_2$ benzylidene acetate

4. CH$_3$ – C = CH – C = CH$_3$

#### B. TRUE / FALSE

1. **False**: Benzaldehyde has no $\alpha$-hydrogen atom hence it does not undergo aldol condensation but undergoes Cannizzaro reaction.

2. **False**: Saponification is alkaline hydrolysis of esters.

3. **True**: Aldehydes (from primary alcohols) may further be oxidised easily to acids as compared to ketones (from secondary alcohols).

4. **False**: Grignard reagents react with ketones to form ter-alcohols; hence here ter-butanol will be formed.

5. **False**: H-bonding in propionic acid is stronger (carboxylic acids can form dimers) than that in butanol.

#### C. MCQs with ONE Correct Answer

1. **(b)** Fehling solution, Schiff’s reagent & Tollens’ reagent react only with aldehydes but Grignard reagents react both with aldehydes and ketones.

2. **(c)** CH$_3$CHO + 2Cu$^{2+}$ + OH$^-$ $\rightarrow$ CH$_3$COOH + Cu$_2$O $\downarrow$
   Fehling solution (red)

3. **(b)** **TIPS/Formulæ:**
   The compound containing $\alpha$-H atom does not undergo Cannizzaro’s reaction.
   Acetaldehyde does not undergo Cannizzaro reaction since it has $\alpha$-H atoms while formaldehyde, trimethylacetalddehyde and benzaldehyde undergo Cannizzaro reaction since they do not contain $\alpha$-hydrogen atoms.

4. **(c)** **TIPS/Formulæ:**
   Iodoform test is given by compounds having –COCH$_3$ group.
   In acetone –COCH$_3$ group is present. Further ethanol and isopropyl alcohol get oxidised to acetaldehyde and acetone respectively (both having –COCH$_3$ group) in presence of I$_2$ and they in turn give the test. Thus only diethyl ketone does not give this test.

5. **(d)** **NOTE**: –CHO produces –R effect i.e. it withdraws electrons from the double bond or from a conjugated system towards itself.

#### 6.

(a) $\text{CH}_3 - \overset{\text{keto form}}{\text{C}} - \text{CH}_3$

(b) $\text{CH}_3 - \overset{\text{enolic form}}{\text{C}} - \text{CH}_2$

No. of $\sigma$ bonds in enolic form: $3 + 1 + 1 + 1 + 2 = 9$

No. of $\pi$ bonds in enolic form: $1$

No. of lone pairs of electrons in enolic form = 2

#### 7.

**NOTE**: $m$-Chlobenzaldehyde does not contains $\alpha$-H atom. It is an example of Cannizzaro reaction.

$\text{CHO}$ $\xrightarrow{\text{conc. KOH}}$ $\text{COOK} + \text{CH}_2\text{OH}$

#### 8.

**NOTE**: This reaction is known as Rosenmund’s reaction.

C$_6$H$_5$COCl + H$_2$ $\xrightarrow{\text{Pd, BaSO}_4}$ C$_6$H$_5$CHO + HCl

#### 9.

**(a)** **TIPS/Formulæ:**
LiAlH$_4$ is a reducing agent, it reduces –COOH group to –CH$_2$OH group.

C$_6$H$_5$COOH $\xrightarrow{\text{LiAlH}_4}$ C$_6$H$_5$CH$_2$OH

#### 10.

**(a)** C$_6$H$_5$OCH$_3$ $\xrightarrow{\text{HI}}$ C$_6$H$_5$OH + CH$_3$I

**(b)** The possible mechanism is

(i) Ph$\text{C}=\text{O} + \text{OH}^- \rightleftharpoons \text{PhC}=\text{O}^-$

(ii) Ph$\text{C}=\text{O} + \text{PhC}=\text{O}^- \rightleftharpoons \text{PhC}=\text{O}^-$

**NOTE**: The slowest step is the transfer of hydride to the carbonyl group as shown in step (ii).

11. **(d)** C$_2$H$_5$COOH + NaHCO$_3$ $\rightarrow$

12. **(d)** C$_2$H$_5$COOH + NaHCO$_3$ $\rightarrow$

13. **(b)** Remember that $\alpha$ - H's of carbonyl group are easily replaced by D of D$_2$O.

14. **(a)** Compound (a) undergoes dehydration easily as the product obtained is conjugated and thus more stable.

15. **(c)** C$_6$H$_5$ COOH + SOCl$_2$ $\rightarrow$ C$_6$H$_5$COCl + SO$_2$ + HCl
16. (b) Zn(Hg), HCl cannot be used when acid sensitive group like –OH is present, but NH₂, NH₃, OH⁻ can be used.

17. (a) **TIPS/Formulæ:**
Both compounds do not contain α-hydrogen hence undergo Crossed Cannizzaro reaction. Initially OH⁻ attacks at the carbonyl carbon of HCHO than that of PhCHO because carbonyl carbon of HCHO is (i) more electrophilic (ii) less sterically hindered to give hydroxalkoxide which acts as hydride donor in next step to give sodium formate.

\[ \text{C}_2\text{H}_5\text{CHO} + \text{HCHO} \xrightarrow{\text{NaOH}} \text{HCOONa} + \text{C}_6\text{H}_5\text{CH}_2\text{OH} \]

18. (c) **TIPS/Formulæ:**
Ketone (non-reducing) and aldehyde (reducing) can be distinguished by Fehling solution.

\[ \text{P} \xrightarrow{\text{H}_2\text{O}^+} \text{H}_2\text{C} \xrightarrow{\text{OH}^-} \text{C} \xrightarrow{\text{CH}_3} \text{C} = \text{O} \]

Ketone

\[ \text{Q} \xrightarrow{\text{H}_2\text{O}^+} \text{H}_2\text{C} \xrightarrow{\text{OH}^-} \text{C} \xrightarrow{\text{CHO}} \text{Aldehyde} \]

19. (b) Recall that, esters react with excess of Grignard reagents to form 3° alcohols having at least two identical alkyl groups corresponding to Grignard reagent.

\[ \text{O} \quad \xrightarrow{\text{OH}^- / 100^\circ} \quad \text{HOH}_2^+ \]

Intramolecular Cannizzaro reaction

\[ \text{CH}_3\text{OH} \xrightarrow{\text{OH}^-} \text{HOH}_2^+ \]

COOH

20. (a) The optically active acid will react with d and l forms of alcohol present in the racemic mixture at different rates to form two diastereomers in unequal amounts leading to optical activity of the product.

21. (a) This is simply an acid-base reaction.

\[ \text{SO}_3\text{H} + \text{CH}_3\text{COO}^- \xrightarrow{\text{Na}^+} \xrightarrow{\text{H}_2\text{O}} \text{CH}_3\text{CH}_2\text{OH} \]

Strong acid

22. (c) **TIPS/Formulæ:**
Reaction of PhMgBr with carbonyl compounds is an example of nucleophilic addition on carbonyl group which increases with the increase in electron-deficiency of carbonyl carbon.

\[ \text{O} \quad \xrightarrow{\text{C} \xrightarrow{\text{H}} \delta^- \delta^+ \text{C}_6\text{H}_5\text{MgBr}} \quad \text{O} \quad \xrightarrow{\text{C} \xrightarrow{\text{H}} \text{C}_6\text{H}_5} \]

Thus acetaldehyde is most reactive while C₆H₅COC₆H₅ least.

23. (c) **TIPS/Formulæ:**

24. (c) **TIPS/Formulæ:**

This reaction is an example of “Perkin reaction”. The compound X should be (CH₃CO)₂O.

In this step the carbanion is obtained by removal of an α-H atom from a molecule of an acid anhydride, the anion of the corresponding acid acting as a necessary base.

25. (a) This is simply an acid-base reaction.

\[ \text{SO}_3\text{Na}^+ + \text{CH}_3\text{COO}^- \xrightarrow{\text{Na}^+} \xrightarrow{\text{H}_2\text{O}} \text{CH}_3\text{COOH} \]

Strong base

26. (c) **TIPS/Formulæ:** (β-keto acid)

\[ \text{PhC} \xrightarrow{\text{OH}} \xrightarrow{\text{Heat}} \text{PhC} \xrightarrow{\text{CO}_2} \text{Ph}_3\text{C} \xrightarrow{\text{CH}_3} \]

(E)

Since here Grignard reagent is CH₃MgBr, the 3° alcohol should have at least two methyl groups. Thus, the choice with at least two methyl groups at the carbon linked with –OH group will be the correct choice. Hence (a) is the correct choice.
27. (a) Carboxylic acid is stronger acid than phenol. The presence of electron withdrawing group (e.g. Cl) increases acidic strength, while presence of electron donating group (e.g. CH₃) decreases acidic strength.

28. (c)

\[
\text{H}_3\text{C}\text{C}_\text{O} \quad \text{H}_2\text{N}\text{C}_\text{NH}_2 \
\xrightarrow{(1) \text{NaOH/Br}_2} \text{Me}\cdot\text{C}_\text{O} \quad \text{NH}_2 \
\xrightarrow{-\text{HCl}} \text{Me}\cdot\text{C}_\text{O} \quad \text{N} = \text{C} \quad \text{HO} \quad \text{OH} 
\]

(Ascorbic acid) (Aspirin)

32. (a) \[
\text{CH}_3\text{CH}_2\text{C}_\text{C}_\text{H}_3 \xrightarrow{\text{CN}} \text{CH}_3\text{CH}_2\text{C}_\text{C}_\text{H}_3 
\]

\[
\text{CH}_3\text{CH}_2\text{C}_\text{C}_\text{H}_3 \xrightarrow{95\% \text{H}_2\text{SO}_4} \text{CH}_3\text{CH}_2\text{C}_\text{C}_\text{H}_3 
\]

\[
\xrightarrow{\Delta} \text{CH}_3\text{CH} = \text{C}_\text{H}_3 
\]

33. (b) β-Ketoacids undergo decarboxylation easily.

34. (d) Carbolic acid (Phenol) is weaker acid than carbonic acid and hence does not liberate CO₂ on treatment with aq. NaHCO₃ solution.

35. (d)

36. (a) (stabilizes by more H bonding)

.. acidity order is I > II > III > IV
Aldehydes, Ketones and Carboxylic Acids

37. (a) 

\[
\begin{array}{c}
\text{Aldehyde} \\
\text{(Cross aldol reaction)} \\
\end{array}
\]

\[
\text{CH}_3\text{COCl} \xrightarrow{\text{KCN(alc.)}} \text{CH}_3\text{COCN} + \text{KCl}
\]

\[
2\text{C}_6\text{H}_5\text{CHO} \xrightarrow{\text{KCN(alc.)}} \text{C}_6\text{H}_5\text{CHOHCOC}_6\text{H}_5
\]

Thus only chlorobenzene does not react.

4. (b,d) Keto-enol tautomerism is shown in compounds having \(\alpha\)-hydrogen on the \(\text{C}\) adjacent to the \(\text{CO}\) group.

5. (a, b) NOTE:
Aldehydes and ketones containing \(\alpha\)-Hydrogen atom undergo aldol condensation.

6. (b, d) (a) \(\text{HCHO} \xrightarrow{\text{OH}^-} \text{CH}_3\text{OH} + \text{HCOO}^-\)  
(No new \(\text{C} - \text{C}\) bond is formed)  
(b) \(\text{C}_6\text{H}_6 + \text{CH}_3\text{Cl} \xrightarrow{\text{AlCl}_3} \text{C}_6\text{H}_5 - \text{CH}_3\)  
(New \(\text{C} - \text{C}\) bond is formed)

(c) \(\text{C} = \text{O} \xrightarrow{\text{Na/H}_2\text{O}} \text{CH}_2\)  
(No new \(\text{C} - \text{C}\) bond is formed)  
(d) \(\text{(New } \text{C} - \text{C} \text{ bond is formed)}\)

7. (b) TIPS/Formulæ:  
Three \text{Cl} of chloral makes its carbonyl carbon highly electron deficient, hence \(\text{H}_2\text{O}\), a nucleophile easily adds on it forming chloral hydrate, \(\text{CCl}_3\text{(OH)}_2\), which is quite stable due to intramolecular \(\text{H}\)-bonding between two \(-\text{OH}\) groups.

8. (a,b,d) TIPS/Formulæ:  
Carbonyl compounds having \(\alpha - \text{H}\) or \(\alpha - \text{D}\) undergo aldol condensation.

(a) \(\text{CH}_3\text{CHO}\)  
(b) \(\text{CH}_3\text{CH}_2\text{CHO}\)  
(c) \(\text{CH}_3\text{CHO}\)  
(d) \(\text{C}_3\text{H}_7\text{CHO}\)  
(No \(\alpha - \text{I}\))  
(\(\alpha - \text{D}\) present)

9. (d) 
\(\text{Intramolecular Cannizzaro reaction}\) 
\(\xrightarrow{\text{OH}^-}\) 
\(\xrightarrow{\text{H}^+}\) 
\(\text{COOH} + \text{H}_2\text{O}\)
10. (c) \[ \text{Isopropylbenzene (cumene, P)} \]
\[ + \text{CH}_3\text{CH}_2\text{CH}_2\text{Cl} \xrightarrow{\text{AlCl}_3} \]
\[ \text{O} \quad \text{O} \quad \text{O} \]
\[ \text{Cumene hydroperoxide} \]
\[ \xrightarrow{\text{H}_2\text{O}} \]
\[ \text{Phenol} + \text{Acetone (Q)} \]

11. (b) \[ \text{C} = \text{O} + \text{NH}_2\text{OH} \rightarrow \text{N} \quad \text{C} = \text{O} \]
\[ \text{H}_3\text{C} \quad \text{CH}_3 \]
\[ \text{H}_3\text{C} \quad \text{CH}_3 \]
\[ \text{(same compound)} \]
\[ \text{optically active oximes} \]

12. (b, d) (A) Both are soluble in NaOH, hence in separable.
(B) Only benzoic acid (C\textsubscript{6}H\textsubscript{5}COOH) is soluble in NaOH and NaHCO\textsubscript{3}, while benzyl alcohol (C\textsubscript{6}H\textsubscript{5}CH\textsubscript{2}OH) is not. Hence, separable.
(C) Although NaOH can enable separation between benzyl alcohol (C\textsubscript{6}H\textsubscript{5}CH\textsubscript{2}OH) and phenol (C\textsubscript{6}H\textsubscript{5}OH) as only the later is soluble in NaOH. However, in NaHCO\textsubscript{3}, both are insoluble. Hence, in separable.
(D) \( \alpha \)-Phenylacetic acid (C\textsubscript{6}H\textsubscript{5}CH\textsubscript{2}COOH) is soluble in NaOH and NaHCO\textsubscript{3}. While benzyl alcohol (C\textsubscript{6}H\textsubscript{5}CH\textsubscript{2}OH) is not. Hence, separable.

13. (a, c, d)
\[ \text{O} \]
\[ \text{H}_3\text{C} \quad \text{C}_\text{C}_\text{H}_5 \]
\[ \text{LiAlH}_4 \rightarrow \text{H}_3\text{C} \quad \text{C}_\text{C}_\text{H}_5 \]
\[ \text{(U)} \quad \text{(no chiral centre)} \]
\[ \xrightarrow{\text{excess (CH}_3\text{CO}_2}\text{H}} \]
\[ \text{OCOCH}_3 \quad \text{OCOCH}_3 \]
\[ \text{(W)} \quad \text{(C}_6\text{H}_4\text{O}_2) \]
\[ \xrightarrow{\text{CrO}_3 / \text{H}^+} \]
\[ \text{O} \quad \text{O} \]
\[ \text{HO} \quad \text{OH} \]
\[ \text{(V)} \quad \text{(Effervescence with NaHCO}_3) \]
14. (h, d)

\[
\text{OH} \quad \xrightarrow{\text{Cl}(\text{Cl}_3)} \quad \text{O} \quad \xrightarrow{\text{H}_3\text{C}} \quad \text{CHCl}_2 \quad \xrightarrow{\text{(Minor)}} \quad \text{(Q)} \quad \xrightarrow{\text{CH}_3} \quad \text{(Major)}
\]

\[\text{CHCl}_3 + \text{OH} \rightarrow \text{CCl}_2 + \text{H}_2\text{O} + \text{Cl}^-\]

\[\text{CH}_3 \quad \xrightarrow{\text{OH}^-} \quad \text{CH}_3 + \text{H}_2\text{O}\]

\[
\text{O}^- \quad \xrightarrow{\text{+: CC}_2} \quad \text{O} \quad \xrightarrow{\text{H}} \quad \text{OH} \quad \xrightarrow{\text{CHCl}_2} \quad \text{OH} \quad \xrightarrow{\text{CHCl}_2} \quad \text{CH}_3 \quad \text{(major)}
\]

\[\text{O}^- \quad \xrightarrow{\text{+: CC}_2} \quad \text{O} \quad \xrightarrow{\text{H}_2\text{O}} \quad \text{OH} \quad \xrightarrow{\text{CHCl}_2} \quad \text{CHCl}_2 \quad \text{(minor)}
\]

15. (c)

**Reaction I:**

\[
\text{O} \quad \xrightarrow{\text{CH}_3} \quad \text{CH}_3 \quad \xrightarrow{\text{Br}_2(1.0 \text{ mol})} \quad \text{Na}^\text{+} \text{OH}^- \quad \xrightarrow{\text{CH}_3\text{COONa} + \text{CHBr}_3 + \text{CH}_3}\quad \text{(U)} \quad \text{(unreacted)}
\]

**Reaction II:**

\[
\text{O} \quad \xrightarrow{\text{CH}_3} \quad \text{CH}_3 \quad \xrightarrow{\text{Br}_2(1.0 \text{ mol})} \quad \text{CH}_3\text{COOH} \quad \xrightarrow{\text{CH}_3\text{CH}_2\text{Br}} \quad \text{(P)}
\]

16. (a)

\[
\text{CH}_3 \quad \xrightarrow{\text{KOH, H}_2\text{O}} \quad \text{O} \quad \xrightarrow{\text{H}^+} \quad \text{CH}_3 \quad \text{(Minor)} \quad \text{CH}_3 \quad \text{(Major)}
\]

\[
\text{(Minor)} \quad \xrightarrow{\text{(Major)}}
\]
17. (a, b, c) Aldehydes and α-Hydroxyketones show positive Tollen’s test.

HCHO + Tollen's Reagent → Silver mirror ↓

PhCHO + Tollen's Reagent → Silver mirror ↓

Diketone

18. (b, c)

\[
\begin{align*}
\text{苯} & \xrightarrow{(i) \text{O}_2} \text{OHHCl} / \text{NaOH} & \xrightarrow{(ii) \text{H}_2\text{O}^+} & \text{Q} \quad \text{(Major)} + \text{R} \quad \text{(Minor)} \\
\text{OH} & \xrightarrow{\text{NaOH} / \text{PhCH}_2\text{Br}} & \text{O} - \text{CH}_2\text{Ph} & \text{CHO} \\
\end{align*}
\]

Q is steam volatile not R.
Q and R show positive test with 1% aqueous FeCl₃ solution.
Q, R, S give yellow precipitate with 2, 4-dinitrophenyl hydrazine.

19. (c, d)

LiAlH₄/(C₂H₅)₂O : Reduces to esters, carboxylic acid, epoxides and aldehydes and ketones.
BH₃ in T.H.F : Reduces to –COOH and aldehydes into alcohols but do not reduce to esters and epoxides.
NaBH₄ in C₂H₅OH : Reduces only aldehydes and ketones into alcohols but not to others.
Raney Ni in T.H.F. : Do not reduce to –COOH, –COOR and epoxide but it can reduce aldehyde into alcohols.

E. Subjective Problems

1. (i)

Hexamethylenetetramine (Urotropine)
Aldehydes, Ketones and Carboxylic Acids

(xi) \( \text{ KCN} + \text{H}_2\text{SO}_4 \rightarrow \text{KHSO}_4 + \text{HCN} \)

\[
\begin{align*}
\text{CH}_3\text{CH}_2 & \quad C \quad O \\
& \quad \text{H} \quad \text{H} \\
\text{C} & \quad \text{O} \\
& \quad \text{H} \quad \text{C} \quad \text{NH}_2 \\
\text{LiAlH}_4 & \rightarrow \\
\text{CH}_3\text{CH}_2 & \quad C \quad \text{OH} \\
& \quad \text{H} \quad \text{C} \quad \text{H}_2 \text{NH}_2 \\
\text{HOCH}_2 & \quad \text{C} \quad \text{O} \\
\text{H}_2\text{SO}_4 & \rightarrow \\
\text{(±)} & \quad \text{HOCH}_2 \\
\end{align*}
\]

(ii) \( \text{CHO} + \text{Ph}_3\text{P} = \text{CH}_2 \rightarrow \text{CHO} \)

\[
\begin{align*}
\text{CHO} + \text{Ph}_3\text{P} = \text{CH}_2 & \quad \text{HOCH}_2 \\
\text{HOCH}_2 & \quad \text{C} \quad \text{O} \\
\text{H}_2\text{SO}_4 & \rightarrow \\
\text{(E)} & \quad \text{H}_2\text{SO}_4 \\
\end{align*}
\]

(iii) \( \text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_3\text{CCOOOC}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_4\text{ONa} \rightarrow \text{C}_2\text{H}_4\text{OH} \)

\[
\begin{align*}
\text{OH} & \quad \text{CH}_3 \quad \text{C} = \text{CHOOC}_2\text{H}_5 \quad \text{H}^+ \rightarrow \\
& \quad \text{CH}_3 \quad \text{C} = \text{CHCOOC}_2\text{H}_5 \\
\text{Ethyl acetooacetate} & \quad \text{Ethyl acetoacetate} \\
\end{align*}
\]

(iv) \( \text{CH}_3\text{CHO} \rightarrow \text{HCOOH} \rightarrow \text{Ca(OH)}_2 \rightarrow \text{Ca} \quad \text{H}_2\text{O} \rightarrow \text{C}_2\text{H}_4\text{OH} \)

\[
\begin{align*}
\text{(HOOC)_2}\text{Ca} & \rightarrow \\
\text{(CH}_3\text{COO}_2)\text{Ca} & \rightarrow \\
\text{CH}_3 & \quad \text{COOH} \\
\text{Acetone} & \quad \text{Acetone} \\
\end{align*}
\]

(v) \( \text{CH}_3\text{COOH} \rightarrow \text{CH}_3\text{CCI} \rightarrow \text{CH}_3\text{COCH}_3 \rightarrow \text{CH}_3\text{CH}_2\text{CHO} \)

\[
\begin{align*}
\text{CH}_3 & \quad \text{CO}_2\text{H} \\
\text{H}_2\text{O} & \rightarrow \\
\text{H}_2 & \quad \text{H}_2 \quad \text{H}_2 \\
\text{H}_2 \quad \text{H}_2 & \rightarrow \\
\text{CH}_3 & \quad \text{CH}_2 \quad \text{COOH} \\
\end{align*}
\]

(vi) \( \text{CH}_3\text{CHO} \rightarrow \text{HCHO} \rightarrow \text{Ca(OH)}_2 \rightarrow \text{Ca} \quad \text{H}_2\text{O} \rightarrow \text{C}_2\text{H}_4\text{OH} \)

\[
\begin{align*}
\text{(CH}_3\text{COO}_2)\text{Ca} & \rightarrow \\
\text{(CH}_3\text{COO}_2)\text{Ca} & \rightarrow \\
\text{CH}_3 & \quad \text{COOH} \\
\text{Acetone} & \quad \text{Acetone} \\
\end{align*}
\]

NOTE: The reaction is an example of benzil-benzilic acid type rearrangement.

(xvii) \( \text{H}_3\text{C} \rightarrow \text{CH} \rightarrow \text{H}_2\text{O} \rightarrow \text{H}_3\text{C} \rightarrow \text{CH} + \text{H}_3\text{I} \)

(xviii) \( \text{C}_6\text{H}_5\text{CH} \rightarrow \text{C}_6\text{H}_5\text{CH} \rightarrow \text{C}_6\text{H}_5\text{CH} \rightarrow \text{C}_6\text{H}_5\text{CH} \)

(xix) \( \text{CH}_3\text{CH} \rightarrow \text{CH}_3\text{CH} \rightarrow \text{CH}_3\text{CH} \rightarrow \text{CH}_3\text{CH} \)

(Ester hydrolysis involves acyl-oxygen fission)
(v) \[ \text{CH}_3\text{COOH} \xrightarrow{\text{PCl}_3} \text{CH}_3\text{COCl} \]

\[ \text{C}_6\text{H}_5\text{MgBr} \rightarrow \text{C}_6\text{H}_5\text{COCH}_3 \]

\[ \text{C}_6\text{H}_5\text{MgBr} \rightarrow \text{CH}_3\text{C}^-\text{OMgBr} \]

\[ \text{C}_6\text{H}_5\text{H} \]

\[ \text{HOH} \rightarrow (\text{C}_6\text{H}_5)_2\text{CCH}_3 \]

\[ \text{Oh} \]

\[ \text{heat} \xrightarrow{-\text{H}_2\text{O}} (\text{C}_6\text{H}_5)_2\text{C} = \text{CH}_2 \]

\[ \text{CrO}_3 \rightarrow \text{C}_6\text{H}_5\text{COC}_6\text{H}_5 + \text{HCOOH} \]

(vi) \[ \text{CH}_3\text{CH}_2 - \text{C} = \text{CH} + \text{Na}^+ \cdot \text{NH}_2^- \]

\[ \rightarrow \text{CH}_3\text{CH}_2 - \text{C} = \text{C}^- : \text{Na}^+ \]

\[ \text{CH}_3 \rightarrow \text{CH}_3\text{CH}_2 - \text{C} = \text{C} - \text{CH}_3 \]

\[ \text{O} \]

\[ \text{HgSO}_4 \xrightarrow{\text{H}_2\text{SO}_4} \text{CH}_3\text{CH}_2\text{CH}_2 - \text{C} - \text{CH}_3 \]

4. \[ \text{CH}_3\text{COCl} + \text{AlCl}_3 \rightarrow \text{CH}_3\text{C}^+ = \text{O} + \text{AlCl}_4^- \]

\[
\begin{array}{c}
\text{CH}_3 \rightarrow \text{C} = \text{O} \\
\text{CH}_3 \rightarrow \text{C} = \text{O} + \text{HOC}_3\text{R} \quad \text{aldehyde}
\end{array}
\]

5. Ozonolysis of (A) to acetone and an aldehyde indicates the following part structure of alkene (A):

\[
\begin{array}{c}
\text{CH}_3 \rightarrow \text{C} = \text{CHR} \\
\text{O}_3
\end{array}
\]

As per problem:

\[
\begin{array}{c}
\text{RCHO} \xrightarrow{[O]} \text{RCOOH}[B] \xrightarrow{\text{P/Br}_2} \\
\text{Bromo compound}[C] \xrightarrow{\text{H}_2\text{O}} \text{Hydroxy acid}[D]
\end{array}
\]

Structure of (D) is determined by the reaction:

\[
\begin{array}{c}
\text{CH}_3 \rightarrow \text{C} = \text{O} \xrightarrow{\text{HCN}} \text{CH}_3 \rightarrow \text{C} \rightarrow \text{O} \xrightarrow{\text{H}_2\text{O} + \text{H}^+} \\
\text{CH}_3 \rightarrow \text{C} \rightarrow \text{OH} \xrightarrow{\text{CH}_3 \rightarrow \text{C} \rightarrow \text{CN}} \\
\text{CH}_3 \rightarrow \text{C} \rightarrow \text{OH} \xrightarrow{\text{D}} \\
\text{CH}_3 \rightarrow \text{C} \rightarrow \text{COOH}
\end{array}
\]

The compound (D) is obtained by hydrolysis of (C) with aqueous alkali since (C) is a bromo compound, therefore it has a bromo group where the compound (D) has a hydroxyl group. Therefore, structure of C is:

\[
\begin{array}{c}
\text{CH}_3 \rightarrow \text{C} \rightarrow \text{Br} \\
\text{CH}_3 \rightarrow \text{C} \rightarrow \text{COOH}
\end{array}
\]

The compound (C) is formed by bromination of compound (B), therefore, the compound (B) is:

\[
\begin{array}{c}
\text{CH}_3 \rightarrow \text{C} \rightarrow \text{H} \\
\text{CH}_3 \rightarrow \text{C} \rightarrow \text{COOH}
\end{array}
\]

The compound (B) is formed by oxidation of an aldehyde therefore the structure of the aldehyde is:

\[
\begin{array}{c}
\text{CH}_3 \rightarrow \text{C} \rightarrow \text{CHO} \\
\text{CH}_3 \rightarrow \text{C} \rightarrow \text{CHO}
\end{array}
\]

The aldehyde and acetone are formed by ozonolysis of alkene. Therefore, the double bond in alkene should be between the carbon atoms of the two carbonyl compounds (the aldehyde and acetone). Therefore, the compounds and the reactions are identified as:

\[
\begin{array}{c}
\text{CH}_3 \rightarrow \text{C} = \text{C} \rightarrow \text{CH}_3 \\
\text{CH}_3 \rightarrow \text{C} = \text{C} \rightarrow \text{CH}_3 \\
\text{CH}_3 \rightarrow \text{C} \rightarrow \text{CHO} \\
\text{CH}_3 \rightarrow \text{C} \rightarrow \text{CHO}
\end{array}
\]

6. (i) TIPS/Formulae:

Formic acid has no alkyl group i.e. no α - H atom, hence it does not undergo halogenation, while acetic acid has a methyl group (i.e. three α - H atoms) on which halogenation takes place.

(ii) \[ \text{H} - \text{C} \rightarrow \text{OH} \xrightarrow{\text{O}} \text{H} - \text{C} \rightarrow \text{O}^- \rightarrow \text{H}^+ \]

\[
\begin{array}{c}
\text{CH}_3 \rightarrow \text{C} \rightarrow \text{OH} \xrightarrow{\text{O}} \text{CH}_3 \rightarrow \text{C} \rightarrow \text{O}^- \rightarrow \text{H}^+ \\
\text{O}
\end{array}
\]

Presence of CH₃ gp in acetate ion shows +1 effect and thereby intensifying charge on O⁻ of acetate ion which is thus destabilized. Thus formate ion is more stable than acetate ion or HCOOH loses proton more easily than CH₃COOH.

(iii) NOTE:

Alcohols show hydrogen bonding.
The boiling points of carbonyl compounds are lower than the corresponding alcohols since former do not show intermolecular H-bonding like alcohols.

\[
\begin{array}{c}
\text{C}_4\text{H}_9 - \text{O} \rightarrow \text{H} \\
\text{H} \rightarrow \text{O} \rightarrow \text{C}_4\text{H}_9
\end{array}
\]
Aldehydes, Ketones and Carboxylic Acids

H-bonding between two butanol molecules
Solubility of butanol in water is due to hydrogen bonding between butanol and water molecules (similarity to butanol).

(iv) TIPS/Formulæ:
In weakly acidic medium carbonyl group is protonated to form conjugate acid.

\[
\text{C} = \text{O} + \text{H}^+ \rightarrow \text{C}^{+} - \text{OH}
\]

more electron becomes
deficient

In strongly acidic medium (pH < 3.5), the unshared pair of electrons of N of the reagent is protonated with the result nucleophile (NH₃H₂₂⁺) is converted to an electrophile (NH₃H₂₂⁻) which cannot react. Hence in highly acidic medium, there is no protonation of the carbonyl group.

(v) NOTE: Hypoiodite (HOI) is a strong base than iodide ion. (O is more electronegative thus easily accommodate negative charge than I in I⁻).

Haloform reaction is base-promoted reaction (the first step involves removal of acidic hydrogen atom of acetone by base). Hypoiodite ion being strong base than iodide ion, can easily remove acidic hydrogen atom.

\[
\text{CH}_3\text{COCH}_3 + \text{HOI} \rightarrow \text{CH}_3\text{COOH} + \text{H}_2\text{I}
\]

(vi) In the acylium ion (R - C = O⁺), each and every element has a complete octet, while in carbonium ion (R - C⁺ = O), carbon bearing positive charge has incomplete octet which makes it more reactive than the former.

\[
\text{acylium ion} \quad \text{carbonium ion}
\]

(Carbon has only six electrons)

(vii) TIPS/Formulæ:
- Both of the resonating structures of benzoate ion are equivalent, while it is not so in phenoxide ion.

Resonating structures of phenoxide ion

Resonating structures of benzoate ion

The benzoate ion is more stabilized because the negative charge on both structures is on the more electronegative oxygen atom, whereas in phenoxide ion, it is on the less electronegative carbon atoms.

(iii) TIPS/Formulæ:
- o-Hydroxybenzaldehyde has intramolecular H-bonding while the p-isomer has intermolecular H-bonding.

\[
\begin{align*}
\text{CH}_3\text{CHO} + \text{H}_2\text{O} & \xrightarrow{\text{H}_2\text{O}} \text{CH}_3\text{COOH} + \text{H}_2\text{O} \\
\text{CH}_3\text{CHO} + \text{H}_2\text{O} & \xrightarrow{\text{H}_2\text{O}} \text{CH}_3\text{COOH} + \text{H}_2\text{O}
\end{align*}
\]

7. (i) \( \text{C}_2\text{H}_5\text{CHO} \xrightarrow{\text{H}_2\text{O}} \text{CH}_3\text{CHO} \xrightarrow{\text{H}_2\text{O}} \text{CH}_3\text{CH}_2\text{OH} \)

(ii) \( \text{CH}_3\text{I} + \text{KCN} (\text{alc.}) \xrightarrow{\text{KI}} \text{CH}_3\text{CN} \)

8. \( \text{H}_2\text{SO}_4(\text{conc.}) \xrightarrow{\text{H}_2\text{O}} \text{H}_2\text{O} + \text{CH}_3\text{COOH} \)

9. \( \text{CH}_3\text{CHO} + \text{AgNO}_3/\text{NH}_4\text{OH} \xrightarrow{\text{Tollen’s reagent}} \text{CH}_3\text{CH}_2\text{COOH} + 2\text{Ag} \)

10. TIPS/Formulæ:
- Acetaldehyde can be distinguished from acetone by using Tollen’s reagent or Fehling solution or Schiff’s reagent. Only acetaldehyde responds to all these tests.

\[
\text{CH}_3\text{CHO} + [\text{Ag(NH}_3\text{)}_2]^{\text{+/2}} \xrightarrow{\text{Tollen’s reagent}} \text{CH}_3\text{CH}_2\text{COOH} + 2\text{Ag}
\]

11. TIPS/Formulæ:
The weaker a base better is its leavability.

This is an example of nucleophilic substitution where the group \( \text{X} (\text{Cl}, \text{NH}_2, \text{OC}_2\text{H}_5, \text{OCOCH}_3) \) is replaced by \( \text{OH} \). The decreasing basic character of the four concerned groups is:

\[
\text{NH}_2^- > \text{OR}^- > \text{OCOR}^- > \text{Cl}^-\]

Hence \( \text{Cl}^- \) (the weakest base) will be lost most easily while \( \text{NH}_2^- \) (the strongest base) will be lost with most difficulty.

Thus the order of hydrolysis becomes.

\[
\text{CH}_3\text{CONH}_2 < \text{CH}_3\text{COOC}_2\text{H}_5 < (\text{CH}_3\text{CO})_2\text{O} < \text{CH}_3\text{COCl}
\]

12. Let us summarise the given facts.

White ppt. \( \xrightarrow{\text{AgNO}_3(A)} \text{C}_6\text{H}_5\text{Cl} \xrightarrow{\text{KOH}} \text{C}_6\text{H}_5\text{CH}_3 \)

\( \text{C}_6\text{H}_5\text{CHO} + \text{C}_6\text{H}_5\text{CH}_3 + \text{CH}_3\text{COCH}_3 + (\text{CH}_3)_2\text{CCH}_3 \)

(i) (ii) (iii) (iv)
**Topic-wise Solved Papers - CHEMISTRY**

**NOTE THIS STEP:** With the help of structures of the four carbonyl compounds, (i) to (iv), we may write the structures of the two isomeric olefins (B) and (C). The two carbonyl compounds should be joined in such a way that the parent olefin has 6 carbon atoms. Two such possibilities are the combination of carbonyl compounds having 2+4 carbon atoms [i.e. (i) + (iv)] and 3+3 carbon atom [i.e. (ii) + (iii)].

\[
\begin{align*}
\text{CH}_3\text{CHO} + \text{OHC.CH}(\text{CH}_3)_2 &\overset{\text{O}_2}{\rightarrow} \text{CH}_3\text{CH} = \text{CH.CH}(\text{CH}_3)_2 \\
\text{(i)} &\quad \text{Olefin B (C}_6\text{H}_{12}) \\
\text{C}_2\text{H}_5\text{CHO} + \text{OC}(\text{CH}_3)_2 &\overset{\text{O}_2}{\rightarrow} \text{C}_2\text{H}_5\text{CH} = \text{C}(\text{CH}_3)_2 \\
\text{(ii)} &\quad \text{Olefin (C}_6\text{H}_{12})
\end{align*}
\]

Thus the compound (A) should be a chloride that can eliminate a molecule of HCl to give B as well as C.

\[
\begin{align*}
\text{Cl} &\quad \text{CH}_3 \\
\text{CH}_2\text{CH}_2\text{CH.CH.CH}_3 &\quad \rightarrow \quad \text{CH}_3\text{CH} = \text{CH.CH.CH}_3 \\
\quad 2-\text{Methyl}-3-\text{chloropentane (A)} &\quad \rightarrow \quad 4-\text{Methylpentene-2 (B)}
\end{align*}
\]

Thus the compound (A) should be a chloride that can eliminate a molecule of HCl to give B as well as C.

\[
\begin{align*}
\text{CH}_3 &\quad \text{CH}_3 \\
\text{CH}_2\text{CH}_2\text{CH.CH.CH}_3 &\quad \rightarrow \quad \text{CH}_2\text{CH} = \text{CH.CH.CH}_3 \\
\quad 2-\text{Methyl-3-chloropentane (A)} &\quad \rightarrow \quad 4-\text{Methylpentene-2 (B)}
\end{align*}
\]

16. **TIPS/Formulae:**

![Chemical structure diagram](image)

The above reactions lead to following conclusions.

(i) Reaction of A with CH₃COOH in presence of H₂SO₄ to form ester B indicates that A is an alcohol.

(ii) Reaction of C with 50% KOH followed by acidification to give alcohol A and the compound D seems to be the Cannizzaro reaction. Hence C must be an aldehyde and D must be an acid. The nature of C as an aldehyde is again consistent with the fact that it is obtained by the mild oxidation of A which has been established as an alcohol.

(iii) Structure of acid D is established by its given facts.

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{C} &- \text{OCH}_2\text{CH}_2\text{CH}_3, \quad \text{CH}_3\text{CH}_2\text{COOH}, \\
\quad \text{(Propyl propanoate) X} &\quad \text{(Propanoic acid) Y}
\end{align*}
\]

17. (i) CH₃C – OC₂H₅

15. (i) **Empirical formula can be calculated as**

<table>
<thead>
<tr>
<th>Element</th>
<th>Percentage</th>
<th>Relative no. of atoms</th>
<th>Simplest ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>69.77</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>H</td>
<td>11.63</td>
<td>11.63</td>
<td>10</td>
</tr>
<tr>
<td>O</td>
<td>18.60</td>
<td>1.16</td>
<td>1</td>
</tr>
</tbody>
</table>

(ii) \text{PCl}_3, \text{NH}_2\text{CH}_2\text{COONH}_4
18. **TIPS/Formulae**:

For this type of problem, students are advised to summarise the whole problem in the form of reactions.

\[
\text{CH}_3 \text{CH}_2 \text{CH}_3 + \text{H}_2 \xrightarrow{\text{HBr}} \text{C}_3\text{H}_{10} \xrightarrow{\text{Markov. addition}} \text{B (having Br)}
\]

\[
\text{B} \xrightarrow{\text{AgOH} (\text{C}_3\text{H}_2\text{O}, \text{alcohol})} \text{C} \xrightarrow{(O)} \text{D (ketone)}
\]

Let us draw some conclusions from the above set of reactions.

(i) The molecular formula \( \text{C}_3\text{H}_{10} \) (\( \text{C}_3\text{H}_8 \)) for \( \text{A} \) indicates that it is an alkene having one double bond.

(ii) Since the alcohol \( \text{C} \) on oxidation gives a ketone \( \text{D} \), \( \text{C} \) must be a secondary alcohol and hence \( \text{B} \) must be a secondary bromide.

(iii) The structure of 2-methylbutane, the hydrogenated product of \( \text{A} \), indicates that the secondary bromide must have following structure.

\[
\begin{align*}
\text{CH}_3 & \quad \text{Br} \\
\text{CH}_3 - \text{CH} - \text{CH} - \text{CH}_3 & \quad (\text{B})
\end{align*}
\]

(iv) Thus the corresponding olefin \( \text{A} \) must have structure \( \text{A} \) which on Markonnikov addition of \( \text{HBr} \) gives the bromide \( \text{B} \), the other possible alkene \( \text{A}' \) will not give \( \text{B} \) when \( \text{HBr} \) is added on it according to Markonnikov rule.

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_2 \\
\text{CH}_3-\text{CH} & \quad = \text{CH}_2 \\
(\text{A}) & \quad (\text{A}')
\end{align*}
\]

Thus the reaction involved can be represented as below:

\[
\begin{align*}
\text{CH}_3 \text{CH}_2 \text{CH} = \text{CH}_2 + \text{HBr} & \rightarrow \text{CH}_3 \text{CH} = \text{CH} - \text{CH}_3 \\
3\text{-Methylbutene-1,A} & \rightarrow 2\text{-Bromo-3-methylbutane,B}
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3 \text{OH} & \xrightarrow{\text{AgOH}} \text{CH}_3 \text{CH} = \text{CH} - \text{CH}_3 \\
3\text{-Methylbutanol-2,C} & \rightarrow \text{CH}_3 \text{CH} = \text{C} - \text{CH}_3 \\
3\text{-Methylbutanone-2,D}
\end{align*}
\]

19. The compound \( \text{A} \), a ketone, undergoes haloform reaction. Thus, it must contain \( \text{CH}_3\text{CO} \) group.

The compound \( \text{C} \) gives mono-ozonide \( \text{D} \), which shows that the compound \( \text{C} \) contains a double bond. Since the hydrolysis of \( \text{D} \) gives only acetaldehyde, the compound \( \text{C} \) would be an alkene having four carbon atoms, i.e. \( \text{CH}_3 - \text{CH} = \text{CH} - \text{CH}_3 \) (butene-2).

The compound \( \text{B} \) is obtained by the reduction of compound \( \text{A} \) (which contains \( \text{CH}_3\text{CO} \) group). Hence, the compound \( \text{B} \) would be an alcohol, which on heating with \( \text{H}_2\text{SO}_4 \) gives \( \text{C} \). Hence \( \text{B} \) and \( \text{A} \) would be

\[
\begin{align*}
\text{CH}_3 - \text{CH} - \text{CH}_2 - \text{CH}_3 & \quad \text{CH}_3 - \text{C} - \text{CH}_2 - \text{CH}_3 \\
\text{butan-2-ol (B)} & \quad \text{butan-2-one (A)}
\end{align*}
\]

The reactions involved:

\[
\begin{align*}
\text{(A) reduction} & \rightarrow \text{(B) conc. H}_2\text{SO}_4 \rightarrow \text{CH}_3 - \text{CH} = \text{CH.CH}_3 \\
\text{(C)} & \rightarrow \text{HOH} \rightarrow 2\text{CH}_3\text{CHO}
\end{align*}
\]

20. **TIPS/Formulae**:

The given set of reactions can be represented as below:

\[
\begin{align*}
\text{aq. NaOH} & \rightarrow \text{Sod. salt of acid A} \\
\text{Gas B} & \rightarrow \text{Sod. salt of acid A} \\
\text{(i) NaOH heat} \rightarrow \text{Dibasic acid, C} \\
\text{(ii) H}_2\text{SO}_4 \rightarrow \text{Dibasic acid, C}
\end{align*}
\]

**Calculation of molecular formula of \( \text{C} \)**

\[
\begin{align*}
\text{A} & = 2 \times \frac{0.08}{18} \times 100 = 2.22% \\
\text{B} & = 12 \times \frac{0.39}{44} \times 100 = 27.30% \\
\text{C} & = 100 - (2.22 + 27.30) = 71.48% \\
\text{By usual method, empirical formula of acid} \text{C} & = \text{CHO}_2
\end{align*}
\]

\[
\text{Eq. wt. of acid C} = \frac{1.0}{0.71} \times 108 = 107 = 45
\]

\[
\text{Mol. wt. of acid C} = 45 \times 2 = 90
\]

\[
\therefore \text{Mol. formula of C} = \text{C}_2\text{H}_4\text{O}_4
\]

Since it is dicarboxylic acid, it must have two-COOH groups.

Hence \( \text{C} \) is \( \text{COOH} \)

\[\text{COOH}\]

Oxalic acid

Going back, compound \( \text{C} \) must be produced from sodium oxalate which in turn is produced from sodium formate. Hence \( \text{A} \) is formic acid and \( \text{B} \) is \( \text{CO}_2 \).

Thus the complete series of reactions can be written as below:

\[
\begin{align*}
2\text{NaOH(aq.)} & \rightarrow 2\text{CO}_2 + \text{HCOONa} + \text{NaOH} \\
+ \text{HCOONa} & \rightarrow \text{COONa} \rightarrow \text{COONa} \xrightarrow{\text{NaOH heat}} \text{COOH} \xrightarrow{\text{H}_2\text{SO}_4} \text{COOH}
\end{align*}
\]

\[
\text{(C)}
\]

\[
\text{(C)}
\]
21. **TIPS/FORMULAE:**

**A** \[ \text{Reduction by LiAlH}_4 \] \[ \text{B} + \text{C} \]

\[ \text{F} \xrightarrow{\text{oxi.}} \text{D} \xrightarrow{(i) \text{aq. OH}^{-}, \text{(ii) heat}} \text{E} \]

**Monobasic acid (Mol. wt. = 60)**

Molecular weight of the monobasic acid (RCOOH) indicates that the R− should be CH$_3$− i.e., acid F should be acetic acid (CH$_3$COOH, mol. wt. 15+45). Thus compound D must be acetaldehyde CH$_3$CHO, and compound B which on oxidation gives CH$_3$CHO must be ethanol, CH$_3$CH$_2$OH.

Acetaldehyde (D) on treating with aqueous alkali will undergo aldol condensation.

\[
2\text{CH}_3\text{CHO} \xrightarrow{\text{OH}^{-}} \text{CH}_3\text{CH}=(\text{CH})\text{CHO} \xrightarrow{\text{heat}} \text{CH}_3\text{CH}=\text{CHCH}_2\text{CHO} \]

**Nature of A.** Thus it is evident that reduction of A with LiAlH$_4$ gives two alcohols; B (ethanol) and C (butanol). Hence A must be an ester i.e., ethyl butanoate (CH$_3$CH$_2$COOCH$_2$CH$_3$).

\[
\text{CH}_3\text{CH}=\text{CHCH}_2\text{COOCH}_2\text{H}_5 \xrightarrow{\text{LiAlH}_4} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} + \text{C}_6\text{H}_5\text{OH} \]

**22. Empirical formula of A and B.**

<table>
<thead>
<tr>
<th>Element</th>
<th>Relative No. of atoms</th>
<th>Simplest ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>12 0.308 x 0.108 x 100 = 77.77</td>
<td>6.48 0.92 = 7</td>
</tr>
<tr>
<td>H</td>
<td>2 0.072 x 0.108 x 100 = 7.40</td>
<td>7.40 0.92 = 8</td>
</tr>
<tr>
<td>O</td>
<td>100 - (77.77 + 7.40) 14.83 x 0.16 = 0.92</td>
<td>0.92 = 1</td>
</tr>
</tbody>
</table>

.: % of C = 77.77

.: % of H = 7.40

.: % of O = 14.83

.: Empirical formula of A is C$_8$H$_{16}$O$_3$.

**Nature of (A):** Since A is insoluble in NaOH and NaHCO$_3$, it can’t have –OH and –COOH groups. Further the reaction of A with conc. HI to give compounds C and D separable by means of ammonical AgNO$_3$ and solubility of D in NaOH indicates that C and D are alkyl halide and phenol respectively. Thus A is an ether i.e. it is C$_6$H$_5$.O.CH$_3$ which explains all the given reactions.

23. (i) C$_6$H$_5$.COOH \[ \xrightarrow{\text{PCl}_5} \text{C}_6\text{H}_4\text{COCl} \xrightarrow{\text{NH}_3} \]

C$_6$H$_5$CONH$_2$ \[ \xrightarrow{\text{PbO}_x} \text{C}_6\text{H}_5$CN \xrightarrow{\text{H}_2/\text{Ni}} \text{C}_6\text{H}_5$.CH$_2$.NH$_2$ \[ (E) \]

(ii) H$_2$.CCH$_3$.CHCHO \[ \xrightarrow{\text{NaBH}_4} \text{CH}_3$.CH = CH–CH$_2$.OH \]

HCl \[ \xrightarrow{\text{ZnCl}_2} \text{CH}_3$.CH = CHCH$_2$.Cl \]

KCN \[ \xrightarrow{\text{H}^+} \text{CH}_3$.CH = CHCH$_2$.COOH \]

24. For empirical formula of (Y)

<table>
<thead>
<tr>
<th>Element</th>
<th>%</th>
<th>Relative no. of atoms</th>
<th>Simplest ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>49.31</td>
<td>4,10</td>
<td>3</td>
</tr>
<tr>
<td>H</td>
<td>9.59</td>
<td>9.59</td>
<td>7</td>
</tr>
<tr>
<td>N</td>
<td>19.18</td>
<td>1.37</td>
<td>1</td>
</tr>
<tr>
<td>O</td>
<td>21.92</td>
<td>1.37</td>
<td>1</td>
</tr>
</tbody>
</table>

.: Empirical formula of (Y) is C$_3$.H$_2$.NO.

(Y) reacts with Br$_2$ and NaOH to give (Z) and (Z) reacts with HNO$_2$ to give ethanol and thus (Y) seems to have —CONH$_2$ group.

25. **TIPS/Formulae:**

\[ \text{C}_6\text{H}_5$.OH \[ \xrightarrow{\text{Carboxylic acid}} \text{B} + \text{C} \]

\[ \text{CH}_3\text{CH}_2$.NH$_2$ \[ \xrightarrow{\text{HNO}_2} \text{CH}_3\text{CH}_2$.OH \]

Y is formed from (X) having Cl on treatment with NH$_3$ and so (X) is CH$_3$.CH$_2$.COCl i.e. propanoyl chloride.

CH$_3$.CH$_2$.COCl + NH$_3$ → CH$_3$.CH$_2$.CONH$_2$
Aldehydes, Ketones and Carboxylic Acids

(i) Since E (C₂H₅O) forms a 2, 4-dinitrophenylhydrazone but does not reduce Tollen’s reagent and Fehling solution, it must be a ketone, CH₃.CO.CH₃.

(ii) The compound E (established as ketone) is obtained by heating compound B with Ca(OH)₂, B must be CH₃.COOH.

(iii) Compound B is obtained by the oxidation of D, the latter must be ethyl alcohol, C₂H₅OH and hence C must be ethyl acetate, CH₃.COOCH₃.

(iv) Since compound A when treated with ethyl alcohol gives acetic acid (B) and ethyl acetate (C), it must be acetic anhydride.

\[
\begin{align*}
\text{CH₃CO.O.CO.CH₃} + \text{C₂H₅OH} & \rightarrow \text{CH₃COOH} + \text{CH₃COOC₂H₅} \\
(A) & \rightarrow (B) \rightarrow (C)
\end{align*}
\]

\[
\begin{align*}
\text{CH₃COCH₂} & \xrightarrow{\text{Ca(OH)}₂\text{, heat}} \text{CH₃COOH} + \text{C₂H₅OH} \\
(E) & \rightarrow (B) \rightarrow (C)
\end{align*}
\]

26. CH₃CHO<CH₂COCH₃

<CH₂COCH₂.COCH₃<CH₂COCH₂CH₁

27. PCl₅ + SO₂ \rightarrow SOCl₂ + POCl₃

(A) \rightarrow (B)

SOCl₂ + CH₃COOH \rightarrow CH₃COCl + SO₂ + HCl

(A) \rightarrow (B)

2CH₃COCl+(CH₃)₂Cd \rightarrow 2CH₃-CO-CH₃+CdCl₂

(C) \rightarrow (D)

28. TIPS/Formulae:

A \xrightarrow{\text{dry KOH}} \text{B} \text{Ct}

\[
\begin{align*}
\text{Zn/} & \text{H₂O} \text{but-2-ene} \\
\text{CH₃CHO}
\end{align*}
\]

The reaction of gas (A) with but-2-ene followed by treatment with Zn/H₂O gives CH₃CHO. This shows that the gas (A) is ozone (O₃).

\[
\begin{align*}
\text{CH₃CH=CHCH₃+O₃} & \rightarrow \text{CH₃CH} \\
\text{O} & \rightarrow \text{CHCH₃} \\
\text{Zn/} & \text{H₂O} \rightarrow 2\text{CH₃CHO}+\text{H₂O₂}
\end{align*}
\]

Reaction of ozone with KOH.

3KOH + 2O₃ \rightarrow 2KO₃ + KOH.H₂O + ½O₂↑

(A) \rightarrow (C)

Pot. ozonide, B (Red colour)

29. TIPS/Formulae:

C₆H₆ \xrightarrow{\text{dil. H₂SO₄}} \text{B \xrightarrow{\text{anhydrous AlCl₃}}} \text{RCOCl + C₆H₆}

(A) \rightarrow (B) \rightarrow (C)

C + Yellow compound (D)

(i) Formation of (B) from benzene and acid chloride in presence of anhydrous AlCl₃ (Friedel-Craft reaction) indicates that it is a ketone, C₆H₅.COR.

(ii) Further the ketone (B) reacts with alkaline iodine forming yellow compound (D) (haloform reaction). This indicates that one of the alkyl groups in ketone B is - CH₃. Hence it should be C₆H₅.CO.CH₃.

(iii) Since ketone (B) is also formed from the hydrocarbon C₆H₆ (A) by reaction with dil. H₂SO₄ and HgSO₄, the hydrocarbon (A) must have an acetylenic hydrogen atom, i.e. = C = H grouping. Hence (A) must be C₆H₅.C=CH.

Thus compounds (A) to (D) are

C₆H₅.C=CH C₆H₅.CO.CH₃ C₆H₅.COOGH CH₃

(A) (B) (C) (D)

Formation of (B) from (A)

\[
\begin{align*}
\text{C₆H₅.C=CH} & \xrightarrow{\text{dil.H₂SO₄}} \text{C₆H₅.C=CH}_2 \\
\text{Phenylacetylene (A)} & \xrightarrow{\text{HgSO₄}} \text{C₆H₅.CO.CH₃} \\
\text{Acetophenone (B)} & \xrightarrow{\text{rearranges}} \text{C₆H₅.CO.CH₃}
\end{align*}
\]

30. (i) β-Keto acids are unstable and undergo decarboxylation most readily.

31. CH₃

\[
\begin{align*}
\text{CH₃} & \xrightarrow{\text{dil KMnO₄}} \text{CH₃} \\
\text{CH₃} & \xrightarrow{\text{H₂O₄}} \text{OH}
\end{align*}
\]

The last step is intramolecular aldol condensation.

32. We know that esters on treatment with excess of methyl magnesium chloride either give secondary alcohols (from alkyl formates) or tertiary alcohols (from esters other than formates). However, tertiary alcohols are not easily oxidised, hence the alcohol should be secondary alcohol and thus ester is alkyl formate. Hence ester A (C₄H₉.O₂) should be HCOO.C₂H₅. Thus the various reactions and nature of compound B can be established as below:

\[
\begin{align*}
\text{O} & \rightarrow \text{OMgBr} \\
\text{C-OC₃H₇} & \rightarrow \text{CH₃MgBr} \rightarrow \text{CH₃-C-OC₃H₇} \rightarrow \text{CH₃-C-OC₃H₇} \\
\text{H} & \rightarrow \text{H₂O} \rightarrow \text{CH₃-C-O(OH)} \rightarrow \text{CH₃-C-O(OH)} \\
\text{H} & \rightarrow \text{Ethanal}
\end{align*}
\]

H⁺

\[
\begin{align*}
\text{CH₃-C-OH} & \rightarrow \text{CH₃} \\
\text{H} & \rightarrow \text{Isopropanol [B]}
\end{align*}
\]

\[
\begin{align*}
\text{NaCl} & \rightarrow \text{O} \\
\text{CH₃-C-ONa} & \rightarrow \text{H⁺} \rightarrow \text{CH₃COOH}
\end{align*}
\]

(haloform reaction)
33. Following informations are provided by the problem.
   (i) Since aldehyde A (C_11H_8O) gives C_6H_5CHO on ozonolysis, it must have a benzene nucleus and a side chain. The side chain should have five carbon (C_1-C_5), three hydrogen (H_8-H_3=H_2) and one oxygen atom, i.e., it should be C_5H_3O. Further the compound A has an aldehydic group, so the side chain can be written as C_5H_3CHO.
   (ii) Formation of two moles of B from one mole of A by ozonolysis indicates that the side chain must possess two unsaturated linkages, one of which must be alkyne type, suggested by very low number of hydrogen atoms.
   (iii) Further since the aldehyde A does not undergo aldol condensation, α-hydrogen is absent and hence triple bond should be present between C_2 and C_3.
   (iv) Thus the side chain C_5H_3CHO of A can be written as –CH=CH–C=C–CHO.
   (v) Thus compound A should possess following structure which explains all the given reactions.

34. C_6H_5 – CH – C = CH \xrightarrow{H^+} C_6H_5 – CH – C = CH + OH_2
   \xrightarrow{-H_2O} C_6H_5C\equiv H \xrightarrow{C = CH} C_6H_5CH = C = CH
   \xrightarrow{H_2O} C_6H_5CH = C = CH \xrightarrow{H^+} C_6H_5CH = C = CH + OH_2
   \xrightarrow{\text{heat (-CO_2)}} C_6H_5CH = CH – COOH

35. \xrightarrow{(C) C_4H_9CHO} \xrightarrow{(i) LiAlH_4 (ii) H^+, \Delta} \xrightarrow{(i) LiAlH_4 (ii) H^+, \Delta}

36. D C\equiv C \xrightarrow{(4) C_6H_5CO_2H}
   D C\equiv C \xrightarrow{(5) CH_3MgBr}
   D C\equiv C \xrightarrow{(6) H_2O / H^+ (-Mg(OH)Br)}

37. C_2H_5OC \xrightarrow{NaOCl} C_2H_5OC \xrightarrow{Br} C_2H_5OC \xrightarrow{(i) KOH (i) HCl} C_2H_5OC \xrightarrow{\text{heat (-CO_2)}} C_2H_5OC

38. TIPS/Formulae:
The given reaction can be summarised as below:
[A] C_7H_6O \xrightarrow{(i) CH_3MgBr (ii) H^+} [B] \xrightarrow{[C]} O_3 \xrightarrow{HBr} [D] \xrightarrow{[E]}

Conclusions from the set of reactions
(i) Carbon-hydrogen ratio of A indicates that it is a cyclic compound.

LiAlH_4 reduces only ketonic group to 2° alcoholic group without affecting double bond.
Aldehydes, Ketones and Carboxylic Acids

(ii) Reaction of A with CH₂MgBr indicates that it should have a ketonic group.
(iii) As B undergoes ozonolysis to form C, it must have a double bond, and C must have two carbonyl groups.
(iv) Reaction of C (a dicarbonyl compound) with a base gives a cyclic compound, it indicates that intramolecular condensation have occurred during this conversion. Thus A is cyclohexanone which explains all the given reactions.

41. \[ \text{Ba}^\ddagger \text{CO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{CO}_2 \uparrow \]

CH₂ = CHBr \( \xrightarrow{\text{(i) Mg \text{ ether}}} \) CH₂ = CHMgBr \( \xrightarrow{\text{(ii) CO}_2(X)} \)

CH₂ = CHCOOH \( \xrightarrow{\text{LiAlH}_4} \) CH₂ = CHCH₂OH

\[ \text{(Y)} \]

Formation of CH₂O from (Z)

CH₂ = CHCH₂OH \( \xrightarrow{\text{H}^+} \)

[CH₂ = CHCH₂ \( \xrightarrow{\text{H}^+} \) CH₂CH₂] \( \xrightarrow{\text{Br}^-} \)

BrCH₂CH = CH₂ \( \xrightarrow{\text{O}_3} \) CH₂ = O

42. (i) As both the compounds A and B form a silver mirror with Tollens’ reagent, they have aldehydic group in their structure. In these compounds, B gives positive test with FeCl₃ solution, so it must also have phenolic group in its structure.

Hence, compound A is p-methoxybenzaldehyde and B is p-hydroxyphenylacetaldheyde.

(ii) Compound C gives positive iodoform test, so it must have CH₃CO– group in its structure. Hence compound C is p-hydroxyphenylmethyl ketone.

(iii) Compound D is readily extracted in aqueous NaHCO₃, so it must have -COOH group in its structure. So, compound D is p-methylbenzoic acid.

(iv) Compound E on hydrolysis gives 1,4-dihydroxybenzene. So, compound E is p-hydroxyphenyl vinyl ether.

Hence the structures of all the five compounds are:

43. TIPS/Formulae:
Meso forms are optically inactive.

CH₃CH₂ – C = C – H

\[ \xrightarrow{\text{(i) NaNH₂, (-2HBr)}} \]

CH₂ = C = CH₂

\[ \xrightarrow{\text{HgSO₄, H}_2\text{SO₄}}} \]

CH₂COCH₂

\[ \xrightarrow{\text{NaOH/H}_2\text{O (Aldol condensation)}} \]

CH₂CH₂ – C = C – CH₂CH₃

\[ \xrightarrow{\text{(i) CH₂CH₂Br}} \]

CH₂CH₂ – C = C – CH₂CH₃

\[ \xrightarrow{\text{H}_2\text{Pd} - \text{BaSO₄, (cis-addition of H atoms)}} \]

\[ \xrightarrow{\text{Alkaline KMnO}_4, \text{syn-hydroxylation}}} \]

\[ \text{H}_2\text{O} \]

\[ \text{H} \]

\[ \text{H} \]

CH₂CH₃ (Z)
Thus the possible polymer should be
\[ \text{CH}_3 \]
\[ n\text{CH}_2 = \text{C} - \text{CH} = \text{CH}_2 \longrightarrow \left\{ \begin{array}{l}
\text{CH}_2 - \text{C} = \text{CH} - \text{CH}_2 \\
\text{H} \\
\text{CH}_3 \\
\end{array} \right\}_n \]
Structure of all cis configuration of the polymer.

All cis form

F. Match the Following

1. (A) - r, s; (B) - p, q; (C) - p, q, r; (D) - p, s

2. (a)

\[ \begin{align*}
(1) \quad & \text{C}_9\text{H}_8\text{Cl}_2 \quad \text{CH}_3 \\
& \rightarrow \text{C}_9\text{H}_8\text{CH}_2 + \text{CO}_2 + \text{CH}_3 - \hat{\text{O}} \\
(3) \quad & \text{C}_9\text{H}_8\text{H}_2 \quad \text{CH}_3 \\
& \rightarrow \text{CO}_2 + \text{C}_9\text{H}_8\text{CH}_2 + \text{CH}_3 - \hat{\text{O}} \\
& \text{CH}_3 - \text{C}_9\text{H}_8 \\
(4) \quad & \text{C}_9\text{H}_8 \quad \text{CH}_3 \\
& \rightarrow \text{C}_9\text{H}_8 - \hat{\text{O}} + \hat{\text{O}} - \text{CH}_3 \\
& \text{CH}_3 \\
(2) \quad & \text{C}_6\text{H}_5 \quad \text{CH}_3 \\
& \rightarrow \text{C}_6\text{H}_5 - \hat{\text{O}} + \text{CH}_3 - \hat{\text{O}} \\
\end{align*} \]

G. Comprehension Based Questions

1. (d) \[ \text{CH}_3 - \text{C} = \text{CH}_2 - \text{CHO} \]
Hex-3-ynal

\[ \begin{align*}
1. \text{NaBH}_4 \\
2. \text{PBr}_3 \\
\text{Product 'I'}
\end{align*} \]
Sodium borohydride reduces –CHO
Selectively into –CH_2OH

2. (a)

\[ \begin{align*}
1. \text{Mg} / \text{Ether} \\
2. \text{CO}_2 \\
3. \text{H}_3\text{O}^+ \\
\text{Product 'J'}
\end{align*} \]

Thus "K" is SOCl_2
Aldehydes, Ketones and Carboxylic Acids

For 4-6.
Iodoform test of compound P points out that P has −COCH₃ group which shows that it may be either option (a) or (b) of Q. 16. Further since the dicarbonyl compound R has at least one α-H atom w.r.t to one of the carbonyl groups which is possible when R is produced from (b) of Q. 18; (a) option of Q. 16 will give dicarbonyl compound having two −CHO, none of which has α-H atom.

For 7-9.
Let us summarize the given facts of the problem.

Structures of P, Q, R and S can be established on going backward from the known final product.

7. (b) For 10 - 11
11. (a)
Reactions of compound J (C₆H₄O₃) indicates that it has C = C linkage and −COOH group. Thus, J can be written as C₆H₄CH = CH COOH. Since, J is unsaturated carboxylic acid and it is formed by the reactions of compound I with (CH₃CO)₂O and CH₃COONa, compound I should be an aldehyde (recall Perkin reaction). Thus the whole series of reactions can be written as below.

* Structure of R would be R' when P is (A)
12. (b) \[
\begin{align*}
\text{HOOC} & \xrightarrow{\text{C} = \text{C} \xleftarrow{\text{C}} \text{COOH}} \text{COOH} \\
\text{H} & \xrightarrow{\text{C} = \text{C} \xleftarrow{\text{C}} \text{COOH}} \text{COOH}
\end{align*}
\]

\[
\begin{align*}
\text{H} & \xrightarrow{\text{alk.}} \text{H} \\
\text{H} & \xrightarrow{\text{alk.}} \text{H}
\end{align*}
\]

\[
\begin{align*}
\text{Meso (S), optically inactive}
\end{align*}
\]

\[
\begin{align*}
\text{HOOC} & \xrightarrow{\text{C} = \text{C} \xleftarrow{\text{C}} \text{COOH}} \text{COOH} \\
\text{H} & \xrightarrow{\text{C} = \text{C} \xleftarrow{\text{C}} \text{COOH}} \text{COOH}
\end{align*}
\]

\[
\begin{align*}
\text{H} & \xrightarrow{\text{alk.}} \text{OH} \\
\text{OH} & \xrightarrow{\text{alk.}} \text{OH}
\end{align*}
\]

\[
\begin{align*}
\text{COOH} & \xrightarrow{\text{C} = \text{C} \xleftarrow{\text{C}} \text{COOH}} \text{COOH} \\
\text{H} & \xrightarrow{\text{C} = \text{C} \xleftarrow{\text{C}} \text{COOH}} \text{COOH}
\end{align*}
\]

\[
\begin{align*}
\text{OH} & \xrightarrow{\text{alk.}} \text{OH} \\
\text{OH} & \xrightarrow{\text{alk.}} \text{OH}
\end{align*}
\]

\[
\text{(Racemic Mixture), optically inactive}
\]

13. (a) \[
\text{HOOC-CH=CH-COOH} \xrightarrow{\text{H}_2 / \text{Ni}} \text{Q}
\]

\[
\text{Q} \xrightarrow{\text{H}_2 \text{PO}_4} \text{V}
\]

\[
\text{V} \xrightarrow{\text{Zn-Hg, HCl}} \text{OH}
\]

H. Assertion & Reason Type Questions

1. (d) TIPS/Formulae:
Acetate ion is resonance stabilized while methoxide ion is not.

\[
\text{CH}_3^- \xrightarrow{\text{C}} \text{O}^- \quad \text{Methoxide ion}
\]

\[
\text{Acetate ion}
\]

Hence, acetate ion is less basic than methoxide ion.

2. (c) Haloform reaction is undergone only by ketones, CH₃COOH has 3 α-hydrogens.

3. (a) TIPS/Formulae:
Ozonide can be reduced by (CH₃)₂S to give carbonyl compounds and dimethyl sulphoxide.

\[
\text{R}_\text{C} = \text{O} \xrightarrow{+ (\text{CH}_3)^2 \text{S}} 2\text{R}_\text{C} = \text{O} + (\text{CH}_3)^2 \text{S} = \text{O}
\]
Aldehydes, Ketones and Carboxylic Acids

4. (d) p-Hydroxybenzoic acid has higher boiling point than o-hydroxybenzoic acid due to intermolecular hydrogen bonding. Thus, statement-1 is false. o-Hydroxybenzoic acid shows intramolecular H-bonding thus, statement-2 is true.

I. Integer Value Correct Type

1. 

The number of intra molecular aldol condensation products (α, β - unsaturated carbonyl compound formed from Y is 1.

2. All carboxylic acids and phenols are soluble in aqueous NaOH. Four compounds are soluble in aqueous NaOH.

3. (2) 

No. of –COOH group is '2'

4. (5) General molecular formula for ketones is $C_nH_{2n}O$

\[ C_{12}H_{24}O = 100 \text{ or } 12n + 2n + 16 = 100, n = 6 \]

Possible isomeric ketones with 6 carbon atoms are

(I) \[ \text{CH}_3\text{CH}_2\text{CH}_2\text{C} - \text{CH}_3 \]

(II) \[ \text{CH}_3\text{CH}_2\text{C} - \text{CH}_2\text{CH}_3 \]

(III) \[ \text{CH}_3\text{CH}_2\text{CH}\text{C} - \text{CH}_3 \]

(IV) \[ \text{CH}_3\text{CH}_2\text{C} - \text{CH}_3 \]

(V) \[ \text{CH}_3\text{CH}\text{C} - \text{CH}_2\text{CH}_3 \]

(VI) \[ \text{CH}_3\text{C} - \text{CH}_3 \]

Note that only isomer III has a chiral carbon so on reduction with NaBH$_4$ it will give diastereomeric alcohols, while all other five isomers will give racemic mixture.

5. (4) 

(Guttermann Koch Reaction)
1. (c) \( \text{CH}_3\text{CH}_2\text{COOH} \xrightarrow{\text{Cl}_2 \text{ red P}} \text{CH}_3\text{CHCICOOH} \)

\[ \text{alc.KOH} - \text{HCl} \rightarrow \text{CH}_2 = \text{CHCOOH} \]

2. (b) Aldehydic group gets oxidised to carboxylic group. Double bond breaks and carbon gets oxidised to carboxylic group.

3. (c) 2,4,6-trinitrophenol is also known as picric acid.

4. (a) LiAIH_4 can reduce COOH group and not the double bond.

\[ \text{CH}_2 = \text{CH} - \text{COOH} \xrightarrow{\text{LiAIH}_4} \text{CH}_2 = \text{CH} - \text{CH}_2\text{OH} \]

5. (c) There is no reaction hence the resultant mixture contains CH_3COOC_2H_5 + NaCl.

6. (a) 2-methyl-2-propanol

7. (d) It is Clemmensen’s reduction

8. (b) This reaction is known as cannizarro’s reaction. In this reaction benzaldehyde in presence of 50% NaOH undergoes disproportionation reaction and form one mol of Benzyl alcohol (Red. product) and one mole of sod. benzoate (ox. product)

9. (c) \( pK_a = -\log K_a \), HCOOH is the strongest acid and hence it has the highest \( K_a \) or lowest \( pK_a \) value.

10. (c) \( \text{O} + \text{HN(CH}_3)_2 \rightarrow \text{N(CH}_3)_2\text{OH} \rightarrow \text{N(CH}_3)_2 \)

11. (a) **NOTE**: Addition of HCN to carbonyl compounds is nucleophilic addition reaction. The order of reactivity of carbonyl compounds is Aldehydes (smaller to higher) Ketones (smaller to higher), Then

\[ \text{HCHO} > \text{CH}_3\text{COCH}_3 > \text{Ph.CO.CH}_3 > \text{Ph.COPh} \]

**NOTE**: The lower reactivity of Ketones is due to presence of two alkyl group which shows +I effect. The reactivity of Ketones decreases as the size of alkyl group increases.

12. (a) The correct order of increasing acid strength

\[ \text{CF}_3\text{COOH} > \text{MeOCH}_2\text{COOH} > \text{CH}_3\text{COOH} > (\text{Me})_2\text{CH.COOH} \]

[**NOTE**: Electron withdrawing groups increase the acid strength and electron donating groups decrease the acid strength.]

13. (c) Fruity smell is due to ester formation which is formed between ethanol and acid.

\[ \text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH} \xrightarrow{\text{Conc. H}_2\text{SO}_4} \text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O}. \]

14. (c) CH_3Cl + OH^-

15. (a) Phenol gives a violet colour with neutral ferric chloride solution whereas benzoic acid does not give this test.

16. (d) CCl_3CHO + NaOH

17. (a) CCl_3CHO + NaOH \rightarrow CCl_3CH_2OH + CCl_3COONa

In Cannizarro’s reaction the compounds which do not contain \( \alpha \)-hydrogen atoms undergo oxidation and reduction simultaneously i.e. undergo disproportionation and form one molecule of sodium salt of carboxylic acid as oxidation product and one molecule of alcohol as reduction product.

18. (c) The electron withdrawing (–I) group – Cl withdraws electrons from O–H bond and thus helps the cleavage of the O–H bond releasing hydrogen as H^+. 
23. (d) An excellent reagent for oxidation of 1° alcohols to aldehydes is PCC.

\[
\text{R} - \text{CH}_2 - \text{OH} \xrightarrow{\text{PCC}} \text{R} - \text{CHO}
\]

24. (c) \[\text{CH}_3\text{COOH} \xrightarrow{\text{LiAlH}_4} \text{CH}_3\text{CH}_2\text{OH} \]

\[\xrightarrow{\text{PCl}_5} \]

\[\xrightarrow{\text{Alc. KOH}} \]

\[\text{CH}_2 = \text{CH}_2 \]

Hence the product (C) is ethylene.

25. (b) 

[Diagram showing the Rosenmund's reaction process]
Compounds Containing Nitrogen

Section-A : JEE Advanced/ IIT-JEE

A 1. aniline 2. o-nitrophenol 3. dipolar ion

C 1. (c) 2. (b) 3. (b) 4. (a) 5. (b) 6. (a) 7. (b)
8. (d) 9. (b) 10. (c) 11. (d) 12. (b) 13. (a) 14. (a)
15. (a) 16. (d) 17. (b) 18. (b) 19. (NA) 20. (c) 21. (b)
22. (a) 23. (c)

D 1. (c, e) 2. (a, c) 3. (a, d) 4. (c) 5. (c) 6. (a, d) 7. (b)
8. (b, d) 9. (a, b, e) 10. (a, b, d) 11. (a) 12. (c) 13. (a) 14. (a) 15. (b)

E 3. (i) N, N-dimethyl-p-toluidine, <p-nitroaniline < aniline < p-toluidine.
   (ii) aniline-N-methylanine < methylaniline < dimethylaniline
7. CH₃CH₂CONH₂CH₃CH₂COOH
8. aniline, phenol, phenyl isocyanate, salicylaldehyde, p-hydroxybenzaldehyde
   A B C
9. isopropylamine 11. ethylmethylamine
12. PhNC
14. C₆H₅COCH₃, syn-C₆H₅C(=NOH)CH₃, anti-C₆H₅C(=NOH)CH₃
   A B C
   CH₃CO.NHC₆H₅, CH₃NHCOC₆H₅, C₆H₅NH₂, C₆H₅COOH
   D E F G

21. (CH₃)₂CH–CH–CH₃, (CH₃)₂C–CH₂CH₃

F 1. (A)– p, q, s, t; (B)– s, t; (C)– p; (D)– r 2. (e)

G 1. (d) 2. (d) 3. (b) 4. (a) 5. (b)

H 1. (a) 2. (d) 3. (d) 4. (d)

Section-B : JEE Main/ AIEEE

1. (a) 2. (c) 3. (b) 4. (d) 5. (b) 6. (d) 7. (b)
8. (d) 9. (a) 10. (c) 11. (b) 12. (d) 13. (a) 14. (d)
15. (a) 16. (a) 17. (b)

Section-A

A. Fill in the Blanks

1. aniline.
2. o-Nitrophenol; this isomer involves intramolecular hydrogen bonding whereas the other two isomers have intermolecular hydrogen bonding. Because of this, the former is less polar and hence least soluble in polar solvent water.
3. Dipolar ion. (Salt like)

C. MCQs with ONE Correct Answer

1. (e) NOTE : Secondary amines (aliphatic as well as aromatic) react with nitrous acid to form N-nitrosoamines.
   (C₂H₅)₂NH + HONO → (C₂H₅)₂N – N = O + H₂O
   N-Nitrosodiethylamine
2. (b) CH₃CONH₂ → NaOH + Br₂ → CH₃NH₂
   Acetamide Methylamine
Compounds Containing Nitrogen

3. (b) **NOTE**: Only primary aliphatic and aromatic amines give this test.

\[ \text{CH}_3 + \text{RNH}_2 + 3\text{KOH} \rightarrow \text{RNC} + 3 \text{KX} + 3\text{H}_2\text{O} \]

4. (a) **TIPS/Formulae**: Toluene has electron-donating methyl group. Hence reacts fastest while others have either electron withdrawing groups (*i.e.* -COOH or -NO\(_2\) etc.) or no substituent.

5. (b) **TIPS/Formulae**:

**Empirical Formula = \( n \times \text{Molecular formula} \)**

**Solution**: Since the molecular formula is \( n \) times the empirical formula, therefore, different compounds having the same empirical formula must have different molecular weights.

6. (a) In benzylicamine, electron pair on nitrogen is not delocalised due to lack of conjugation; while in all other compounds it is delocalised and hence lesser available for protonation.

7. (b) **TIPS/Formulae**: The addition is initiated by the attack of \( \text{CN}^- \) group which is a nucleophile.

\[
\begin{align*}
\text{R} - \text{C} = \text{O} & \xrightarrow{(i) \text{CN}^-} \text{R} - \text{C} + \text{OH} \\
& \text{R} - \text{C} \equiv \text{CN} \\
\text{Ketone cyanohydrin} & \\
\end{align*}
\]

8. (d) **TIPS/Formulae**: In the formation of cyanohydrin number of carbon atoms in parent chain increases by one.

\[ \text{CH}_3\text{CH}_2\text{CH}_2\text{Cl} + \text{alc. KCN} \xrightarrow{100^\circ\text{C}} \text{CH}_3\text{CH}_2\text{CH}_2\text{CN} + \text{KCl} \]

9. (b) **TIPS/Formulae**:

\[
\begin{align*}
\text{NH}_3 & \xrightarrow{(-\text{Cl}^-)} \text{Cl} \\
\text{NH}_2 \text{Cl} & \xrightarrow{(-\text{NH}_2)} \text{Cl} \\
\text{NH}_2 \text{CN} & \xrightarrow{(-\text{H}^+)} \text{NH}_2 \text{CN} \\
\text{Benzyne} & \\
\end{align*}
\]

10. (c) N can't have more than 8 electrons in its valence shell as it does not have any \( d \) orbital. In (c), N has 10 electrons.

11. (d) Aliphatic amines are more basic than aromatic amines because in aliphatic amines electron pair on nitrogen is not involved in resonance.

12. (b) **TIPS/Formulae**:

\[
\begin{align*}
\text{CH}_3 - \text{C} & \equiv \text{N} \xrightarrow{\text{II}} \text{CH}_3 - \text{C} & \equiv \text{N} \xrightarrow{\text{H}^+} \\
\text{NH}_2 &dl \text{NH}_2 &dl \text{H}^+ &dl \text{NH}_2 &dl \text{H}^+ \\
\text{CH}_3 - \text{C} & \equiv \text{N} \xrightarrow{\text{II}} \text{CH}_3 - \text{C} & \equiv \text{N} \xrightarrow{\text{H}^+} &dl \text{NH}_2 &dl \text{H}^+ \\
\text{NH}_2 &dl \text{NH}_2 &dl \text{H}^+ &dl \text{NH}_2 &dl \text{H}^+ \\
\text{CH}_3 - \text{C} & \equiv \text{N} \xrightarrow{\text{II}} \text{CH}_3 - \text{C} & \equiv \text{N} \xrightarrow{\text{H}^+} &dl \text{NH}_2 &dl \text{H}^+ \\
\text{NH}_2 &dl \text{NH}_2 &dl \text{H}^+ &dl \text{NH}_2 &dl \text{H}^+ \\
\end{align*}
\]

The protonated form of II would be III which is more stable because here the contributing structures (III) and (IV) are equivalent.

In \( \text{CH}_3 - \text{N} \equiv \text{H} - \text{CH}_3 \), the availability of electron pair increases due to the +1 effect of two \( \text{CH}_3 \) groups while in \( \text{CH}_3\text{CH}_2\text{NH}_2 \), +1 effect of only one ethyl group is operative. In \( \text{CH}_3 - \text{C} = \text{NH}_2 \), the electron availability on nitrogen decreases due to resonance as shown below.

\[
\begin{align*}
\text{CH}_3 - \text{C} & \equiv \text{N} \xrightarrow{\text{II}} \text{CH}_3 - \text{C} & \equiv \text{N} \xrightarrow{\text{H}^+} &dl \text{NH}_2 &dl \text{H}^+ \\
\text{CH}_3 - \text{C} & \equiv \text{N} \xrightarrow{\text{II}} \text{CH}_3 - \text{C} & \equiv \text{N} \xrightarrow{\text{H}^+} &dl \text{NH}_2 &dl \text{H}^+ \\
\text{CH}_3 - \text{C} & \equiv \text{N} \xrightarrow{\text{II}} \text{CH}_3 - \text{C} & \equiv \text{N} \xrightarrow{\text{H}^+} &dl \text{NH}_2 &dl \text{H}^+ \\
\text{CH}_3 - \text{C} & \equiv \text{N} \xrightarrow{\text{II}} \text{CH}_3 - \text{C} & \equiv \text{N} \xrightarrow{\text{H}^+} &dl \text{NH}_2 &dl \text{H}^+ \\
\end{align*}
\]

Therefore, the order of basic strength would be \( 1 > 3 > 2 > 4 \).

13. (a) \( \text{C}_2\text{H}_4 \xrightarrow{\text{K}_2\text{Cr}_2\text{O}_7/\text{H}^+} \text{C}_2\text{H}_4 \xrightarrow{\text{Amn. AgNO}_3} \text{Silver mirror} \xrightarrow{\text{H}_3\text{NCONH}_2\text{HCl}} \text{(C)} \)

**NOTE**: Reaction of (B) indicates that it is an aldehyde which thus should be \( \text{C}_2\text{H}_5\text{CHO} \) or \( \text{CH}_2\text{CH}_2\text{CHO} \), hence C should be \( \text{CH}_3\text{CH}_2\text{CH} = \text{NNHCONH}_2 \).
D. MCQs with ONE or More Than One Correct

1. (c, e) TIPS/Formulæ: Silver nitrite, being a salt of nitrous acid, occurs in two tautomeric forms.

\[
\begin{align*}
\text{Ag} - \text{O} - \text{N} &= \text{O} \quad \text{Ag} - \text{N} \quad \text{O} \\
\text{nitrile form} & \quad \text{nitro form (pentavalent nitrogen)}
\end{align*}
\]

\[
\text{NO}_2^- \text{ ion from AgNO}_2 \text{ may exist in two tautomeric forms, } -\text{O} - \text{N} = \text{O} \text{ (nitrite ion) forming alkyl nitrites,}
\]

\[
2\text{C}_2\text{H}_5\text{Br} + 2\text{AgNO}_2 \rightarrow \text{C}_2\text{H}_5\text{NO}_2 + \text{C}_2\text{H}_5\text{ONO} + 2\text{AgBr}
\]

2. (a, c) This is an example of Hoffmann degradation of amides.

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{R} - \text{C} - \text{NH}_2 + \text{Br}_2 & \rightarrow \text{R} - \text{C} - \text{NHB}r + \text{HBr}
\end{align*}
\]

\[
\begin{align*}
\text{R} - \text{C} \cdot \text{NHB}r + \text{KOH} & \rightarrow \text{R} - \text{C} \cdot \text{N}^- \text{Br} + \text{H}_2\text{O} + \text{KBr}
\end{align*}
\]

\[
\begin{align*}
\text{R} - \text{C} \cdot \text{N}^- \text{Br} & \rightarrow \text{R} - \text{C} \cdot \text{N} \\
\text{rarrangement} & \rightarrow \text{R} - \text{N} = \text{C} = \text{O} \quad \text{H}_2\text{O} \rightarrow \text{R} - \text{NH}_2
\end{align*}
\]

3. (a, d) TIPS/Formulæ: Nitro group decreases the electron density at the meta-position in comparison to ortho and para position due to –I and –M effects.

![Nitro group effect](image)

The above intermediate is a resonance hybrid of three structures, hence is more stable than the corresponding intermediate from ortho and para-attack.

4. (c) In 1³ structure N has complete octet, whereas in II³ structure N has 10e in its valence shell. Because of 1 double and 3 single bonds of N.

5. (c) TIPS/Formulæ: Anilinium hydrochloride has ionisable chlorine whereas chlorobenzene has non ionizable chlorine. Thus anilinium hydrochloride gives white precipitate of AgCl with AgNO₃,

\[
\text{C}_6\text{H}_5\text{NH}^+\text{Cl}^- + \text{AgNO}_3 \rightarrow \text{C}_6\text{H}_5\text{NH}^+\text{NO}_3^- + \text{AgCl} \downarrow
\]

In chloroaniline, –Cl is directly attached to benzene ring, hence it is non-reactive.

6. (a, d) If \(\text{C}_6\text{H}_5\text{NH}_2 + \text{O} = \text{C}(\text{CH}_3)_2 \rightarrow \text{C}_6\text{H}_3\text{N} = \text{C}(\text{CH}_3)_2\),

\[
\begin{align*}
\text{C}_6\text{H}_6\text{NH}_2 + \text{O} &= \text{C}(\text{CH}_3)_2 \rightarrow \text{C}_6\text{H}_3\text{N} = \text{C}(\text{CH}_3)_2 \\
\text{C}_6\text{H}_6\text{NH}_2 + \text{O} &= \text{C}(\text{CH}_3)_2 \rightarrow \text{C}_6\text{H}_3\text{N} = \text{C}(\text{CH}_3)_2
\end{align*}
\]

23. (c) Only primary aromatic amines undergo diazotisation followed by coupling.
7. (b) \[ C_6H_2N_2Cl + \text{OH}^- \xrightarrow{\text{Coupling reaction}} p\text{-Hydroxyazobenzene} \]

8. (b, d) NOTE: Only primary amines give carbamidine test. Hence 2,4-dimethylanilinc and p-methyl-benzylamine both give this test.

9. (a,b,c) Lower amines like \( \text{NH}_3, \text{CH}_3\text{NH}_2 \) and \( (\text{CH}_3)_2\text{NH} \) break diborane molecule unsymetrically, while larger amines like \( (\text{CH}_3)_3\text{N} \), \( \text{C}_2\text{H}_5\text{N} \) break diborane in symmetrical manner.
\[
\text{B}_2\text{H}_6 + 2\text{NH}_3 \rightarrow [\text{H}_2\text{B}(\text{NH}_3)_2]^+ [\text{BH}_4^-] \\
\text{B}_2\text{H}_6 + 2\text{NH}_3 \rightarrow 2\text{H}_2\text{B} \rightleftharpoons \text{N(CH}_3)_3
\]

10. (a, b, d) In ice, water molecules are excessively H-bonded giving a cage-like structure which is lighter than water. Primary amines are more basic than tertiary amine, because the protonated \( 1^\circ \) amines are extensively H-bonded and hence more stable than the corresponding protonated \( 3^\circ \) amines.
\[
\text{R} - \text{NH}_2 + \text{H}^+ \rightarrow \text{R} - \text{NH}_3^+; \text{R}_3\text{N} + \text{H}^+ \rightarrow \text{R}_3\text{NH}^+ \\
\text{R} - \text{OH}_2 > \text{R}_3\text{N} - \text{OH}_2 \\
\text{More stable} \quad \text{Less stable}
\]

Acetic acid undergoes dimerisation in benzene.
\[
\text{H}_3\text{C} - \text{O} - \text{H} - \text{O} - \text{C} - \text{CH}_3
\]

11. (a) \( \text{NH}_3 \) group is acetylated by acetic anhydride in methylene chloride (solvent). Note that \( \text{CONH}_2 \) group does not undergo acetylation because here lone pair of electrons is delocalised.
\[
\text{CH}_2 - \text{NH}_2 + (\text{CH}_3\text{CO})_2\text{O} \xrightarrow{\text{CH}_2\text{Cl}_2} \text{CH}_2 - \text{NH} + \text{CH}_3\text{COOH}
\]

12. (c)

13. (a)

14. (a)

15. (b)
E. Subjective Problems

1. (i) CH₃CH₂Cl + alc. KCN → CH₃CH₂CN
   \[\text{H}_2\text{NiH} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2\]

(ii) \[\text{NH}_2 \rightarrow \text{HNO}_2 \rightarrow \text{N}^+ = \text{NCl}^-\]
   \[\text{Cu}_{2}\text{Cl}_2 \rightarrow \text{Cl}^- \rightarrow \text{N}_2\]

(iii) C₆H₆ \[\text{H}_2\text{SO}_4(\text{conc.}) \rightarrow \text{C}_6\text{H}_5\text{NO}_2 \rightarrow \text{Sn/HCl} \rightarrow \text{C}_6\text{H}_5\text{NH}_2\]

(iv) CH₃CHO \[\text{K}_2\text{Cr}_2\text{O}_7 \rightarrow \text{CH}_3\text{COOH} \rightarrow \text{Ca(OH)}_2 \rightarrow \text{CH}_3\text{COCH}_3 \rightarrow \text{NH}_2\cdot\text{HCl} \rightarrow (\text{CH}_3)_2\text{C}=\text{NOH} \rightarrow \text{Acetoxime}\]

(v) Consult (ii)

(vi) C₆H₅CHO \[\text{Oxi.} \rightarrow \text{C}_6\text{H}_5\text{COOH}\]
   \[\text{HNO}_2 \rightarrow \text{C}_6\text{H}_5\text{CONH}_2 \rightarrow \text{Br}_2 \rightarrow \text{C}_6\text{H}_5\text{NH}_2\]

(vii) CH₃\[\text{alk. KMnO}_4 \rightarrow \text{COOH}\]

(viii) \[\text{NH}_2 \rightarrow \text{Br}_2 \rightarrow \text{m-nitrobenzoic acid}\]

4-Nitroaniline

(ix) \[\text{Br}_2/\text{Fe} \rightarrow \text{Br} \rightarrow \text{Br}\]

\[\text{HNO}_3 \rightarrow \text{H}_2\text{SO}_4 \rightarrow \text{Br}\]

\[\text{H}_2\text{SO}_4 \rightarrow \text{Br}\]

\[\text{NO}_2\]

\[\text{p-bromonitrobenzene}\]

On fractional crystallization para isomer crystallizes first.

(x) \[\text{Benzene} \rightarrow \text{CH}_3\text{Cl} \rightarrow \text{HNO}_3 \rightarrow \text{dil.} \rightarrow \text{CH}_3\text{NO}_2\]

4-nitrobenzaldehyde

(xi) \[\text{NO}_2 \rightarrow \text{SN + HCl} \rightarrow \text{NH}_2\]

Nitrobenzene

(xii) \[\text{NaNO}_2/\text{HCl} \rightarrow \text{CuCN} \rightarrow \text{CN}\]

\[\text{H}_2\text{O, }\text{H}^+ \rightarrow \text{NH}_3 \rightarrow \text{CONH}_2\]

\[\text{Benzamide}\]

(xiii) \[\text{NaNO}_2(\text{HCl}) \rightarrow \text{N}_2\text{Cl}^-\]
Compounds Containing Nitrogen

\[
\begin{align*}
\text{CuCN} & \quad \text{Sn + HCl} \\
\text{COOH} & \quad \text{HNO}_3 \quad \text{H}_2\text{SO}_4 \quad \text{COOH} \quad \text{NO}_2 \\
\text{Sn/HCl} & \quad \text{NaNO}_2 \quad \text{HCl} \quad \text{F} \\
\text{NH}_2 & \quad \text{NaHCO}_3 \quad \text{HNO}_3 \quad \text{NH}_2
\end{align*}
\]

(xiv) Going backward, we can easily solve the problem.

\[
\begin{align*}
\text{NO}_2 & \quad \text{heat} \quad \text{NO}_2 \quad \text{HNO}_3 \quad \text{0-5°C} \quad \text{NO}_2 \\
\text{NH}_2 & \quad \text{H}_2\text{SO}_4 \quad 100°C
\end{align*}
\]

2. (i) Aniline is a weak base than cyclohexylamine because of resonance while there is no resonance in cyclohexylamine.

\[
\begin{align*}
\text{Resonating} & \quad \text{Structures of aniline} \quad \text{Cyclohexylamine (No resonance)}
\end{align*}
\]

(ii) o-nitrophenol shows intramolecular H-bonding and p-nitrophenol shows intermolecular H-bonding and thus its several molecules associate with each other. The ortho isomer goes with the steam due to its low boiling point.

(iii) TIPS/Formulæ: Two factors operate in deciding the basicity of alkyl amines.

(a) Inductive effect
(b) Solvation effect

(a) Inductive effect. The alkyl group being electron releasing increases the charge density on nitrogen. This in turn increases the basicity of amines. The expected order of basicity is

\[
R_3\text{N} > R_2\text{NH} > \text{RNH}_2 > \text{NH}_3
\]

(b) Solvation effect. Because of the positive charge carried by the conjugate acid of an amine, it is stabilised by the hydrogen bonding with the solvent water. The larger the number of hydrogens attracted to the nitrogen in the conjugate acid, the larger is its stability and thus larger is the basicity of the corresponding base. The expected order of basicity of the alkylamines will be

\[
\text{NH}_3 > \text{RNH}_2 > R_2\text{NH} > R_3\text{N}
\]

The inductive and solvent effects predict the opposite trend in the basicity of alkylamines. In going from \(R_2\text{NH}\) to \(R_3\text{N}\) the solvation effect plays a more dominating role as compared to the inductive effect making \(R_2\text{NH}\) more basic than \(R_3\text{N}\).

A simple explanation is that the steric factor in \(R_3\text{N}\) makes the availability of a lone pair of electrons on nitrogen poor than in the dialkylamine, predicting \(R_2\text{NH}\) a stronger base than \(R_3\text{N}\).

(iv) The nitro group in nitrobenzene strongly deactivates the benzene ring due to \(–I\) and \(–M\) effects. This decreases the reactivity of benzene ring towards Friedel-Crafts alkylation.

(v) TIPS/Formulæ: –NO\(_2\) group is electron withdrawing, hence \(m\)-directing whereas –CH\(_2\)NO\(_2\) is not.

(a) Given that compound is an aryl fluoride having electron-withdrawing –NO\(_2\) group at \(para\) position of fluoride atom which activates the fluoride due to –M and –E effects for nucleophilic substitution \((S_NAr)\), hence reaction with NaOH will liberate \(F^-\) as NaF.

(b) The given compound is an aryl fluoride having \(–\text{CH}_2\text{NO}_2\) group in the meta position which is not capable of activating aryl fluoride (absence of \(–M\) and \(–E\) effects because NO\(_2\) group is present in \(m\)-position and also not conjugated to benzene ring) for nucleophilic substitution, hence aq. NaOH will not displace fluorine here, i.e. no \(F^-\) will be formed.

(vi) (a) \(–\text{N} = \text{O}\) group is electron releasing, hence \(o\)-, \(p\)-directing

(b) –NO\(_2\) group is electron withdrawing, hence \(m\)-directing

3. (i) TIPS/Formulæ: Presence of +I group increases the basicity whereas presence of –I group decreases the basicity.

\[
\begin{align*}
\text{NH}_2 & \quad \text{NH}_2 & \quad \text{NH}_2 & \quad \text{CH}_3 – \text{N} – \text{CH}_3 \\
\text{NO}_2 & \quad \text{NH}_2 & \quad \text{NH}_2 & \quad \text{CH}_3 \quad \text{CH}_3 \\
\text{NH}_2 & \quad \text{NHCH}_3 & \quad \text{CH}_2\text{NH}_2 & \quad (\text{CH}_3)_2\text{NH}
\end{align*}
\]

(ii)
The ease with which the lone pair of electron (unshared) on the N-atom co-ordinates with a proton determines the relative basic strength of amines.

4. (i) \[
\begin{align*}
\text{CONH}_2 & \quad \text{CN} & \quad \text{COOH} \\
\text{NH}_2 & \quad \text{N} & \quad \text{O}
\end{align*}
\]

(ii) \[
\begin{align*}
\text{N(CH}_3)_2 & \quad \text{N(CH}_3)_2 \\
\text{O} & \quad \text{NO}_2
\end{align*}
\]

(iii) \[
\begin{align*}
\text{CONH}_2 & \quad \text{CN} & \quad \text{COOH} \\
\text{N} & \quad \text{H}^+ & \quad \text{H}_2\text{O} & \quad \Delta
\end{align*}
\]

(iv) \[
\begin{align*}
\text{NH}_2 & \quad \text{N} & \quad \text{O} \\
\text{NO}_2 & \quad \text{NaNO}_3 & \quad \text{HCl} & \quad \text{C}_2\text{H}_5\text{OCH}_3 & \quad \text{NO}_2 & \quad \text{OCH}_3
\end{align*}
\]

2, 4-Dinitroaniline

5. Hoffmann degradation reaction.

\[
\text{CH}_3\text{CONH}_2 + \text{Br}_2 + 4\text{KOH} \rightarrow \text{CH}_3\text{NH}_2 + \text{K}_2\text{CO}_3 + 2\text{KBr} + 2\text{H}_2\text{O}
\]

6. NOTE: Carbylamine reaction is a distinct test for primary amines. All primary amines (aliphatic or aromatic) on heating with alcoholic KOH and CHCl₃ give unpleasant or foul smell of isocyanide which is easily detected.

\[
\text{C}_2\text{H}_5\text{NH}_2 + \text{CHCl}_3 + 3\text{KOH} (\text{alc}) \rightarrow \text{C}_2\text{H}_5\text{NC} + 3\text{KCl} + 3\text{H}_2\text{O}
\]

Diethyamine, a 2° amine, does not respond this test.

7. Calculation of molecular wt. of (B)

We know, meq. of Ag = meq. of Ag salt

\[
\frac{\text{Wt. of Ag}}{\text{Wt. of salt}} = \frac{\text{Wt. of salt}}{\text{Eq. wt. of Ag}}
\]

\[
\frac{59.67}{108} = \frac{100}{E_{\text{salt}}} \quad \text{or} \quad E_{\text{salt}} = 181
\]

\[
E_{\text{salt}} = E_{\text{Ag}} + E_{\text{Anion}} \quad E_{\text{anion}} = 181 - 108 = 73
\]

For monobasic acid (B), adding one H, Mol. wt. = Eq. wt. + 1 = 73 + 1 = 74

B being monobasic can be represented as \( C_n \text{H}_{2n+1} \text{COOH} \)

\[
74 = 12n + (2n + 1) + 1 + 12 + 16 + 16 + 1 \quad \Rightarrow n = 2
\]

\[ \therefore \text{B} = \text{C}_2\text{H}_5\text{COOH} \]

Nature of A: Since B is obtained by the action of A with NaOH followed by hydrolysis, so A is an amide, \( \text{CH}_3\text{CH}_2\text{CONH}_2 \).

Reaction:

\[
\text{CH}_3\text{CH}_2\text{CONH}_2 \xrightarrow{\text{NaOH}} \text{CH}_3\text{CH}_2\text{COONa} \quad \text{(A)} \quad \text{(Propanamide)}
\]

\[
\text{CH}_3\text{CH}_2\text{COONa} \xrightarrow{\text{HOH}} \text{CH}_3\text{CH}_2\text{COOH} \quad \text{(B)} \quad \text{(Ethanoic acid)}
\]

8. TIPS/Formulae:

(i) Carbarylamine reaction involves reaction of a primary amine with alc. KOH and CHCl₃ which results a product containing isocyanide group with unpleasant smell.

(ii) Rieger-Tiemann reaction of phenol produces o and p isomers.
Compounds Containing Nitrogen

Solution of compound A in chloroform when treated with alcoholic KOH yields compound C (C\textsubscript{6}H\textsubscript{5}NH\textsubscript{2}) having an unpleasant odour which may be due to isocyanide. Hence the above reaction may be an example of carbylamine reaction. Therefore, compound A must be aniline (C\textsubscript{6}H\textsubscript{5}NH\textsubscript{2}) and C must be phenyl isocyanide (C\textsubscript{6}H\textsubscript{5}NC).

\[ \text{C}_{6}\text{H}_{5}\text{NH}_{2} + \text{CHCl}_{3} + 3\text{KOH} \rightarrow \text{C}_{6}\text{H}_{5}\text{NC} + 3\text{KCl} + 3\text{H}_{2}\text{O} \]

Aniline, A  Phenyl isocyanide, C

Alkaline aqueous layer of B when heated with chloroform gives D and E which are isomeric with each other and have molecular formula C\textsubscript{6}H\textsubscript{4}O\textsubscript{2}. This indicates the possibility that Reimer-Tiemann reaction would have taken place. Hence compound B must be phenol and compounds D and E are o- and p-hydroxybenzaldehydes. This can be represented in the following way.

\[ \text{Phenol, B} \quad \text{CHCl}_{3} \quad \text{(i) KOH, heat} \quad \text{(ii) H}^+ \]

\[ \text{OH} \quad \text{CHO} \quad \text{CHO} \]

\[ \text{(D) \quad o- Hydroxybenzaldehyde} \quad (\text{Salicylaldehyde}) \quad \text{p-Hydroxybenzaldehyde} \]

9. Let us summarise the given facts.

112 ml of colourless, odourless gas at S.T.P. + Residue

\[ \text{(i) aq. HCl} \quad \text{(ii) NaNO\textsubscript{2},0\textdegree C} \quad \text{Basic nitrogen compound (0.295 g)} \quad \text{CHCl}_{3} \quad \text{KOH} \quad \text{Foul smelling gas} \]

\[ \text{distilled aq. sol.} \quad \text{OH}^-/\text{I}_2 \quad \text{Yellow ppt.} \]

Organic liquid (no N)

Reaction of the original compound with alcoholic potash and chloroform to give foul smelling gas indicates that it contains a primary --NH\textsubscript{2} group.

\[ \text{R -- NH}_2 + \text{CHCl}_3 + \text{KOH} \rightarrow \text{R -- NC} \uparrow \]

(Basic compound) Carbylamine (foul smelling)

**Determination of mol. weight of the amine:**

112 ml. of gas is evolved at S.T.P. by 0.295 g of amine

\[ \frac{0.295}{112} \times 22400 = 59 \]

Hence the mol. wt. of the amine = 59

\[ \therefore \text{Mol. wt. of the alkyl group} = 59 - 16 = 43 \]

Nature of alkyl gp. of mol. wt. 43 = C\textsubscript{3}H\textsubscript{7}-

Thus the amine may be either

\[ \text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2 \text{ or } \text{CH}_3\text{CH} = \text{CHNH}_2 \]

The reaction of amine with NaNO\textsubscript{2}, at 0\textdegree C and all other reactions may thus be written as below:

\[ \text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2 \xrightarrow{(i) \text{HCl}} \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + \text{N}_2 \uparrow \]

\[ \xrightarrow{(ii) \text{NaNO}_2,0\textdegree C} \text{aq.sol.distill} \]

\[ \xrightarrow{} \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \]

\[ \xrightarrow{\text{OH}^-, \text{I}_2} \text{CH}_3\text{CH}_2\text{NH}_2 \]

No yellow ppt.

\[ (\text{CH}_3)\text{CCHNH}_2 \xrightarrow{} (\text{CH}_3)\text{CCHOH} + \text{N}_2 \uparrow \]

Isopropylamine

\[ \xrightarrow{} (\text{CH}_3)\text{CCH}_2\text{OH} \]

\[ \xrightarrow{\text{OH}^-, \text{I}_2} \text{CH}_3\text{I} \quad \text{(Haloform reaction) } \text{yellow} \]

**NOTE:** Since the given reactions correspond to isopropylamine, the original compound may be propylamine or isopropylamine, (CH\textsubscript{3})\textsubscript{2}CHNH\textsubscript{2}.

10. (i) ring deactivated

\[ \text{(ii) Conc. HNO}_3/\text{conc. H}_2\text{SO}_4 \quad \text{mononitration} \]

\[ \text{ring activated} \]

\[ \text{CH}_3\text{CCH}_2\text{OH} \]

\[ \xrightarrow{\text{NaOCH}_3, \text{heat}} \text{OCH}_3 \]

\[ \text{(nucleophilic substitution, }\text{F}\text{ is activated due to }\text{p-NO}_2\text{ (t)}) \]

\[ \text{(iii) } \text{Deactivated benzene ring due to }\text{C} = \text{O} \quad \text{Activated benzene ring due to }\text{N} \]

11. A (C\textsubscript{3}H\textsubscript{7}NH\textsubscript{2}) is a 2° amine CH\textsubscript{3} -- NH -- C\textsubscript{6}H\textsubscript{5} (ethylmethylamine) because the benzene sulphonyl chloride is solid and insoluble in alkali.

\[ \text{H}_3\text{C} \]

\[ \text{NH} + \text{C}_6\text{H}_5\text{SO}_2\text{Cl} \xrightarrow{} \]

\[ \text{H}_5\text{C}_2 \]

\[ \text{H}_3\text{C} \]
Recall that Beckmann rearrangement involves migration of anti-alkyl or aryl group, i.e.,

Since (D) is formed from (B), and (E) from (C), (B) and (C) should have following structures.

From the above set, following conclusions can be drawn.

(i) Since the oily compound F (C₆H₅N) reacts with acetyl chloride, it must have - NH₂ or > NH group. Thus (F) can be written as C₆H₅NH₂ or C₆H₅-NH-H, i.e., it is C₆H₅NH₂ and hence D is C₆H₅NHCOCH₃.

(ii) Compound E on treatment with alkali followed by acidification gives a white solid compound (G), C₆H₅O₂. Thus (G) seems to be an acid, hence it is C₆H₅COOH.

(iii) Since (D) and (E) are isomers of the formula C₆H₅NO, and give C₆H₅NH₂ and C₆H₅COOH respectively, both should be amides having different alkyl or aryl group. Thus (D) should be C₆H₅NHCOCH₃, and (E) must be CH₃NHCOCH₃.

(iv) Since compounds (D) and (E) are formed by the rearrangement of compounds (B) and (C) respectively. Compounds (B) and (C) should be oximes > C = NOH (recall that oximes rearrange to amides - Beckmann rearrangement). Further oximes having different alkyl (aryl) groups show geometrical isomerism (syn and anti), compounds (B) and (C) must have following structures.
Compounds Containing Nitrogen

16. The reaction proceeds via benzyne formation

17. Reaction involving nitro groups:

18. Reaction involving alkyl groups:

19. Reaction involving carboxylic acids:

20. Reaction involving ketones and carboxylic acids:

Test of phenolic group:

Test of amine group:

Test of COOH group:

 характеристика горького запаха метилендианисида (characteristic foul smell of isocyanide)
21. (i) \((\text{CH}_3)_2\text{CH} -^{\text{t}}\text{CH} - \text{CH}_3\) [X], optically active

\[\text{OH} \xrightarrow{\text{aq NaNO}_2/\text{HCl}} (\text{CH}_3)_2\text{C} - \text{CH}_2\text{CH}_3 + \text{NaCl} + \text{N}_2 + \text{H}_2\text{O}\]

(ii) [Y], a 3° alcohol is optically inactive.
(iii) Formation of [Y] from [X].

\[\text{NH}_2 \xrightarrow{\text{NaNO}_2/\text{HCl}} (\text{CH}_3)_2\text{CH} - \text{CH} - \text{CH}_3\]

\[\xrightarrow{\text{2° carbocation}} (\text{CH}_3)_2\text{C}^{+} - \text{CH} - \text{CH}_3\]

\[\xrightarrow{\text{3° carbocation}} (\text{CH}_3)_2\text{C}^{-} - \text{CH}_2\text{CH}_3\]

2. (c) Scheme (III): H \xrightarrow{\text{Acetylene, P}} \text{Nitration} \xrightarrow{\text{red hot Fe, 873 K}} \text{NH}_4\text{HS} \xrightarrow{\text{NO}_2} \text{NO}_2 \xrightarrow{\text{NaNO}_2} \text{NO}_2 \xrightarrow{\text{H}_2\text{O boil}} \text{NO}_2 \xrightarrow{\text{NH}_4\text{HS}} \text{NH}_2 \xrightarrow{\text{conc H}_2\text{SO}_4} \text{SO}_3\text{H} \xrightarrow{\text{conc H}_2\text{SO}_4} \text{SO}_3\text{H} \xrightarrow{\text{dil H}_2\text{SO}_4} \text{O}_2\text{N}_2\text{NO}_2 \xrightarrow{\text{conc H}_2\text{SO}_4} \text{O}_2\text{N}_2\text{NO}_2 \xrightarrow{\text{conc H}_2\text{SO}_4} \text{O}_2\text{N}_2\text{NO}_2 \xrightarrow{\text{conc H}_2\text{SO}_4} \text{O}_2\text{N}_2\text{NO}_2

F. Match the Following

1. (A) \(\text{CH}_3\text{CH}_2\text{CH}_2\text{CN} \xrightarrow{\text{Pd-C/H}_2 \text{ or DIBAL-H}} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2\)

(B) \(\text{CH}_3\text{CH}_2\text{OOCOCH}_3 \xrightarrow{\text{DIBAL-H}} \text{CH}_3\text{CH}_2\text{OH}\)

(C) \(\text{CH}_3\text{CH} = \text{CH}_2\text{OH} \xrightarrow{\text{Pd-C/H}_2} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}\)

(D) \(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2 \xrightarrow{\text{CHCl}_3/\text{KOH}} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NC}\)

Onitride (foul smelling)
G. Comprehension Based Questions

1. (d) The reagent used in Hofmann bromamide reaction is alkaline halogen (NaOH or KOH + X₂).

2. (d) Conversion of (iii) to (iv) involving rearrangement is the slowest step. Species (iii) is electron deficient (N has only 6 electrons), hence it has a tendency to get its octet completed by migration of alkyl group.

3. (b) Since the reaction is intramolecular, no cross product will be formed.
H. Assertion & Reason Type Questions

1. (a) In o-nitrophenol intramolecular H-bonding is possible because OH and NO₂ groups are close to each other. This makes the ortho isomer less acidic as its capacity to donate a proton (H-atom) decreases. There is no such intramolecular H-bonding in the p-isomer.

2. (d) Chlorobenzene is resonance stabilized. Thus aryl halides (chlorobenzene) do not undergo nucleophilic substitution. Reason is correct.

3. (d) TIPS/FORMULAE: Electron donating tendency to a double bond is called +M effect and the transfer of electrons take place towards the attacking reagent due to +E effect.

In strongly acidic conditions, aniline becomes protonated with the result lone pair of electrons is not available to produce +E and +M effects. Thus here aniline becomes less reactive towards electrophilic

4. (d) The colour of the azo-dye formed will be orange red but not blue. However, the colour of dye can said to be due to extended conjugation due to presence of azo group.

Section-B

JEE Main/ AIEEE

1. (a) \( \text{C}_2\text{H}_5\text{NH}_2 + \text{CHCl}_3 + 3\text{KOH} \rightarrow \text{C}_2\text{H}_5\text{N}=\text{C} + 3\text{KCl} + 3\text{HCl} \) (Ethyl isocyanide)

2. (c) \( \text{CH}_3 + \text{CHCl}_3 + 3\text{KOH} \rightarrow \text{CH}_3 + 3\text{KCl} + 3\text{H}_2\text{O} \)

3. (b) The alkyl groups are electron releasing group (+ I), thus increases the electron density around the nitrogen thereby increasing the availability of the lone pair of electrons to proton or lewis acid and making the amine more basic. Hence more the no. of alkyl group more basic is the amine. Therefore the correct order is \( \text{NH}_3 < \text{CH}_3\text{NH}_2 < (\text{CH}_3)_2\text{NH} \)

4. (d) Ethyl isocyanide on hydrolysis form primary amines.

\[ \text{CH}_3\text{CH}_2\text{N} \equiv \text{C} + \text{H}_2\text{O} \xrightleftharpoons{\text{H}^+} \text{CH}_3\text{CH}_2\text{NH}_2 + \text{HCOOH} \]

Therefore it gives only one mono chloroalkane.

5. (b) Wurtz reaction is for the preparation of hydrocarbons from alkyl halide

\[ \text{RX} + 2\text{Na} + \text{XR} \rightarrow \text{R} - \text{R} + 2\text{NaX} \]

6. (d) Benzylamine \( \text{CH}_2\text{NH}_2 \) is most basic. In others the basic character is suppressed due to Resonance (see applications of resonance).

7. (b) \( \text{Element} \% \quad \text{Relative number Simple Ratio of atoms} \)

<table>
<thead>
<tr>
<th>Element</th>
<th>%</th>
<th>Simple Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>20%</td>
<td>20/12 = 1.66</td>
</tr>
<tr>
<td>H</td>
<td>6.67%</td>
<td>6.67/1 = 6.67</td>
</tr>
<tr>
<td>N</td>
<td>46.67%</td>
<td>46.67/14 = 3.33</td>
</tr>
<tr>
<td>O</td>
<td>26.64%</td>
<td>26.64/16 = 1.66</td>
</tr>
</tbody>
</table>

The compound is \( \text{CH}_4\text{N}_2\text{O} \)

Empirical weight = 60; Mol. wt. = 60; \( \therefore n = \frac{60}{60} = 1 \)

Molecular formula = \( \text{CH}_4\text{N}_2\text{O} \) \( \text{NH}_2 - \text{C} - \text{NH}_2 \)

On heating urea loses ammonia to give Biuret

\( 2\text{NH}_2\text{CONH}_2 \rightarrow \text{H}_2\text{NCO.NHCONH}_2 + \text{NH}_3 \)

Biuret with alkaline CuSO₄ gives violet colour. Test for \( -\text{CONH}^- \) group.

8. (d) NOTE: Aromatic amines are less basic than aliphatic amines. Among aliphatic amines the order of basicity is \( 2° > 1° > 3° \). The electron density is decreased in 3° amine due to crowding of alkyl group over N atom which makes the approach and bonding by a proton relatively difficult. Therefore the basicity decreases. Further Phenyl group show -1 effect, thus decreases the electron density on nitrogen atom and hence the basicity.

\( \therefore \text{dimethylamine} (2° \text{ aliphatic amine}) \text{ is strongest base among given choices.} \)

\( \therefore \text{The correct order of basic strength is} \)

Dimethylamine > Methyl amine > Trimethyl amine > Aniline.
9. (a) This is carbylamine reaction.
\[ \text{CH}_3\text{CH}_2\text{NH}_2 + \text{CHCl}_3 + 3\text{KOH} \]
\[ \rightarrow \text{C}_2\text{H}_5\text{NC} + 3\text{KCl} + 3\text{H}_2\text{O} \]

10. (c) Primary aromatic amines react with nitrous acid to yield arene diazonium salts.
\[ \text{ArNH}_2 + \text{NaNO}_2 + 2\text{HX} \xrightarrow{\text{cold}} \text{Ar}^-\text{N} = \text{N}^+\text{X}^- + \text{NaX} + 2\text{H}_2\text{O} \]

1° Aromatic amine

Arenediazonium salt

The diazonium group can be replaced by fluorine by treating the diazonium salt with fluoroboric acid (HBF₄). The precipitated diazonium fluoroborate is isolated, dried and heated until decomposition occurs to yield the aryl fluoride. This reaction is known as the Balz-Schiemann reaction.

\[ \text{Ar}^-\text{N} = \text{N}^+\text{X}^- \xrightarrow{\text{HBF}_4} \text{Ar}^-\text{N}^+\text{BF}_4^- \xrightarrow{\text{heat}} \text{Ar}^-\text{F} + \text{BF}_3 + \text{N}_2 \]

11. (b) \[ \text{R} = \text{NH}_2 + \text{CH}_3 - \text{C} = \text{Cl} \xrightarrow{\text{HCl}} \]
Mol. Mass = 16

Now since the molecular mass increases by 42 unit as a result of the reaction of one mole of CH₃COCl with one-NH₂ group and the given increase in mass is 210. Hence the number of NH₂ group is \(210/42 = 5\)

12. (d) \[ \text{A} = \text{NH}_3 \xrightarrow{\text{B}} \text{B} \xrightarrow{\text{C}} \text{Br}_2 \xrightarrow{\text{KOH}} \text{CH}_3\text{CH}_2\text{NH}_2 \]

Reaction (III) is a Hofmann bromamide reaction formation of CH₃CH₂NH₂ is possible only from a compound CH₃CH₂CONH₂ which can be obtained from the compound CH₃CH₂COO⁻NH₄⁺ (B) in (II) reaction further propanic acid (CH₃CH₂COOH) on reaction with NH₃ produce CH₃CH₂COO⁻NH₄⁺ (reaction I) hence the reaction will be

13. (a) Methyl isocyanate CH₃–N = C = O

14. (d) \[ \text{R} = \text{CH}_2 = \text{NH}_2 + \text{CHCl}_3 + 3\text{KOH (alc)} \rightarrow \]
Carbylamine reaction
\[ \text{R} = \text{CH}_2 = \text{NC} + 3\text{KCl} + 3\text{H}_2\text{O} \]

Alkyl isocynide

15. (a) Arylamines are less basic than alkyl amines and even ammonia. This is due to resonance. In aryl amines the lone pair of electrons on N is partly shared with the ring and is thus less available for sharing with a proton.

In alkylamines, the electron releasing alkyl group increases the electron density on nitrogen atom and thus also increases the ability of amine for protonation. Hence more the no. of alkyl groups higher should be the basicity of amine. But a slight discrepancy occurs in case of trimethyl amines due to steric effect. Hence the correct order is

\( (\text{CH}_3)_2\text{NH} > \text{CH}_3\text{NH}_2 > (\text{CH}_3)_3\text{N} > \text{C}_6\text{H}_5\text{NH}_2 \)

16. (a)

17. (b) 4 moles of NaOH and one mole of Br₂ is required during production of one mole of amine during Hoffmann's bromamide degradation reaction.
Section-A : JEE Advanced/ IIT-JEE

C. MCQs with ONE Correct Answer

1. (d) Glucose being an aldose responds to Tollen’s test while fructose, although a ketose, undergoes rearrangement in presence of basic medium (provided by Tollens's reagent) to form glucose, which then responds to Tollens's test.

2. (b) The two isomeric forms (α - and β -) of D-glucopyranose differ in configuration only at C-1; hence these are called anomers.

3. (a) Cellulose is a polysaccharide composed of only D-glucose units. Every adjacent glucose units are joined by β-glycosidic linkage between C1 of one glucose and C1 of the next.

NOTE: Thus in every glucose units only three -OH groups are free to form triacetate.

4. (d) Nylon and cellulose, both have intermolecular hydrogen bonding, polyvinyl chloride has dipole-dipole interaction, while natural rubber has van der Waal forces which are weakest.

5. (a)

6. (b) It is a β-pyranose hence it is an aldohexose.

7. (a)

D. MCQs with ONE or More Than One Correct

1. (b,c) We know that carbohydrates having acetal linkage are non-reducing while that with hemiacetal linkage are reducing. In the give structure,
Carbohydrates, Amino Acids, Polymers & Miscellaneous Match the Following

X has acetal linkage, hence non-reducing.
Y has hemiacetal linkage, hence reducing.
Further X is α-anomer, while Y is β-anomer of D-(+)-glucose.

2. (a.b.c.d)
Condensation polymers are formed by condensation of a diol or diamine with a dicarboxylic acid.

H₂CO - C - (CH₂)₄ - C - OCH₃ → H₂O/Ni →
HOH₂C - (CH₂)₄ - CH₂OH

O
O

H₂N - C - (CH₂)₄ - C - NH₂ → H₂O/Ni →
H₂NCH₂ - (CH₂)₄ - CH₂NH₂

O
O

H₂N - (CH₂)₄ - NH₂ → H₂O/Ni →
H₂NCH₂ - (CH₂)₄ - CH₂NH₂

O
O

H₂N - (CH₂)₄ - NH₂ → H₂O/Ni →
H₂NCH₂ - (CH₂)₄ - CH₂NH₂

O
O

2. TIPS/Formulæ:
pH = 2 indicates acidic character whereas pH = 10 indicates basic character.

CH₃
H₃N⁺ - C - COOH
H
H

pH = 2

CH₂ - C₆H₅

H₂N - C - COO⁻
H

pH = 10

3. H₂N - CH - CONH - CH - COOCH₃

CH₂ - COOH

Aspartame (Aspartamine)

(i) Four functional groups present in aspartamine are
(a) -NH₂ (Amine)
(b) -COOH (Carboxylic acid)
(c) - C - NH - (Amide)
(d) - C - O - CH₃ (Ester)

(ii) Zwitterion structure is given as follows:

\[
\begin{align*}
\text{CH}_2\text{C}_6\text{H}_5 \\
\text{H}_3\text{N} - \text{CH} - \text{CONH} - \text{CH} - \text{COOCH}_3 \\
\text{CH}_2 - \text{COO}^- \\
\text{H}_2\text{N} - \text{CH} - \text{C} - \text{NH} - \text{CH} - \text{COOCH}_3 \\
\text{CH}_2\text{COOH}
\end{align*}
\]
4. The structure of two possible dipeptides are

5. L-Glucose is an enantiomer of D-glucose, hence

6. In the two disaccharides structure A will be reducing sugar since both monosaccharides units are not linked through their reducing centers, while in structure B both the monosaccharide units are linked through their reducing centers, hence it will be non-reducing.

F. Match the Following

1. (A) : (p) and (s)
   Cellulose is a natural polymer and has a $C_1 - C_4$ $\beta$-glycosidic linkage.

2. (B) : (q) and (r)
   Nylon-6, 6 is a synthetic polymer of hexamethylenediamine and adipic acid and has amide linkages.

(C) : (p) and (r)
Proteins are natural polymers of $\alpha$ amino acids joined by amide linkages (peptide bonds).

(D) : (s)
Sucrose is a disaccharide of $\alpha$-D glucose and $\beta$-D-fructose and has an $\alpha, \beta$-glycosidic linkage.

2. (A) $-$ (r), (s) ; (B) $-$ (t) ; (C) $-$ (p), (q) ; (D) $-$ (r)

H. Assertion & Reason Type Questions

1. (c) Statement-1 is correct, but statement-2 is incorrect because glucose on reaction with Fehling solution gives $Cu_2O$ and not $CuO$.

I. Integer Value Correct Type

1. The basic groups in the given form of lysine is $NH_2$ (not $NH_3$) and $CO_2^-$.

2. Molecular weight of decapptide = 796 g/mol
   Total bonds to be hydrolysed = $(10 - 1) = 9$ per molecule
   Total weight of $H_2O$ added = $9 \times 18 = 162$ g/mol
   Total weight of hydrolysis products = $796 + 162 = 958$ g
   Total weight % of glycine (given) = 47%

   Total weight of glycine in product = $\frac{958 \times 47}{100}$ g = 450 g
   Molecular weight of glycine = 75 g/mol
   Number of glycine molecules = $\frac{450}{75}$ = 6

3. (8)

4. Peptides with isoelectric point (pI) more than 7, would exist as cation in neutral solution (pH = 7) which means the given polypeptide is of basic nature, so it must contain two or more amino groups. Hence IV, VI, VIII and IX are correct options.

5. According to question C $-$ Terminal must be alanine and N $-$ Terminal do have chiral carbon means it should not be glycine. So possible sequence is : 
   Val Phe Gly Ala
   Val Gly Phe Ala
   Phe Val Gly Ala
   Phe Gly Val Ala

6. (1) On hydrolysis, the given peptide gives only one naturally occurring amino acid (glycine).
Section-B

1. (a) Polymerisation starts either by condensation or addition reactions between monomers. Condensation polymers are formed by the combination of monomers with the elimination of simple molecules. Where as the addition polymers are formed by the addition together of the molecules of the monomer or monomers to form a large molecule without elimination of anything.

2. (b) In RNA, the sugar is D-ribose and base is uracil whereas in DNA, the sugar is D-2 deoxyribose and the nitrogenous base is thymine.

3. (c) The given compound is aspirin which is antipyretic and analgesic.

4. (b) Liquid hydrogen and liquid oxygen are used as excellent fuel for rockets. H₂O (l) has low mass and high enthalpy of combustion whereas oxygen is a strong supporter of combustion.

5. (b) Nylon is a polyamide polmer.

6. (b) Cellulose is a linear polymer of β-D-glucose in which C₁ of one glucose unit is connected to C₄ of the other through β-D glucosidic linkage. It does not undergo hydrolysis easily. However on heating with dilute H₂SO₄ under pressure, it does undergo hydrolysis to give only D-glucose.

   \[(C₆H₁₀O₅)n + nH₂O \rightarrow nC₆H₁₂O₆\]  
   \[\text{D-Glucose}\]

7. (b) DNA consists of two polynucleotide chains, each chain forms a right handed spiral with ten bases in one turn of the spiral. The two chains coil to double helix and run in opposite direction held together by hydrogen bonding.

8. (c) RNA contains cytosine and uracil as pyrimidine bases while DNA has cytosine and thymine. Both have the same purine bases i.e., Guanine and adenine.

9. (b) Insulin is a biochemically active peptide hormone secreted by pancreas.

10. (a) Photochemical smog is caused by oxides of sulphur and nitrogen.

11. (c) Nylon is a general name for all synthetic fibres forming polyamides.

12. (c) An antipyretic is a drug which is responsible for lowering the temperature of the feverish organism to normal but has no effect on normal temperature states.

13. (b) In DNA and RNA heterocyclic base and phosphate ester are at C₁ and C₅ respectively of the sugar molecule.

14. (c) Teflon is polymer of CF₂ = CF₂.

15. (b) Cyclization of the open chain structure of D-(+)-glucose has created a new stereocenter at C₁ which explains the existence of two cyclic forms of D-(+)-glucose, namely α- and β-. These two cyclic forms are diastereomers, such diastereomers which differ only in the configuration of chiral carbon developed on hemiacetal formation (it is C₁ in glucose and C₂ in fructose) are called anomers and the hemiacetal carbon (C₁ or C₂) is called the anomeric carbon.
16. (a) The pyrimidine bases present in DNA are cytosine and thymine.

17. (b) The secondary structure of a protein refers to the shape in which a long peptide chain can exist. There are two different conformations of the peptide linkage present in protein, these are α-helix and β-conformation. The α-helix always has a right-handed arrangement. In β-conformation all peptide chains are stretched out to nearly maximum extension and then laid side by side and held together by intermolecular hydrogen bonds. The structure resembles the pleated folds of drapery and therefore is known as β-sheet.

18. (c) **NOTE**: Ozone layer acts as a shield and does not allow ultraviolet radiation from sun to reach earth. It does not prevent infra-red radiation from sun to reach earth.

Thus option (c) is a wrong statement and so it is the correct answer.

19. (d) Bakelite is formed by the reaction of formaldehyde (HCHO) and phenol so the correct answer is (d).

20. (e) Since α-D-(+)-glucose and β-D-(+)-glucose differ in configuration at C-1 atom so they are anomers.

**NOTE**: Anomers are those diastereomers that differ in configuration at C-1 atom. i.e., (c) in the correct answer.

21. (c) The cross linked polymers will be formed by RSiCl₃

\[ nRSiCl_3 + 3nH_2O \rightarrow nR-Si-OH \]

The correct choice is (c)

22. (b) Buna – N is a copolymer of butadiene \((\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2)\) and acrylonitrile \((\text{CH}_2=\text{CHCN})\).

23. (e) **NOTE**: Glucose is considered as a typical carbohydrate which contains –CHO and –OH group.

24. (a) Biuret test produces violet colour on addition of dilute \(\text{CaSO}_4\) to alkaline solution of a compound containing peptide linkage.

Polypeptides, proteins and urea have \(-\text{C} = \text{NH} -\)

(amide) linkage while carbohydrates have glycosidic linkages. So, test of carbohydrates should be different from that of other three.

25. (b) Nylon 6-6 has amide linkage capable of forming hydrogen bonding.
26. (b) RNA has D (−) - ribose and the DNA has 2–Deoxy D (−) – ribose as the carbohydrate unit.

From the structures it is clear that 2\textsuperscript{nd} carbon in DNA do not have OH group.

27. (b) **Molisch's Test**: This is a general test for carbohydrates. One or two drops of alcoholic solution of \(\alpha\)-naphthol is added to 2 ml glucose solution. 1 ml of conc. \(\text{H}_2\text{SO}_4\) solution is added carefully along the sides of the test tube. The formation of a violet ring at the junction of two liquids confirms the presence of a carbohydrate or sugar.

28. (c) Lewis acids are the most common compounds used for initiation of cationic polymerisation. The more popular Lewis acids are SnCl\(_4\), AlCl\(_3\), BF\(_3\) and TiCl\(_4\).

29. (c) With the exception of glycine all the 19 other common amino acids have a uniquely different functional group on the central tetrahedral alpha carbon.

30. (a) Aspirin (Acetyl salicylic acid)

31. (a) \(6\text{CO}_2 + 12\text{NADPH} + 18\text{ATP} \rightarrow \text{C}_6\text{H}_12\text{O}_6 + 12\text{NADP}^{-} + 18\text{ADP}\)

32. (a) Except Dacron all are additive polymers. Terephthalic acid condenses with ethylene glycol to give Dacron.

33. (a) DNA contains ATGC bases

So quinoline is not present in DNA.

34. (c) Water-soluble vitamins dissolve in water and are not stored by the body. The water soluble vitamins include the vitamin B-complex group and vitamin C.

35. (a) Phenelzine is an antidepressant, while others are antacids.

36. (d) Glyptal is used in the manufacture of paints and lacquers.

37. (a) The maximum limit of nitrate in drinking water is 50 ppm. Excess nitrate in drinking water can cause disease such as methemoglobinemia ('blue baby' syndrome).

38. (d) Sodium lauryl sulphate (C\(_{11}\)H\(_{23}\)\(\text{SO}_4\)\(\text{Na}^+\)) is an anionic detergent. Glyceryl oleate is a glyceryl ester of oleic acid. Sodium stearate (C\(_{17}\)H\(_{35}\)\(\text{COO}^-\)\(\text{Na}^+\)) is a soap. Cetyltrimethyl ammonium bromide

\[\left[\text{CH}_3(\text{CH}_2)_{15}^+\text{N(CH}_3)_3\right]^-\text{Br}^-\] is a cationic detergent.

39. (b) High density polythene is used in the manufacture of housewares like buckets, dustbins, bottles, pipes etc. Low density polythene is used for insulating electric wires and in the manufacture of flexible pipes, toys, coats, bottles etc.
MISCELLANEOUS — MATCH THE FOLLOWING FOR IIT-JEE

I. (i) Free radical substitution  (ii) Thermite process
   (iii) Nucleophilic addition  (iv) Cyanamide process;
   (v) Nucleophilic substitution  (vi) Baeyer’s process
   (vii) Homologous pair
   (viii) Electrophilic substitution  (ix) Ostwald’s process
   (x) Homolytic addition.

II. A. (i) (g)  (ii) (d)  (iii) (e)  (iv) (a)
   (v) (f)  (vi) (b)  (vii) (c)
   B. (viii) (o)  (ix) (m)  (x) (k)  (xi) (l)
   (xii) (n)  (xiii) (j)
   C. (xiv) (s)  (xv) (r)  (xvi) (q)  (xvii) (p)
   D. (xviii) (w)  (xix) (v)  (xx) (u)  (xxi) (t).

III. A. (i) (b)  (ii) (c)  (iii) (d)  (iv) (a)
   B. (i) (c)  (ii) (a)  (iii) (d)  (iv) (b)
   C. (i) (b)  (ii) (c)  (iii) (d)  (iv) (a)
   D. (i) (d)  (ii) (b)  (iii) (a)  (iv) (c).

IV. (i)-(f)-6; (ii)-(c)-2; (iii)-(d)-4; (iv)-(b)-1; (v)-(a)-5; (vi)-(e)-3.

V. A. (i) (a)  (ii) (c)  (iii) (b)  (iv) (e)  (v) (d)
   B. (v) (h)  (vii) (j)  (viii) (i)  (ix) (g)  (x) (f)
   C. (x) (n)  (xii) (l)  (xiii) (o)  (xiv) (m)  (xv) (k)
   D. (xvi) (i)  (xvii) (r)  (xviii) (s)  (xxi) (p)  (xx) (q)

VI. (i) (g)  (ii) (h)  (iii) (f)  (iv) (c)
   (v) (e)  (vi) (d)  (vii) (b)  (viii) (a)

VII. (i) Invar/Fe, Ni/watch spring; Nichrome/Co, Ni/heating element; Rydberg/cm⁻¹/109677; Stainless steel/Fe, Cr, Ni, C/cutlery; Boltzmann/kJ deg⁻¹/1.3805 × 10⁻²⁶
   (ii) Friedel-Craft/Lewis acid/anhydrous AlCl₃;
        Fermentation/yeast/ethanol; Dehydrogenation/alcoholic alkali/alkene; Sandmeyer/cuprous chloride/chlorobenzene; Saponification/oil/soap.

VIII. A-(c)-(ii); B-(e)-(iii); C-(a)-(iv); D-(b)-(v); E-(d)-(i).

IX. (A)→(p), (s)  \((\text{CH}_3)_2\text{SiCl}_2 + 2\text{H}_2\text{O}\)

\[\text{Polymerisation} \rightarrow [\text{(CH}_3)_2\text{Si-O}]_n \]

(B)→(p), (q), (r), (t)  \(\text{XeF}_4 + \text{H}_2\text{O} \rightarrow \text{Xe} + \text{XeO}_3 + \text{H}_2\text{F}_2 + \text{O}_2\)

\(\text{SiO}_2 + 4\text{HF} \rightarrow \text{SiF}_4 + 2\text{H}_2\text{O}\)

\(\text{SiF}_4 + 2\text{HF} \rightarrow \text{H}_2[\text{SiF}_6]\)

Solvable hexathorosilicic(IV) acid

(C)→(p), (q)  \(\text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HCl} + \text{HOCI}\)

(D)→(p), (q)  \(\text{VCl}_3 + 7\text{H}_2\text{O} \rightarrow [\text{V(H}_2\text{O})_6]^{3+} + 3\text{Cl}^- + \text{HCl} + \text{HOCI}\)
Analytical Chemistry

Section-A : JEE Advanced/ IIT-JEE

A 1. Fe$^{3+}$ 2. CrO$_2$Cl$_2$
B 1. T 2. T
C 1. (d) 2. (a) 3. (c) 4. (d) 5. (d) 6. (c) 7. (a)
   8. (c) 9. (b) 10. (b) 11. (b) 12. (a) 13. (d)
D 1. (a, b) 2. (a, b, d) 3. (b, c) 4. (c, d) 5. (a or a, c)
E 3. CO$_2$, H$_2$O, NaHCO$_3$, Na$_2$CO$_3$, BaCO$_3$
   A B X Y Z
   4. FeCl$_2$, NH$_4$Cl
   5. FeSO$_4$, H$_2$SO$_4$, FeSO$_4$, NO, Fe$_2$O$_3$, SO$_2$, SO$_3$
   A B C D E F
   6. CO$_2$, H$_2$O, KHCOS, K$_2$CO$_3$, BaCO$_3$
   A B X Y Z
   7. NH$_4$+, Fe$^{2+}$, SO$_4^{2-}$, Cl$^-$
   8. NH$_4$+, Fe$^{2+}$, SO$_4^{2-}$, FeSO$_4$(NH$_4$)$_2$SO$_4$, 6H$_2$O
   9. (NH$_4$)$_2$CrO$_7$, Cr$_2$O$_7^{2-}$, N$_2$, Mg$_3$N$_2$, NH$_3$
   A B C D E
   10. K$_2$O, K$_2$SO$_4$, Al$_2$(SO$_4$)$_3$, 24 H$_2$O
       A B C D
   11. Pb$_2$O$_4$, PbO$_2$, PbI$_2$
       A B C
   12. NH$_3$, CaCO$_3$
       A B
   13. Cu$^{2+}$
       A B C D E
   14. CrO$_2$Cl$_2$, Na$_2$CrO$_4$, PbCrO$_4$, iodide of Millon’s base, NH$_4$Cl
       A B C D
   15. Hgl$_2$, KI, HgS, Hg
       A B C D
   16. (d) 2. (c) 3. (b) 4. (a) 5. (d) 6. (b) 7. (d)
   17. (b) 2. (b)
   18. (c) 2. (b) 3. (a) 4. (a) 5. (b)

Section-B : JEE Main/ AIEEE

A. Fill in the Blanks
1. Fe$^{3+}$; Without oxidation with HNO$_3$, the Fe$^{2+}$ ions present would not be converted into Fe$^{3+}$. So Fe(OH)$_2$ will not be precipitated as its solubility product is higher than that of Fe(OH)$_3$, and as NH$_4$Cl suppresses the ionisation of NH$_4$OH, this solubility product is not reached.
2. Chromyl chloride (CrO$_2$Cl$_2$).

B. True/ False
1. True : Function of ammonium chloride is to suppress the ionisation of NH$_4$OH and thus check the precipitation of Mg(OH)$_2$ because the solubility product of Mg(OH)$_2$ is high. This is used in salt analysis when 3rd group radicals are precipitated. The group reagent are NH$_4$OH in presence of NH$_4$Cl.
2. True : K$_{sp}$ of CuS is less than K$_{sp}$ of ZnS. On passing H$_2$S in acidic medium, the dissociation of H$_2$S is suppressed due to common ion effect and it provides [S$^{2-}$] which is just sufficient to cross over K$_{sp}$ of CuS and not K$_{sp}$ of ZnS. Thus only CuS gets precipitated.

C. MCQs with ONE Correct Answer
1. (d) Sn$^{2+}$ can be precipitated by H$_2$S but not by HCl.
2. (a) NOTE : The ions of group II of salt analysis are precipitated by HCl and H$_2$S whereas members of group IV are precipitated by H$_2$S in alkaline medium.
   i. Bi$^{3+}$ and Sn$^{4+}$ both belong to group II
   ii. They will be precipitated by HCl in presence of H$_2$S.
   Both Bi$^{3+}$ and Sn$^{4+}$ belong to group II of qualitative inorganic analysis and will get precipitated by H$_2$S.
3. (c) **NOTE:**

Only group I cations are precipitated by dil. HCl

\[ \text{SO}_3^{2-} + \text{H}_2\text{SO}_4 \rightarrow \text{SO}_2 + \text{H}_2\text{O} + \text{SO}_4^{2-} \]  

\[ \text{(X)} \]

\[ 3\text{SO}_2 + \text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4 \rightarrow \text{K}_2\text{SO}_4 + \text{Cr}_2(\text{SO}_4)_3 + \text{H}_2\text{O} \]  

\[ \text{green colour solution} \]

Only PbCl\(_2\) and Hg\(_2\)Cl\(_2\) will precipitate as Pb\(^{2+}\) and Hg\(_2\)\(^{2+}\) as first group basic radicals and their solubility product is less than the other radicals.

**NOTE:**: dil. HCl is the first group reagent.

4. (d) Sodium salts are highly soluble. Cu\(^{2+}\) belongs to the II\(^{\text{nd}}\) group in salt analysis and is precipitated as CuS, whereas Zn\(^{2+}\) belongs to the IV group and is precipitated as ZnS after CuS because of higher \(K_{sp}\) of ZnS.

5. (d) \(\text{Pb}^{2+} + 2\text{HCl} \rightarrow \text{PbCl}_2 \downarrow \text{H}_2\text{S} \downarrow \text{PbS} \downarrow \text{H}_2\text{O} \)  

White ppt dissolves on boiling  
[Soluble in hot water]

6. (c) Since the saturated aqueous solution of (X) give white ppt with AgNO\(_3\), so (X) may be Cl\(_2\). Hence

\[ \text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{HCl} \]  

\[ \text{(X)} \]

\[ \text{HCl} + \text{AgNO}_3 \rightarrow \text{AgCl} \downarrow + \text{HNO}_3 \]  

white

\[ 2\text{HCl} + \text{Mg} \rightarrow \text{MgCl}_2 + \text{H}_2 \uparrow \]  

\[ \text{(Y)} \]

7. (a) SO\(_3\) and H\(_2\)S, both being reducing agents, can turn acidified dichromate solution green. SO\(_2\) can be obtained by the action of acid upon sulphite, while H\(_2\)S is evolved by the action of acid upon sulphide. However, SO\(_2\) has a burning sulphur smell which is irritating. H\(_2\)S has rotten egg like smell.

8. (c) **TIPS/Formulae:** For precipitation,

Ionic product > solubility product

HgS having the lowest \(K_{sp}\) among the given compounds will precipitate first.

9. (b) \(\text{Bi(NO}_3)\_3(\text{aq}) + 3\text{KI(aq)} \rightarrow \text{BiI}_3(\text{s}) + 3\text{KNO}_3(\text{aq}) \)

\[ \text{Black} \]

\[ \text{BiI}_3(\text{s}) + \text{KI(aq)} \rightarrow \text{K}[\text{BiI}_4] \]

Orange

The metal ion is Bi\(^{3+}\).

10. (b) Precipitate of Zn(OH\(_2\)) formed at initial stage dissolves in excess of NH\(_4\)OH due to the formation of tetrammine Zn(II) complex.

11. (b) \(\text{Hg}^{2+} + 2\text{KI} \rightarrow \text{Hgl}_2 \downarrow + 2\text{K}^+ \)  

\[ \text{red ppt} \]

\[ \text{Hgl}_2 + 2\text{KI} \rightarrow \text{K}_2[\text{Hgl}_4] \]

\[ \text{Hg}^{2+} + \text{Co}^{2+} + 4\text{SCN}^- \rightarrow \text{Co}[\text{Hg(SCN)}_4] \downarrow \]  

\[ \text{deep blue crystalline} \]

12. (a) In presence of acid, ionisation of H\(_2\)S is suppressed, so less number of S\(^{2-}\) are furnished. Hence only those sulphides are precipitated which has low solubility product \(K_{sp}\); thus only CuS and HgS are precipitated.

13. (d) The group reagent of fourth group is ammoniacal H\(_2\)S by which Zn\(^{2+}\) ion will be precipitated as ZnS, whereas Fe\(^{3+}\) ion and Al\(^{3+}\) ions will be precipitated as hydroxides.

**D. MCQs with ONE or More Than One Correct**

1. (a,b) Al\(^{3+}\) (third group radical) and Cu\(^{2+}\) (fifth group radical) precipitate out as their hydroxide with NH\(_3\)Cl and eq. NH\(_4\) (NH\(_4\)OH) which are the group reagents.

2. (a,b,d) The reactions are

\[ 4\text{NaCl} + 3\text{K}_2\text{Cr}_2\text{O}_7 + 6\text{H}_2\text{SO}_4 \rightarrow 2\text{Cr}_2\text{O}_2\text{Cl}_2 + 4\text{NaHSo}_4 + 2\text{KHSO}_4 + 3\text{H}_2\text{O} \]  

(Red vapours)

\[ \text{Cr}_2\text{O}_2\text{Cl}_2 + 4\text{NaOH} \rightarrow \text{Na}_2\text{CrO}_4 + 2\text{NaCl} + 2\text{H}_2\text{O} \]

chromyl yellow chloride solution

3. (b,c) The blue precipitate of Fe\(^{2+}\) ions with potassium ferricyanide is due to formation of Turnbull’s blue

KFe\(^{II}\)[Fe\(^{III}\)(CN)\(_6\)]

Fe\(^{2+}\) + K\(_3\)[Fe(CN)\(_6\)] \rightarrow K. Fe\(^{II}\)[Fe\(^{III}\)(CN)\(_6\)] + 2K\(^+\)

Potassium ferri cyanide

The red colouration of Fe\(^{3+}\) ions with potassium thiocyanate is due to the formation of [Fe(CNS)\(_3\)]

Fe\(^{2+}\) + 3KCN \rightarrow [Fe(CNS)\(_3\)] + 3K\(^+\)  

(Ferric thiocyanate red colour)

4. (c,d) Only group II cations precipitate as sulphide with H\(_2\)S in acidic medium that is (Cu\(^{2+}\), Pb\(^{2+}\)) and (Hg\(^{2+}\), Bi\(^{3+}\))

<table>
<thead>
<tr>
<th>(\text{S}^{2-})</th>
<th>(\text{SO}_4^{2-})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(^{2+})</td>
<td>CuS (pH)</td>
</tr>
<tr>
<td>Ba(^{2+})</td>
<td>BaS (Soluible)</td>
</tr>
<tr>
<td>Pb(OAc)(_2)</td>
<td>PbS (pH)</td>
</tr>
<tr>
<td>Na(_2)[Fe(CN)(_3)]NO</td>
<td>Na(_4)<a href="NOS">Fe(CN)(_3)</a> Colour (not a pH)</td>
</tr>
<tr>
<td></td>
<td>CuSO(_4)(Soluible)</td>
</tr>
<tr>
<td></td>
<td>BaSO(_4)(pH)</td>
</tr>
<tr>
<td></td>
<td>PbSO(_4)(pH)</td>
</tr>
</tbody>
</table>
E. Subjective Problems

1. HNO₃ is strong oxidising agent and it oxidises H₂S to S. So HNO₃ cannot be used to precipitate second group elements.

2. (i) (A) is FeSO₄.₇H₂O because it is light green crystalline solid. Which dissolves in water containing H₂SO₄.

(ii) On strong heating FeSO₄ both SO₂ (B) and SO₃ (C) are evolved. The colour of KMnO₄ disappears due to the formation of MnSO₄.

(iii) SO₂ being a reducing agent turns a dichromate solution green and forms H₂SO₄ in the solution. SO₃ dissolves in water to give H₂SO₄. Therefore, white ppt of BaSO₄ is formed with a solution of Ba(NO₃)₂.

(iv) The brown residue left behind is Fe₂O₃ which is reduced to Fe on heating in charcoal cavity. Fe is magnetic substance.

3. Representing the given facts in the form of equation.

\[(X)(g) \xrightarrow{\text{heat}} A(g) + B(g) + Y(s)\]

16.8g 4.4g 1.8g

The above equation leads to the following facts:

(i) Since the gas A turned lime water milky, it must be CO₂.

(ii) NOTE: The compound Y gives alkaline solution in water which when treated with BaCl₂ forms a white precipitate of Z. Since the compound Z when treated with acid gives effervescence of CO₂, Z and hence Y must be metal carbonate, CO₃²⁻. Hence Y may be written as metal carbonate MCO₃ or M₂CO₃.

(iii) When X is heated, it yields a carbonate (Y) along with the evolution of CO₂ (A) and another gas (B), it must be a bicarbonate.

(iv) The above facts point out that B may be water vapour. Thus the above reaction can be written as below.

\[2\text{MCO}_3 \xrightarrow{\text{heat}} \text{CO}_2 + \text{H}_2\text{O} + \text{M}_2\text{CO}_3\]

16.8g 4.4g 1.8g

Calculation of molecular weight of MCO₃

4.4g of CO₂ is given by 16.8g of MCO₃

\[2 \times \frac{16.8}{4.4} \times 44 = 168 \text{g} \]

Since two molecules of MCO₃ are taking part in the reaction, the molecular weight of

\[\text{MCO}_3(X) = \frac{168}{2} = 84\]

Calculation of atomic weight of metal M

\[\text{MCO}_3 = 84; M + 1 + 12 + 48 = 84\]

\[M + 61 = 84; M = 84 - 61 = 23\]

Thus the metal must be Na and hence the given salt X is NaHCO₃. The above facts coincide with the given thermal decomposition.

\[2\text{NaHCO}_3 \xrightarrow{\text{heat}} \text{CO}_2 + \text{H}_2\text{O} + \text{Na}_2\text{CO}_3\]

\[(X) \quad (A) \quad (B) \quad (Y)\]

\[\text{Na}_2\text{CO}_3 + \text{BaCl}_2 \rightarrow \text{BaCO}_3 + 2\text{NaCl}\]

\[(Z) \quad \text{white}\]

\[\text{BaCO}_3 + \text{HCl} \rightarrow \text{BaCl}_2 + \text{H}_2\text{O} + \text{CO}_2\quad \uparrow\]

Thus A is CO₂, B is H₂O₂, Y is Na₂CO₃.

4. (A) Test (i) of the problem indicates that the mixture contains Cl⁻ ion which is liberated as Cl₂, (yellowish green gas) when heated with MnO₂ and conc. H₂SO₄.

(B) Test (ii) indicates the presence of NH₄⁺ ion in the mixture which gives ammonia when heated with NaOH solution. Since ammonia is basic in nature, it turns red litmus blue. Presence of NH₄⁺ in the mixture is further confirmed by the given test (iv) according to which the gas (NH₃) gives brown precipitate with Nessler’s reagent (alkaline solution of K₄[HgI₄]).

(C) Test (iii) indicates Fe²⁺ ion in the mixture which gives blue precipitate with potassium ferricyanide (note that potassium ferricyanide gives brown ppt. with Fe³⁺ ions).

(D) Red colouration with ammonium thiocyanate indicates that the mixture also contains Fe³⁺ ions which are believed to be formed by the oxidation of Fe²⁺ ions by air.

\[2\text{Fe}^{2+} + 2\text{H}^+ + (\text{O}) \rightarrow 2\text{Fe}^{3+} + \text{H}_2\text{O}\]

Thus the mixture contains FeCl₂ and NH₄Cl.

Ionic reactions:

(i) \[2\text{Cl}^- + \text{MnO}_2 + \text{H}_2\text{SO}_4 + 2\text{H}^+ \rightarrow \text{Mn}^{2+} + \text{SO}_4^{2-} + 2\text{H}_2\text{O} + \text{Cl}_2\uparrow \quad \text{(Yellowishgreen)}\]

(ii) \[\text{NH}_4^+ + \text{OH}^- \xrightarrow{\text{heat}} \text{NH}_3 \uparrow + \text{H}_2\text{O}\]

turns red litmus blue

(iii) (a) \[3\text{Fe}^{3+} + 2[\text{Fe(CN)}_6]^{3-} \rightarrow \text{Fe}_3[\text{Fe(CN)}_6]_2 \quad \text{(blue ppt.)}\]

(b) \[\text{Fe}^{3+} + 3\text{CNS}^- \rightarrow \text{Fe(CNS)}_3 \quad \text{Ferric thiocyanate}\]

(blood red colour)

5. (i) (A) on heating loses water of crystallization and thus it is a hydrated salt.

(ii) Anhydrous salt (B) on heating gives two gases and brown residue and so (B) is FeSO₄. Thus (A) is FeSO₄.₇H₂O

\[\text{FeSO}_4 \quad 7\text{H}_2\text{O} \xrightarrow{\Delta} \text{FeSO}_4 + 7\text{H}_2\text{O}\]

(A) (B)

\[2\text{FeSO}_4 \xrightarrow{\Delta} \text{Fe}_2\text{O}_3 + \text{SO}_2 \uparrow + \text{SO}_3 \uparrow \quad \text{(s)}\]

(B) (D) (E) (F)

Brown

(iii) (B) is soluble in water and reacts with NO to give brown compound.
FeSO₄(aq) + NO → FeSO₄·NO

Brown ring (C)

(iv) Gaseous mixture decolorizes acidified KMnO₄.

5SO₂ + 2KMnO₄ + 2H₂O → K₂SO₄ + 2MnSO₄ + 2H₂SO₄

(v) Gaseous mixture on passing through BaCl₂, gives white ppt. of BaSO₄.

SO₃ + H₂O → H₂SO₄

BaCl₂ + H₂SO₄ → BaSO₄ + 2HCl

white ppt.

6. Representing the given facts in the form of equation, we get

\[
\text{(X)} \quad \text{(g)} \underset{\text{heat}}{\rightarrow} \quad \text{(A)} \quad \text{(g)} + \text{(B)} \quad \text{(g)} + \text{(Y)} \quad \text{(s)}
\]

20.02 g 4.4 g 1.8 g 13.8 g

The above equation leads to the following facts:

(i) Since the gas A turned lime water milky, it must be CO₂.

(ii) **NOTE**: The compound Y is alkaline to litmus and when treated with BaCl₂ forms a white precipitate of Z. Since the compound Z when treated with acid gives effervescences of CO₂, Z and hence Y must contain carbonate, CO₃²⁻. Hence Y may be written as metal carbonate MCO₃ or M₂CO₃.

(iii) When X is heated, it yields a carbonate (Y) along with the evolution of CO₂ (A) and a neutral gas (B), it must be a bicarbonate.

(iv) B changes anhydrous CuSO₄ blue, which point out that B is water.

Thus the above reaction can be written as below:

\[
2\text{MHC}_3 \underset{\text{heat}}{\rightarrow} \text{CO}_2 + \text{H}_2\text{O} + \text{M}_2\text{CO}_3
\]

20.02 g 4.4 g 1.8 g

*Calculation of molecular weight of MHC₃*

4.4 g of CO₂ is given by 20.02 g of MHC₃

\[
\frac{44 \text{ g of CO}_2}{4.4} = 200.2 \text{ g}
\]

Since two molecules of MHC₃ are taking part in the reaction, the molecular weight of

\[
\text{MHC}_3 (X) = \frac{200.2}{2} = 100
\]

*Calculation of atomic weight of Metal M*

MHC₃ = 100; M + 1 + 12 + 48 = 100

M + 61 = 100; M = 39

Thus the metal must be K and hence the given salt X is KHCO₃. The above facts coincide with the given thermal decomposition.

\[
2\text{KHCO}_3 \underset{\text{heat}}{\rightarrow} \text{CO}_2 + \text{H}_2\text{O} + \text{K}_2\text{CO}_3
\]

X = KHCO₃, Y = K₂CO₃, Z = BaCO₃, A = CO₂, B = H₂O

7. Let us summarise the given facts of the question.

Red vapours of (A) \(\xrightarrow{\text{K}_2\text{Cr}_2\text{O}_7 \text{conc. H}_2\text{SO}_4, \text{heat}}\) Mixture of two salts

Mixtures of two salts \(\xrightarrow{\text{Heat with NaOH}}\) Gas \(\xrightarrow{\text{Alk. K}_2\text{[HgI}_4]}\) Reddish brown ppt.

Deep blue colour, (B) \(\xrightarrow{\text{BaCl}_2}\) Aq. solution of the mixture \(\xrightarrow{\text{White ppt. sparingly soluble in conc. HCl}}\)

The given reactions lead to the following conclusions.

(i) Formation of reddish brown precipitate on treatment with alk. K₂[HgI₄] indicates the evolution of NH₃ gas and hence the presence of NH₄⁺ in the mixture of salts.

(ii) Heating of mixture with K₂Cr₂O₇ and conc. H₂SO₄ to give red vapours of (chromyl chloride) indicates the presence of Cl⁻ ion in the mixture.

(iii) Reaction of aqueous solution of the mixture with barium chloride solution to give white ppt. (of BaSO₄ sparingly soluble in conc. HCl) indicates the presence of SO₄²⁻ ions in the mixture.

(iv) **NOTE**: Reaction of aqueous solution of the mixture with potassium ferriyanide solution to give deep blue colour indicates the presence of Fe⁺² ions in the mixture.

Hence the mixture contains following four ions:

NH₄⁺, Fe₂⁺, SO₄²⁻, and Cl⁻.

Equations for the formation of A and B.

\[
4\text{NaCl} + \text{K}_2\text{Cr}_2\text{O}_7 + 3\text{H}_2\text{SO}_4 \underset{\text{Heat}}{\rightarrow} \text{K}_2\text{SO}_4 + 2\text{Na}_2\text{SO}_4 + 2\text{CrO}_2\text{Cl}_2 \uparrow + 3\text{H}_2\text{O}
\]

Chromyl chloride (orange)(A)

\[
3\text{Fe}^{2+} + 2\text{K}_3\text{[Fe(CN)}_6]\text{]} \rightarrow \text{Fe}_3\text{[Fe(CN)}_6]\text{]}^{3+} + 6\text{K}^+
\]

(Blue ppt.) (B)

8. ‘Compound gives brown ppt. with alkaline K₂[HgI₄] and so contain NH₄⁺ ions.’

‘Compound gives blue colour with K₃[Fe(CN)₆] and so contains Fe²⁺ ions.’

‘Solution of compound in HCl gives white ppt. with BaCl₂ and so it contains SO₄²⁻ ions.’

‘ Bluish green compound with NH₄⁺, Fe²⁺ and SO₄²⁻ suggests that it is Mohr’s salt i.e.’

\[
\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4·6\text{H}_2\text{O}
\]

Reactions:

\[
3\text{NaOH} + \text{NH}_3 + 2\text{K}_2\text{[HgI}_4]\]

\[
\rightarrow \text{O}<\text{Hg}\rightarrow \text{NH}_2\text{I + 4KI + 3NaI + 2H}_2\text{O}
\]

Brown ppt.
9. Let us summarise the given facts

White dense fumes \( \xrightarrow{\text{HCl}} \) \( \text{H}_2\text{O} \) \( \xrightarrow{(E)} \) White solid (D)

(i) Formation of white dense fumes by gas (E) with HCl indicates that the gas (E) is ammonia \((\text{NH}_3)\).

(ii) Formation of ammonia (E) by the hydrolysis of white solid (D) indicates that (D) should be magnesium nitride, \(\text{Mg}_3\text{N}_2\).

(iii) Since compound (D) is formed by reaction of gas (C) with magnesium, the colourless gas (C) must be nitrogen.

(iv) Orange colour of the original compound (A) and green colour of the residue (B) indicates that compound (A) is ammonium dichromate, \((\text{NH}_4)_2\text{Cr}_2\text{O}_7\).

**Reactions:**

\[(\text{NH}_4)_2\text{Cr}_2\text{O}_7 \xrightarrow{\Delta} \text{N}_2 \uparrow + \text{Cr}_2\text{O}_3 + 4\text{H}_2\text{O}\]

Ammonium dichromate

Orange Solid (A)

N\(_2\) + 3Mg \(\xrightarrow{\Delta}\) Mg\(_3\)N\(_2\)

(C) Green residue

Mg\(_3\)N\(_2\) + 6H\(_2\)O \(\rightarrow\) 3Mg(OH)\(_2\) + 2NH\(_3\) \(\uparrow\)

(D) (E)

NH\(_3\) + H\(_2\)O \(\rightarrow\) NH\(_4\)Cl

(White fumes)

10. As the solid B forms a hydrated salt C with Al\(_2\)(SO\(_4\))\(_3\); B should be sulphate of a monovalent cation, i.e. \(\text{M}_2\text{SO}_4\),

Now since sulphate of a monovalent cation contains one sulphur atom per mol, weight of metal sulphate obtained by 32.1 g (at. wt. of S) should be the molecular weight of the metal sulphate. Thus, 0.321 g of sulphur is present in 1.743 g of B

\[\therefore 32.1 \text{ g of sulphur is present in } = \frac{1.743}{0.321} \times 32.1 = 174.3 \text{ g}\]

Thus mol. wt. of B (M\(_2\)SO\(_4\)) = 174.3 g mol\(^{-1}\)

2x + 32.1 + 64 = 174.3 (at wt. of M = x)

2x = 78.2 \(\Rightarrow\) x = 39.1

Atomic weight 39.1 corresponds to metal potassium, K.

Thus B is K\(_2\)SO\(_4\), and C is K\(_2\)SO\(_4\). Al\(_2\)(SO\(_4\))\(_3\), 24H\(_2\)O

**Nature of compound A:** Since A is a binary compound of potassium and it reacts with sulphur to form K\(_2\)S\(_2\), it must be oxide of potassium, probably potassium superoxide \((\text{KO}_2)\), which is supported by the given data.

11. Summary of the given facts.

\[(A) \xrightarrow{\text{conc HNO}_3} (B) \downarrow + \text{Sulphur} \rightarrow \text{Filtrate} \xrightarrow{(i) \text{NaOH}} (C) \downarrow \]

\[\text{Warm with conc. HNO}_3 \text{ in presence of Mn(NO}_3)_2\]

Pink coloured solution (D)

From the colour of the known compound and reaction involved, it is clear that (A) is red lead \((\text{Pb}_2\text{O}_4)\) and its various reactions can be represented as below:

\[\text{Pb}_2\text{O}_4 + 4\text{HNO}_3 \rightarrow \text{PbO}_2 + 2\text{Pb(NO}_3)_2 + 2\text{H}_2\text{O}\]

A) Scarlet

(B) Brown

\[\text{Pb(NO}_3)_2 + 2\text{KI} \rightarrow \text{PbI}_2 \downarrow + 2\text{KNO}_3\]

Filtrate

\[5\text{PbO} + 2\text{Mn(NO}_3)_2 + 4\text{HNO}_3 \rightarrow \text{Pb(Mn(NO}_3)_2} + 4\text{Pb(NO}_3)_2 + 2\text{H}_2\text{O}\]

Ppt. (B)

Pink colouration

12. The reactions are given as follows:

3Ca + N\(_2\) \(\rightarrow\) Ca\(_3\)N\(_2\)

Calcium nitride

(white powder)

Ca\(_3\)N\(_2\) + 6H\(_2\)O \(\rightarrow\) 3Ca(OH)\(_2\) + 2NH\(_3\) \(\uparrow\)

A)

Ca(OH)\(_2\) + CO\(_2\) \(\rightarrow\) CaCO\(_3\) + H\(_2\)O

from air

Solid layer (B)

13. Let us summarise the given facts.

\[(\text{coloured salt}) \xrightarrow{250^\circ\text{C}} (\text{liquid at room temp, neutral}) \rightarrow (\text{neutral oxide}) \rightarrow \text{P} \rightarrow \text{Strong white dehydrating agent}\]

(i) Since the resulting dehydrating agent is derived from P, it is likely to be \(\text{P}_4\text{O}_{10}\).
(ii) $P_4O_{10}$ is produced by burning phosphorus in excess of neutral oxide (B) which is likely to be $NO_2$.

(iii) Thus the salt A should be $NH_4NO_3$ which explains all given reactions.

$$NH_4NO_3 \xrightarrow{250^oC} N_2O + H_2O \quad (A) \quad (B) \quad (C)$$

$$P_4 + 10N_2O \rightarrow P_4O_{10} + 10N_2$$

14. The solubility products of CuS and ZnS are $K_{sp}$(CuS) $\approx 10^{-38}$ and $K_{sp}$(ZnS) $\approx 10^{-22}$

Since $K_{sp}$(CuS) $< K_{sp}$(ZnS), very small concentration of $S^{2-}$ is sufficient to cause the precipitation of $Cu^{2+}$ ions. In order to have very small concentration of $S^{2-}$ ions, acidic medium is used. Due to the common ion $H^+$, the ionisation of $H_2S$ is suppressed:

$$H_2S \rightleftharpoons 2H^+ + S^{2-}$$

The available concentration of $S^{2-}$ ions in acidic medium causes only the precipitation of CuS and not that of ZnS.

15. (i) The substance is Na$_2$O$_2$. When dissolved in water, the solution becomes alkaline with the liberation of $H_2O$

Na$_2$O$_2$ + 2$H_2$O $\rightarrow$ 2NaOH + $H_2O$

**NOTE:** Due to the alkaline solution, the red litmus paper will turn into blue, which subsequently changes into white due to oxidation caused by $H_2O_2$.

(ii) The substance Na$_2$O merely produces alkaline solution and the red litmus paper will turn into blue.

Na$_2$O + $H_2$O $\rightarrow$ 2NaOH

16. Sodium iodide on reaction with Hgl$_2$ gives colourless complex salt, Na$_3$[Hgl$_4$]

Hgl$_2$ + 2NaI $\rightarrow$ Na$_3$[Hgl$_4$]

Colour is due to presence of residual Hgl$_2$

But on addition of excess NaI, it becomes colourless due to change of residual Hgl$_2$ into Na$_3$[Hgl$_4$]

Hgl$_2$ + 2NaI (excess) $\rightarrow$ Na$_3$[Hgl$_4$] (colourless)

The orange colour of Hgl$_2$ reappears due to conversion of Na$_3$[Hgl$_4$] into Hgl$_2$ by means of NaOCl

3Na$_2$Hgl$_4$ + 2NaOCl + $H_2$O

$$\rightarrow 3Hgl_2 + 2NaCl + 4NaOH + 2NaI$$

Orange colour

17. Summary of the given facts

$$MSO_4 \xrightarrow{H^+} MS \downarrow Black (A) \xrightarrow{warm KOH} Insoluble$$

$$Kl, H^+$$

yellow solution (B)

The reaction corresponds to copper sulphate.

$$CuSO_4 + H_2S \xrightarrow{H^+} CuS \downarrow Black (A) + H_2SO_4$$

18. Na$_2$B$_4$O$_7$. $10H_2O \xrightarrow{\Delta} Na_2B_4O_7 \xrightarrow{740^oC} 2NaBO_2 + B_2O_3$ Transparent

Salt of Co $\xrightarrow{\Delta} CoO + gas$

CoO + B$_2$O$_3$ $\rightarrow$ Co(BO$_2$)$_2$ Cobalt metaborate (blue)

19. A (white) $\xrightarrow{dil. H_2SO_4}$ B (colourless gas) + C (colourless solution)

$$\xrightarrow{K_2Cr_2O_7+H^+}$$

Green solution + D (burns in air to form gas E) (coloured)

E $\uparrow$ + B $\uparrow$ $\rightarrow$ D + Colourless liquid $\rightarrow$ CuSO$_4$. Blue colour

C (aq. NH$_3$ or NaOH) $\rightarrow$ White precipitate excess of reagent $\rightarrow$ Clear solution

The above set leads to following conclusions.

(i) Since the gas (B) is colourless and turns acidified K$_2$Cr$_2$O$_7$ solution green, it should be $H_2S$.

(ii) Since $H_2S$ gas is obtained by the reaction of dil. $H_2SO_4$ on A, the latter must be sulphide.

(iii) The white colour of the sulphide (A) points out towards ZnS.

Thus the various reactions can be written as given below.

ZnS + $H_2SO_4$ (dil)$\rightarrow$ ZnSO$_4$ + $H_2S$ $\uparrow$

(A) (C) (B)

3$H_2$S + K$_2$Cr$_2$O$_7$ + 4$H_2$SO$_4$

$$\rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3S$$

(D)

S + $O_2 \rightarrow SO_3 \xrightarrow{2H_2SO_4(B)} 2H_2O + 3S \downarrow$

(D) (E) (colourless liq) D

CuSO$_4$ + 5$H_2$O $\rightarrow$ CuSO$_4 . 5H_2$O (blue)

(C) (Hydrated CuSO$_4$)

$ZnSO_4 + 2NaOH \rightarrow Zn(OH)$_2$ $\downarrow$ white ppt

$$\xrightarrow{2NaOH (excess)} Na_3ZnO$_2$ + 2$H_2$O (soluble)$$
20. Let us summarise the given facts.

\[
\begin{align*}
X + K_2Cr_2O_7 + H_2SO_4 & \rightarrow A \uparrow \text{ (Reddish brown)} \quad \text{NaOH} \\
& \rightarrow B \text{ (Yellow coloured solution)} \\
\text{NaOH solution} & \\
\text{Colourless gas} & \\
& \rightarrow K_3\text{[Hgl}_4\text{]} \text{ solution} \\
& \rightarrow D \text{ (Reddish brown ppt.)}
\end{align*}
\]

**NOTE:** Reaction of compound X with NaOH solution and subsequent treatments indicate that X has NH₄⁺ radical. On the other hand, reaction of X with K₂Cr₂O₇ solution, conc. H₂SO₄ and subsequent treatments indicate that A has Cl⁻ radical. Thus compound X is NH₄Cl which explains all the above reactions.

\[
\begin{align*}
4\text{NH}_4\text{Cl} + K_2\text{Cr}_2O_7 + 3H_2SO_4 & \rightarrow K_2SO_4 + 2(\text{NH}_4)_2SO_4 + 2\text{CrO}_2\text{Cl}_2 \uparrow + 3H_2O \\
& \text{Chromyl chloride, (A) (reddish brown)}
\end{align*}
\]

\[
\begin{align*}
\text{CrO}_2\text{Cl}_2 + 4\text{NaOH} & \rightarrow 2\text{NaCl} + \text{Na}_2\text{CrO}_4 + 2H_2O \\
& \text{Sod. chromate, (B) (yellow coloured Solution)}
\end{align*}
\]

\[
\begin{align*}
\text{Na}_2\text{CrO}_4 + (\text{CH}_3\text{COO})_2\text{Pb} & \rightarrow 2\text{CH}_3\text{COONa} + \text{PbCrO}_4 \downarrow \\
& \text{Lead chromate, (C) (yellow ppt.)}
\end{align*}
\]

\[
\begin{align*}
\text{NH}_4\text{Cl} + \text{NaOH} & \rightarrow \text{NH}_3 \uparrow + \text{NaCl} + H_2O \\
& \text{(X)}
\end{align*}
\]

\[
\begin{align*}
\text{NH}_3 + 2K_2\text{Hgl}_4 + 3\text{KOH} & \rightarrow \begin{array}{c}
\text{Hg} \\
\text{Hg}
\end{array} + 7\text{KI} + 2H_2O \\
& \text{Iodide of Millor's base, (D) (reddish brown ppt.)}
\end{align*}
\]

21. \[[A = \text{Hgl}_2\text{(yellow), B = KI(colourless)}]\]

\[
\begin{align*}
\text{Hgl}_2 + H_2S & \rightarrow \text{HgS} + 2\text{HI} \quad \text{Hgl}_2 \rightarrow \text{aqu regia} \rightarrow \text{HgCl}_2 \\
& \text{(C)}
\end{align*}
\]

\[
\begin{align*}
\text{HgCl}_2 + \text{SnCl}_2 & \rightarrow \text{Hg} \downarrow + \text{SnCl}_4 \\
& \text{(greyish black) (D)}
\end{align*}
\]

\[
\begin{align*}
2\text{KI} + \text{Hgl}_2 & \rightarrow K_2\text{[Hgl}_4\text{]} \quad \text{(orange)}
\end{align*}
\]

\[
\begin{align*}
2K_2\text{[Hgl}_4\text{]} + \text{NH}_3 + 3\text{KOH} & \rightarrow [\text{HgOH}_3\text{NHg}_3]\downarrow + 7\text{KI} + 2H_2O \\
& \text{Iodide of Millor's base (brown)}
\end{align*}
\]

\[
\begin{align*}
\text{Hgl}_2 + \text{Na}_2\text{CO}_3 & \rightarrow 2\text{NaI} \quad \text{CCl}_4 \rightarrow \text{Violet layer} \\
& \rightarrow \text{AgNO}_3 \\
& \rightarrow \text{AgI} \downarrow \text{(Yellow)} \\
& \text{Insoluble in ammonia}
\end{align*}
\]

**G. Comprehension Based Questions**

For 1-3

**Reaction of Y indicates that it is Fe³⁺ salt.**

\[
\begin{align*}
4\text{Fe}^{3+} + 3[\text{Fe(CN)}_6]^{3-} & \rightarrow \text{Fe}_4[\text{Fe(CN)}_6]_3 \downarrow \\
& \text{Y hexacyanoferrate (II) or ferrocyanide Intense blue ppt. soluble in excess of ferrocyanide}
\end{align*}
\]

\[
\begin{align*}
\text{Fe}^{3+} + [\text{Fe(CN)}_6]^{3-} & \rightarrow \text{Fe[Fe(CN)}_6] \downarrow \\
& \text{Y hexacyanoferrate (III) or ferrocyanide Brown colour}
\end{align*}
\]

**NOTE:** since the product formed (methylene blue) has sulphur in its structure, it should be supplied by the compound X which is thus Na₂S.

\[
\begin{align*}
\text{Na}_2\text{S} + 2\text{H}^+ & \rightarrow \text{H}_2\text{S} + 2\text{Na}^+ \\
\text{FeCl}_3 + \text{H}_2\text{S} & \rightarrow \text{FeCl}_2 + 2\text{HCl} + \text{S}
\end{align*}
\]

\[
\begin{align*}
\text{Me}_2\text{N} & + \text{S} + \text{H}_2\text{N}-\text{Me}_2 \\
& \rightarrow \text{H}^+ \rightarrow \text{Me}_2\text{N} \text{[S]} \text{[Me}_2\text{N]} \text{[H]+[H]} \\
& \text{Methylene blue}
\end{align*}
\]

Thus

1. (d)  
2. (c)  
3. (b)  
4. (a) Lead salts give white precipitate of PbCl₂ with dil. HCl which is soluble in hot water. \(\text{Pb}^{2+} + 2\text{Cl}^- \rightarrow \text{PbCl}_2 \) (White ppt) soluble in hot water
5. (d) The filtrate on treatment with ammoniacal H₂S gives a precipitate which dissolves in aqueous NaOH containing H₂O₂ giving a coloured solution. It contains Cr³⁺ ion.

\[
\begin{align*}
\text{Cr}^{3+} + 3\text{NH}_4\text{OH} & \rightarrow \text{H}_2\text{S in ammoniacal medium} \rightarrow \text{Cr(OH)}_3 \downarrow \\
& \text{(Green)}
\end{align*}
\]

\[
\begin{align*}
2\text{Cr(OH)}_3 \rightarrow 3\text{H}_2\text{O}_2 + 4\text{NaOH} & \rightarrow 2\text{Na}_2\text{CrO}_4 + 8\text{H}_2 \\
& \text{(yellow colour)}
\end{align*}
\]

6. (b) \[\text{Ni}^{2+} + 4\text{HCl} \] (M1) \[\rightarrow [\text{NiCl}_4]^{2-} \] (Q) Tetrahedral

\[
\begin{align*}
\text{Ni}^{2+} + 4\text{KCN} & \rightarrow [\text{Ni(CN)}_4]^{2-} \quad \text{R} \quad \text{Square planar}
\end{align*}
\]

**[Note:** \(\text{Co}^{2+} + 6\text{CN}^- \rightarrow [\text{Co(CN)}_6]^{4-} \) Octahedral]**
**H. Assertion & Reason Type Questions**

1. (d) Cd$^{2+}$ is a 2nd group radical and Ni$^{2+}$ is a 4th group radical. So solubility product of NiS has to be more than CdS. Further Cd$^{2+}$ gives yellow colour of CdS with H$_2$S, but Ni$^{2+}$ gives black colour of NiS with H$_2$S.

2. (b) Sulphate is estimated as BaSO$_4$ because of its insolubility in water. BaSO$_4$ forms a white ppt. Therefore reason is correct but do not explain the assertion.

**Section-B JEE Main/ AIEEE**

1. (e) When H$_2$S is passed through Hg$_2$S we get a mixture of mercurous sulphide and mercury (Hg$_2$S + Hg).

2. (b) When we add NH$_4$Cl, it suppresses the ionisation of NH$_3$OH and prevents the precipitation of higher group hydroxide in gp(III).

   **NOTE:** Further ferric chloride and chromium chloride form different colour precipitates with NH$_3$OH.

   \[
   \text{FeCl}_3 + 3\text{NH}_4\text{OH} \longrightarrow \text{Fe(OH)}_3 \downarrow + 3\text{NH}_4\text{Cl} \quad \text{reddish brown}
   \]

   \[
   \text{CrCl}_3 + 3\text{NH}_4\text{OH} \longrightarrow \text{Cr(OH)}_3 + 3\text{NH}_4\text{Cl} \quad \text{Bluish green}
   \]

3. (a) Between AgCl and AgI, AgI is less soluble, hence ammonia can dissolve ppt. of AgCl only due to formation of complex as given below:

   \[
   \text{AgCl} + 2\text{NH}_3 \rightarrow [\text{Ag(NH}_3)_2]\text{Cl}
   \]

4. (a) Prussian blue Fe$_4$[Fe(CN)$_6$]$_3$ is formed in lassaigne test for nitrogen.

   \[
   3\text{Na}_4[\text{Fe(CN)}_6] + 4\text{Fe}^{3+} \rightarrow \text{Fe}_4[\text{Fe(CN)}_4]_6 + 12\text{Na}^+
   \]

   **Prussian blue**

5. (b) The complex [CoCl(NH$_3$)$_5$]$^+$ decomposes under acidic medium, so

   \[
   [\text{CoCl(NH}_3)_5]^+ + 5\text{H}^+ \rightarrow \text{Co}^{2+} + 5\text{NH}_4^+ + \text{Cl}^-
   \]