PRACTICE PAPER (Solved)

General Instructions :

Read the following instructions very carefully and strictly follow them :

- (i) Question paper comprises two parts A and B.
- (ii) Part A : Q. no. 1 to 26 are objective type questions.
 - ${\sf Q}.$ no. 1 to 19 are objective type questions carrying one mark each.
 - Q. no. 20 to 24 are objective type questions carrying two marks each.
 - Q. no. 25 to 26 are case based objective type questions carrying three marks each.
- (iii) Part B : Q. no. 27 to 37 are subjective/descriptive type questions.
 - Q. no. 27 to 30 are short answer type-I questions carrying two marks each.
 - Q. no. 31 to 34 are short answer type-II questions carrying three marks each.
 - Q. no. 35 to 37 are long answer type questions carrying five marks each.
- (iv) There is no overall choice in the question paper. However, internal choices have been provided in both part A and Part B.
- (v) Use of calculators and log tables is not permitted.

Time allowed : 3 hours

PART - A : Objective Type

- In which of the following, the number of carbon atoms does not remain same when carboxylic acid is obtained by oxidation?
 (a) CH₃COCH₃
 (b) CCl₃CH₂CHO
 (c) CH₃CH₂CH₂OH
 (d) CH₃CH₂CHO
- 2. One mole of the complex compound $Co(NH_3)_5Cl_3$, 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) $[Co(NH_3)_5Cl]Cl_2$
 - (b) $[Co(NH_3)_3Cl_2]\cdot 2NH_3$
 - (c) $[Co(NH_3)_4Cl_2]Cl\cdot NH_3$
 - (d) $[Co(NH_3)_4Cl]Cl_2 \cdot NH_3$

OR

The oxidation state of Cr in $[Cr(NH_3)_4Cl_2]^+$ is (a) +3 (b) +2 (c) +1 (d) 0

- **3.** Replacement of Cl of chlorobenzene to give phenol requires drastic conditions. But chlorine of 2,4-dinitrochlorobenzene is readily replaced because
 - (a) NO₂ donates e^- at *meta* position
 - (b) NO₂ withdraws e[−] from ortho/para positions

(c) NO₂ makes ring electron rich at *ortho* and *para* positions

Maximum marks: 70

- (d) NO₂ withdraws e^{-} from meta position.
- 4. Which of the following is more basic than aniline?
 - (a) Benzylamine (b) Diphenylamine
 - (c) Triphenylamine (d) *p*-Nitroaniline
- 5. Which one of the following statements regarding helium is incorrect?
 - (a) It is used to fill gas in balloons instead of hydrogen because it is lighter and noninflammable.
 - (b) It is used as a cryogenic agent for carrying out experiments at low temperatures.
 - (c) It is used to produce and sustain powerful superconducting magnets.
 - (d) It is used in gas-cooled nuclear reactors.
- 6. The vapour pressure of a solvent decreased by 10 mm of mercury when a non-volatile solute was added to the solvent. The mole fraction of the solute in the solution is 0.2. What should be the mole fraction of the solvent if the decrease in the vapour pressure is to be 20 mm of mercury?
 - (a) 0.4 (b) 0.6 (c) 0.8 (d) 0.2 OR

A 5% solution of cane sugar (mol. wt. = 342) is isotonic with 1% solution of a substance *X*.

The molecular weight of *X* is

(a) 68.4 (b) 171.2 (c) 34.2 (d) 136.8

- 7. Which one of the following complexes is an outer orbital complex?
 - (a) $[Fe(CN)_6]^{4-}$ (b) $[Mn(CN)_6]^{4-}$ (c) $[Co(NH_3)_6]^{3+}$ (d) $[Ni(NH_3)_6]^{2+}$ [Atomic nos.: Mn = 25, Fe = 26, Co = 27, Ni = 28]
- 8. Increasing order of acid strength among *p*-methoxyphenol, *p*-methylphenol and *p*-nitrophenol is
 - (a) *p*-nitrophenol, *p*-methoxyphenol, *p*-methylphenol
 - (b) *p*-methylphenol, *p*-methoxyphenol, *p*-nitrophenol
 - (c) *p*-nitrophenol, *p*-methylphenol, *p*-methoxyphenol
 - (d) *p*-methoxyphenol, *p*-methylphenol, *p*-nitrophenol.
- 9. The ability of anion, to bring about coagulation of a given colloid, depends upon
 - (a) magnitude of the charge
 - (b) both magnitude and charge
 - (c) its charge only
 - (d) sign of the charge alone.
- **10.** In cube of any crystal *A*-atom placed at every corners and *B*-atom placed at every centre of face. The formula of compound is

| (a) | AB | (b) | AB_3 |
|-------------------|-----|-----|--------|
| $\langle \rangle$ | 4 D | (1) | 4 D |

| 33 |
|----|
| 3 |

OR

If *a* stands for the edge length of the cubic systems: simple cubic, body-centred cubic and face-centred cubic, then the ratio of radii of the spheres in these systems will be respectively

(a)
$$\frac{1}{2}a : \frac{\sqrt{3}}{2}a : \frac{\sqrt{2}}{2}a$$

(b) $1a : \sqrt{3}a : \sqrt{2}a$
(c) $\frac{1}{2}a : \frac{\sqrt{3}}{4}a : \frac{1}{2\sqrt{2}}a$
(d) $\frac{1}{2}a : \sqrt{3}a : \frac{1}{\sqrt{2}}a$

11. The reaction $A \longrightarrow B$ follows first order kinetics. The time taken for 0.8 mole of *A* to produce 0.6 mole of *B* is 1 hour. What is the

time taken for conversion of 0.9 mole of *A* to produce 0.675 mole of *B* ?

- (a) 1 hour (b) 0.5 hour
- (c) 0.25 hour (d) 2 hours

12. Arrange Ce^{3+} , La^{3+} , Pm^{3+} and Yb^{3+} in increasing order of their ionic radii.

- (a) $Yb^{3+} < Pm^{3+} < Ce^{3+} < La^{3+}$
- (b) $Ce^{3+} < Yb^{3+} < Pm^{3+} < La^{3+}$
- (c) $Yb^{3+} < Pm^{3+} < La^{3+} < Ce^{3+}$
- (d) $Pm^{3+} < La^{3+} < Ce^{3+} < Yb^{3+}$

OR

Of the following outer electronic configurations of atoms, the highest oxidation state is achieved by which one of them?

- (a) $(n-1)d^8ns^2$ (b) $(n-1)d^5ns^1$
- (c) $(n-1)d^3ns^2$ (d) $(n-1)d^5ns^2$.
- **13.** A solution contains Fe^{2+} , Fe^{3+} and I^- ions. This solution was treated with iodine at 35 °C. E° for Fe^{3+}/Fe^{2+} is + 0.77 V and E° for $I_2/2I^-$ = 0.536 V. The favourable redox reaction is
 - (a) I_2 will be reduced to I^-
 - (b) there will be no redox reaction
 - (c) I^- will be oxidised to I_2
 - (d) Fe^{2+} will be oxidised to Fe^{3+} .
- **14.** The atomic numbers of vanadium (V), chromium (Cr), manganese (Mn) and iron (Fe) are respectively 23, 24, 25 and 26. Which one of these may be expected to have the highest second ionisation enthalpy?

(a) V (b) Cr (c) Mn (d) Fe

Questions 15 to 19 :

- (a) Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).
- (b) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).
- (c) Assertion (A) is correct, but Reason (R) is incorrect statement.
- (d) Assertion (A) is incorrect, but Reason (R) is correct statement.
- **15. Assertion :** Equivalent conductance of all electrolytes decreases with increasing concentration.

Reason : Lesser number of ions are available per g equivalent at higher concentration.

Assertion : A negative value of standard reduction potential means that reduction takes place on this electrode with reference to standard hydrogen electrode.

Reason : The standard electrode potential of a half cell has a fixed value.

16. Assertion : The high melting points of transition elements are indicative of high heats of sublimation.

Reason : The ionisation potential of transition metal lies between that for the *s*- and *p*-block elements.

17. Assertion : Addition of Grignard reagent to dry ice followed by hydrolysis gives ketones.Reason : Ketones can be converted into acids by haloform reaction.

OR

Assertion : In formaldehyde, all the four atoms are in the same plane.

Reason : The carbon atom in formaldehyde is sp^2 -hybridised.

18. Assertion : The value of crystal field splitting depends not only on the ligand but also on the charge on the central metal ion.

Reason : The higher the positive charge on the metal ion, the more closely the ligands are pulled into the metal, the greater the interaction between the ligands and the *d*-electrons of the metal and greater the difference between the t_{2g} and the e_g levels.

19. Assertion : In any ionic solid (*MX*) with Schottky defects, the number of positive and negative ions is the same.

Reason : Equal number of cation and anion vacancies are present.

- **20.** Consider the reaction, $2A + B \rightarrow$ products. When concentration of *B* alone was doubled, the half-life did not change. When the concentration of *A* alone was doubled, the rate increased by two times. The unit of rate constant for this reaction is
 - (a) s^{-1} (b) $L \mod^{-1} s^{-1}$
 - (c) no unit (d) mol $L^{-1} s^{-1}$.

OR

For the reaction, N₂ + 3H₂ \longrightarrow 2NH₃, if $\frac{d[\text{NH}_3]}{dt} = 2 \times 10^{-4} \text{ mol } \text{L}^{-1} \text{s}^{-1}, \text{ the value of}$ $\frac{-d[H_2]}{dt} \text{ would be}$ (a) $4 \times 10^{-4} \text{ mol } \text{L}^{-1} \text{ s}^{-1}$ (b) $6 \times 10^{-4} \text{ mol } \text{L}^{-1} \text{ s}^{-1}$ (c) $1 \times 10^{-4} \text{ mol } \text{L}^{-1} \text{ s}^{-1}$ (d) $3 \times 10^{-4} \text{ mol } \text{L}^{-1} \text{ s}^{-1}$

- **21.** Number of isomeric alcohols of molecular formula $C_6H_{14}O$ which give positive iodoform test is
 - (a) three (b) four

(c) five (d) two.

- **22.** In which of the following arrangements the given sequence is not strictly according to the property indicated against it?
 - (a) HF < HCl < HBr < HI : increasing acidic strength
 - (b) $H_2O < H_2S < H_2Se < H_2Te$: increasing pK_a values
 - (c) $NH_3 < PH_3 < AsH_3 < SbH_3$: increasing acidic character
 - (d) $CO_2 < SiO_2 < SnO_2 < PbO_2$: increasing oxidising power
- 23. The vapour pressure of CCl₄ at 25°C is 143 mm Hg. If 0.5 g of a non-volatile solute (mol. weight = 65) is dissolved in 100 g CCl₄, the vapour pressure of the solution will be
 (a) 199.34 mm Hg
 (b) 143.99 mm Hg
 (c) 141.43 mm Hg
 (d) 94.39 mm Hg.
- 24. Which one of the following is an inner orbital complex as well as diamagnetic in behaviour?
 (a) [Zn(NH₃)₆]²⁺
 (b) [Cr(NH₃)₆]³⁺
 (c) [Co(NH₃)₆]³⁺
 (d) [Ni(NH₃)₆]²⁺
 (Atomic number : Zn = 30, Cr = 24, Co = 27, Ni = 28)

OR

 $[Cr(H_2O)_6]Cl_3$ (At. no. of Cr = 24) has a magnetic moment of 3.83 B.M. The correct distribution of 3*d* electrons in the chromium of the complex is

- (a) $3d_{xy}^{1}, 3d_{yz}^{1}, 3d_{z^{2}}^{1}$ (b) $3d_{(x^{2}-y^{2})}^{1}, 3d_{z^{2}}^{1}, 3d_{xz}^{1}$ (c) $3d_{xy}^{1}, 3d_{(x^{2}-y^{2})}^{1}, 3d_{yz}^{1}$ (l) $a d_{xy}^{1}, a d_{xy}^{1}, a d_{xy}^{1}$
- (d) $3d_{xy}^1, 3d_{yz}^1, 3d_{xz}^1$

Read the following passage and answer the questions 25 and 26.

A 10 g mixture of isobutane and isobutene requires 20 g of bromine (in CCl_4) for complete addition. 10 g of the mixture is catalytically hydrogenated and the entire alkane is monobrominated in the presence of light at 127°C.

25. The final product is

- (a) isobutane
- (b) tertiary butyl bromide
- (c) 1, 2-dibromo-2-methylbutane
- (d) None of these.

26. The mass of the final product formed is

- (a) 15.85 g (b) 20.12 g
- (c) 24.21 g (d) 30 g.

PART - B : Subjective / Descriptive Type

- 27. Explain the following observations :
 - (i) Lyophilic colloid is more stable than lyophobic colloid.
 - (ii) Coagulation takes place when sodium chloride solution is added to a colloidal solution of ferric hydroxide.
- **28.** (i) Arrange the following compounds in the decreasing order of their boiling points :
 - (a) Pentan-1-ol
 - (b) 2-Methylbutan-2-ol
 - (c) 3-Methylbutan-2-ol
 - (ii) Which type of alcohol does not react with Lucas reagent at room temperature?

OR

Explain the following with an example for each :

- (i) Kolbe's reaction,
- (ii) Reimer Tiemann reaction.
- **29.** 0.90 g of a non-electrolyte was dissolved in 87.90 g of benzene. This raised the boiling point of benzene by 0.25°C. If the molecular mass of the non-electrolyte is 103.0 g mol⁻¹, calculate the molar elevation constant for benzene.
- **30.** Write down the structures and names of the products formed when *D*-glucose is treated with
 - (a) Bromine water
 - (b) hydrogen iodide (prolonged heating).

- **31.** From the following compounds:
 - 2-Bromopentane, 2-Bromo-2-methylbutane, 1-Bromopentane
 - (i) Which compound is most reactive towards S_N^2 reaction?
 - (ii) Which compound is optically active?
 - (iii) Which compound is most reactive towards β -elimination reaction?
- **32.** (a) Which point defect of its crystals decreases the density of a solid?
 - (b) Calculate the number of unit cells in 8.1 g of aluminium if it crystallizes in a *fcc* structure.

(Atomic mass of $Al = 27 \text{ g mol}^{-1}$)

OR

Silver crystallises in *fcc* lattice. If the edge length of the unit cell is 4.077×10^{-8} cm and density of the crystal is 10.5 g cm⁻³, calculate the atomic mass of silver.

- **33.** How will you convert :
 - (i) Ethanoic acid into methanamine
 - (ii) Ethanamine into methanamine
 - (iii) Nitromethane into dimethylamine
- 34. Explain the following observations :
 - (a) The electron gain enthalpy of sulphur atom has a greater negative value than that of oxygen atom.
 - (b) Nitrogen does not form pentahalides.
 - (c) In aqueous solutions HI is a stronger acid than HCl.
- **35.** (a) (i) What is order of reaction?
 - (ii) The thermal decomposition of HCOOH is a first order reaction with a rate constant of 2.4×10^{-3} s⁻¹ at a certain temperature. Calculate how long will it take for three fourth of initial quantity of HCOOH to decompose.

(Given : $\log 4 = 0.6021$)

(b) For the reaction, $2N_2O_{5(g)} \longrightarrow 4NO_{2(g)} + O_{2(g)}$, the rate of formation of $NO_{2(g)}$ is 2.8×10^{-3} M s⁻¹. Calculate the rate of disappearance of $N_2O_{5(g)}$.

OR

For a homogeneous gas phase reaction $A_{(g)} \rightarrow B_{(g)} + C_{(g)} + D_{(g)}$, the pressure of the

reaction mixture increases by 40% in 20 minute. Calculate rate constant of a reaction.

36. (a) Write the product of the following reactions:

(i)
$$\longrightarrow$$
 O + H₂N - OH \longrightarrow

(ii)
$$2C_6H_5CHO + \text{conc. NaOH} \rightarrow$$

(iii) CH₃COOH
$$\xrightarrow{\text{Cl}_2/P}$$

- (b) Arrange the following compounds in an increasing order of their property as indicated:
 - (i) Acetaldehyde, acetone, methyl-*tert*butyl ketone (reactivity towards HCN)
 - (ii) CH₃CH₂CH(Br)COOH, CH₃CH(Br)CH₂COOH, (CH₃)₂CHCOOH (acid strength)

OR

- (i) Give a chemical test to distinguish between the following :
 - (a) Benzoic acid and ethyl benzoate
 - (b) Benzophenone and acetophenone.
- (ii) Complete the following reaction :

(iii) Identify *A*, *B* and *C* in the following sequence :

- **37.** (a) State reasons for the following :
 - (i) Transition metals and their many compounds act as good catalyst.
 - (ii) Unlike Cr^{3+} , Mn^{2+} , Fe^{3+} and the subsequent other M^{2+} ions of the 3*d* series of elements, the 4*d* and the 5*d* series metals generally do not form stable cationic species.
 - (b) Discuss the general trends in the following properties of the 3*d*-transition elements :
 - (i) Atomic size
 - (ii) Oxidation states
 - (iii) Formation of coloured ions.

OR

On the basis of Lanthanoid contraction, explain the following :

- (i) Nature of bonding in La_2O_3 and Lu_2O_3 .
- (ii) Trends in the stability of oxo salts of lanthanoids from La to Lu.
- (iii) Stability of the complexes of lanthanoids.
- (iv) Radii of 4*d* and 5*d* block elements.
- (v) Trends in acidic character of lanthanoid oxides.

Detailed Solutions

1. (a) : Ketones on oxidation give carboxylic acids with lesser number of carbon atoms *i.e*,

CH₃COCH₃
$$\xrightarrow{[O]}$$
 CH₃COOH + CO₂ + H₂O
2. (a) : [Co(NH₃)₅Cl]Cl₂ \rightleftharpoons [Co(NH₃)₅Cl]²⁺
+ 2Cl⁻

 \Rightarrow 3 ions.

 $[Co(NH_3)_5Cl]Cl_2 + 2AgNO_3 \longrightarrow [Co(NH_3)_5Cl]$ $(NO_3)_2 + 2AgCl$

(a): Let the oxidation state of Cr in $[Cr(NH_3)_4Cl_2]^+$ = x x + 4(0) + 2(-1) = +1 \Rightarrow x - 2 = +1 \Rightarrow x = +1 + 2 = +3

3. (b):
$$\bigcup_{NO_2}^{Cl} NO_2$$

Withdrawal of electrons by $-NO_2$ groups from *ortho/para* positions cause easier removal of -Cl atom due to the development of positive charge on *o*- and *p*- positions.

4. (a) : Any group $(-NO_2, -CN, -SO_3H, -COOH, -Cl, -C_6H_5$, etc.) which when present on benzene ring has electron withdrawing effect, decreases basicity of aniline *e.g.*, aniline is more basic than nitroaniline. Lone pair electrons

are more delocalised in diphenylamine and triphenylamine, thus these are less basic than aniline. In benzylamine the electron pair present on nitrogen is not delocalised with the benzene ring hence it is more basic than aniline.

5. (a) : Helium is twice as heavy as hydrogen, its lifting power is 92 percent of that of hydrogen.

6. (b): x_1 (mole fraction of solute) = 0.2 From Raoult's law,

 $\frac{P^{\circ} - P_s}{P^{\circ}} = x_1 \implies \frac{10}{P^{\circ}} = 0.2 \implies P^{\circ} = 50 \text{ mm}$ Again, when $P^{\circ} - P_s = 20 \text{ mm}$, then $P^{\circ} - P_s = 20 \text{ mm}$

 $\frac{P^{\circ} - P_s}{P^{\circ}} = \text{mole fraction of solute} = \frac{20}{50} = 0.4$ $\Rightarrow \text{ mole fraction of solvent} = 1 - 0.4 = 0.6$

OR

| (a) : | Cane Sugar | X |
|-------|------------------------|------------------------|
| | $W_1 = 5 \text{ g}$ | $W_2 = 1 \text{ g}$ |
| | $V_1 = 100 \text{ mL}$ | $V_2 = 100 \text{ mL}$ |
| | = 0.1 L | = 0.1 L |
| | $M_1 = 342$ | $M_2 = ?$ |

For isotonic solutions, $C_1 = C_2$

7.

$$\frac{W_1}{M_1 V_1} = \frac{W_2}{M_2 V_2} \implies \frac{5}{342 \times 0.1} = \frac{1}{M_2 \times 0.1}$$
$$\implies M_2 = \frac{342}{5} = 68.4$$

| (d): Complex ion | Hybridization of |
|---------------------|-----------------------|
| | central ion |
| $[Fe(CN)_{6}]^{4-}$ | d^2sp^3 (inner) |
| $[Mn(CN)_6]^{4-}$ | d^2sp^3 (inner) |
| $[Co(NH_3)_6]^{3+}$ | d^2sp^3 (inner) |
| $[Ni(NH_3)_6]^{2+}$ | $sp^{3}d^{2}$ (outer) |
| | |

8. (d): $-OCH_3$, $-CH_3$ are electron donating groups and decrease the acidic character of phenols. $-NO_2$, is an electron withdrawing group that tend to increase the acidic character. Thus, the order is

p-methoxyphenol < *p*-methylphenol

< *p*-nitrophenol.

9. (b): Both magnitude and nature of charge effect coagulation of a given colloid. Greater the magnitude of the charge, quicker will be the coagulation.

10. (b): '*A*' atoms are at '8' corners of the cube. Thus, no. of '*A*' atoms per unit cell = $8 \times \frac{1}{8} = 1$ '*B*' atoms are at the face centre of six faces. Thus, no. of '*B*' atoms per unit cell = $6 \times \frac{1}{2} = 3$ The formula is *AB*₃.

OR

(c) : For simple cubic : r = a/2For body centred : $r = a\sqrt{3}/4$ For face-centred : $r = \frac{a}{2\sqrt{2}}$ where a = edge length, r = radius.

3

1

| ÷ | Ratio of r | adii of the | three will be | $e^{\frac{a}{2}}:\frac{a\sqrt{3}}{4}$ | $:\frac{a}{2\sqrt{2}}$ |
|-----|------------|-----------------|---------------|---------------------------------------|------------------------|
| 11. | (a) : In c | ase I | In cas | se II | |
| | A — | $\rightarrow B$ | A — | $\rightarrow B$ | |
| | 0.8 | 0 | 0.9 | 0 | |
| | 0.2 | 0.6 | 0.225 | 0.675 | |

The time taken for the completion of same fraction of change is independent of initial concentration.

1

3

12. (a) : According to their positions in the periods, these values are in the order:

 $\label{eq:2.1} \begin{array}{ccc} Yb^{3+} < Pm^{3+} < Ce^{3+} < La^{3+} \\ \mbox{At. Nos.} & 70 & 61 & 58 & 57 \\ \mbox{Ionic radii (pm)} & 86 & 98 & 103 & 106 \\ \mbox{Ionic size decreases from } La^{3+} \mbox{ to } Lu^{3+} \mbox{ due to } \\ \mbox{Ianthanide contraction.} \end{array}$

| | | | | | | OR |
|-------|---|----|--------|----|---|----|
| | | (1 | ı – 1) |)d | | ns |
| (d) : | 1 | 1 | 1 | 1 | 1 | 11 |

 $(n-1)d^5 ns^2$ can achieve the maximum oxidation state of +7.

13. (c) : Since the reduction potential of Fe^{3+}/Fe^{2+} is greater than that of I_2/I^- , Fe^{3+} will be reduced and I^- will be oxidised.

 $2Fe^{3+} + 2I^- \longrightarrow 2Fe^{2+} + I_2$

14. (b): The second ionisation potential value of Cr is highest among the given elements. This is because of the electronic configuration of Cr⁺ which is $3d^5$ (half-filled), *i.e.*, for the second ionisation potential, the electron is to be removed from very stable configuration.

15. (c): At higher concentration no. of ions per unit volume actually increases. Hence the equivalent conductance decreases on dilution.

OR

(d) : A negative value of standard reduction potential means that oxidation takes place on this electrode with reference to SHE.

16. (b)

17. (d): Addition of Grignard reagent to dry ice followed by hydrolysis gives carboxylic acid not ketone.

$$RMgX + O = C = O \xrightarrow[ether]{Dry} R - \stackrel{||}{C} - OMgX$$
$$\xrightarrow[H^+/H_2O]{OR} R - \stackrel{||}{C} - OH$$

(a) : Since C — O bonds utilise sp^2 -hybrid orbitals, they lie in the same plane and are 120° apart. Hence carbonyl group is planar.

18. (a) 19. (a)

20. (b): Rate = $k [A]^x [B]^y$

When [B] is doubled, keeping [A] constant halflife of the reaction does not change.

Now, for a first order reaction $t_{1/2} = \frac{0.693}{L}$

i.e., $t_{1/2}$ is independent of the concentration of the reactant. Hence the reaction is first order with respect to B. Now when [A] is doubled, keeping [B] constant, the rate also doubles. Hence the reaction is first order with respect to A.

 \therefore Rate = $[A]^1[B]^1$

 \therefore order = 2

Now for a n^{th} order reaction, unit of rate constant is $(L)^{n-1} (mol)^{1-n} s^{-1}$; when n = 2, unit of rate constant is $L \mod^{-1} s^{-1}$.

OR

(d) : For reaction, N₂ + 3H₂
$$\longrightarrow$$
 2NH₃
Rate $= \frac{1}{2} \frac{d[NH_3]}{dt} = -\frac{1}{3} \frac{d[H_2]}{dt} = -\frac{d[N_2]}{dt}$
Given, $\frac{d[NH_3]}{dt} = 2 \times 10^{-4} \text{ mol } \text{L}^{-1} \text{ s}^{-1}$
 $\therefore -\frac{d[H_2]}{dt} = \frac{3}{2} \frac{d[NH_3]}{dt} = \frac{3}{2} \times 2 \times 10^{-4}$

$$\Rightarrow -\frac{d[\mathrm{H}_2]}{dt} = 3 \times 10^{-4} \text{ mol } \mathrm{L}^{-1} \mathrm{s}^{-1}$$

21. (b): The iodoform test is positive for alcohols with formula R — CHOH — CH₃. Among $C_6H_{14}O$ isomers, the ones with positive iodoform test are:

I.
$$CH_3 - CH_2 - CH_2 - CH_2 - CHOH - CH_3$$

2-Hexanol

II. $CH_3 - CH_2 - CH(CH_3) - CHOH - CH_3$ 3- Methyl-2-pentanol

- III. $(CH_3)_2CH CH_2 CHOH CH_3$ 4- Methyl-2-pentanol
- IV. $(CH_3)_3C CHOH CH_3$ 3, 3- Dimethyl-2-butanol

22. (b): Acidic strength of hydrides increase with increase in molecular mass.

Thus, order of acidic strength is HF < HCl < HBr < HI $H_2O < H_2S < H_2Se < H_2Te$ $NH_3 < PH_3 < AsH_3 < SbH_3$

and as acidic strength increases, pK_a decreases. Thus order of pK_a

 $H_2O > H_2S > H_2Se > H_2Te$

23. (c) : Vapour pressure of pure solvent $(P_A^{\circ}) = 143 \text{ mm Hg}$, weight of solute (w) = 0.5 g, weight of solvent (W) = 100 g, molecular weight of solute (m) = 65 and molecular weight of solvent (M) = 154.

$$\frac{p_{A}^{\circ} - p}{p_{A}^{\circ}} = \frac{wM}{mW} \text{ or } \frac{143 - P}{143} = \frac{0.5 \times 154}{65 \times 100}$$

or $P = 141.31 \text{ mm Hg}$
24. (c) : $[\text{Co}(\text{NH}_{3})_{6}]^{3+}$: $\text{Co}(27)$ $[\text{Ar}]^{18} 3d^{7}4s^{2}$
$$\underbrace{3d}_{4s} \underbrace{4s}_{4p} \underbrace{4p}_{4s} \underbrace{4p}_{4$$

tron pair from six ligands(NH₃) $d^2sp^3 \rightarrow$ inner octahedral complex and diamagnetic.

OR

(d) : Magnetic moment =
$$\sqrt{n(n+2)}$$

 $3.83 = \sqrt{n(n+2)} \implies (3.83)^2 = n(n+2)$ $\implies 14.6689 = n^2 + 2n$ On solving the equation, n = 3 $\operatorname{Cr}^{3+} \rightarrow [\operatorname{Ar}]3d^3$ $\boxed{\begin{array}{c}1 \\ d_{xy} \\ d_{yz} \\ d_{zx} \\ d_{x^2-y^2} \\ d_{z^2}\end{array}}$

25. (b)

26. (c) : Let the weight of isobutane is *x* g. Weight of isobutene is *y* g. Then x + y = 10 g.

Now, it is isobutene which will add bromine molecule not isobutane.

$$CH_{3}-C=CH_{2}+Br_{2} \longrightarrow CH_{3}-C-CH_{2}$$

$$CH_{3} \xrightarrow{(160 g)} Br Br$$

Isobutylene (56 g) 1, 2-dibromo-2-methylbutane Since 160 g of Br₂ reacts with 56 g of isobutene, hence 20 g of Br₂ reacts with = 7 g of isobutene *i.e.*, y = 7 g, hence x = 10 - 7 = 3 g.

Now, 56 g of isobutene gives 58 g of isobutane.

Hence 7 g of isobutene gives $\frac{7 \times 58}{56} = 7.25$ g.

Now total amount of isobutane available for 10 g mixture = 7.25 + 3 = 10.25.

$$CH_{3} - CH - CH_{3} \xrightarrow{Br_{2}/h_{U}} CH_{3} \xrightarrow{|}{} CH_{3} \xrightarrow{|}{} CH_{3} \xrightarrow{|}{} CH_{3} \xrightarrow{|}{} CH_{3}$$

$$(58 g) CH_{3} \xrightarrow{(137 g)} CH_{3}$$
Tertiary butylbromide

Now 58 g of isobutane gives 137 g of tertiary butyl bromide.

 $\therefore \quad 10.25 \text{ gof isobutane gives } \frac{10.25 \times 137}{58} = 24.21 \text{ g}$ of tertiary butylbromide.

27. (i) A lyophilic colloid is stable due to the charge as well as solvation of the sol particles. Such a solution can only be coagulated by adding an electrolyte and by adding a suitable solvent which can dehydrate the dispersed phase.

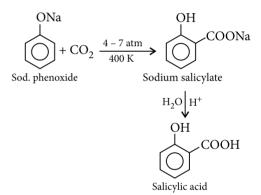
On the other hand, a lyophobic sol is stable due to charge only and hence can be easily coagulated by adding small amount of an electrolyte. (ii) Ferric hydroxide solution adsorbs Cl⁻ ions of NaCl and get neutralised. Thus the colloidal particles get precipitated *i.e.*, ferric hydroxide is precipitated when NaCl solution is added.

28. (i) (a) > (c) > (b). This is because with branching the shape becomes spherical and therefore, van der Waals' forces decrease. As a result, boiling point decreases.

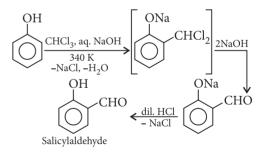
(ii) 1°-Alcohol does not react with Lucas reagent at room temperature.

OR

(i) **Kolbe's reaction :** When sodium phenoxide is heated with carbon dioxide under pressure, it gives salicylic acid.



(ii) Reimer-Tiemann reaction :



29. $w_1 = 0.90 \text{ g}, w_2 = 87.90 \text{ g}, \Delta T_b = 0.25^{\circ}\text{C}$ $M_1 = 103 \text{ g mol}^{-1}, \Delta T_b = K_b m$ $\Delta T_b = K_b \times \frac{w_1}{M_1} \times \frac{1000}{w_2}, K_b = \frac{\Delta T_b \times M_1 \times w_2}{w_1 \times 1000}$ $\Rightarrow K_b = \frac{0.25 \times 103 \times 87.90}{0.90 \times 1000} \Rightarrow K_b = \frac{2263.42}{900}$ $\Rightarrow K_b = 2.5149 = 2.515 \text{ K kg mol}^{-1}$ **30.** (a) *D* - Glucose gets oxidised to six carbon carboxylic acid (gluconic acid) on reaction with bromine water.

| CHO | СООН |
|-----------------------|-------------------------------------------------------------|
| (CHOH) ₄ - | $\xrightarrow{\text{Br}_2\text{water}}$ (CHOH) ₄ |
| CH,OH | CH ₂ OH |
| D-Glucose | Gluconic acid |

(b) On prolonged heating with HI, D-glucose forms n-hexane.

CHO

$$|$$

 $(CHOH)_4 \xrightarrow{HI, \Delta} CH_3 - (CH_2)_4 - CH_3$
 $|$
 CH_2OH
 D -Glucose

- **31.** (i) 1-Bromopentane (CH₃CH₂CH₂CH₂CH₂Br, 1°halide)
- (ii) 2-Bromopentane

$$(CH_3CH_2CH_2 - CH_3H - CH_3)$$

(iii) 2-Bromo-2-methylbutane

$$(CH_{3}CH_{2} - CH_{3}) = CH_{3}$$

- 32. (a) Schottky defect
- (b) As 27 g of Al will contain 6.023×10^{23} atoms
- \therefore 8.1 g Al will contain

$$= \frac{6.023 \times 10^{23}}{27} \times 8.1 \text{ atoms} = 1.8069 \times 10^{23} \text{ atoms}$$

In *fcc*, 4 atoms are present in one unit cell \therefore 1.8069 × 10²³ atoms will be present in $\frac{1.8069 \times 10^{23}}{10^{23}} = 4.517 \times 10^{22}$ unit cells

$$\frac{1}{4}$$
 = 4.517 × 10²² un

Given, edge length, $a = 4.077 \times 10^{-8}$ cm density, d = 10.5 g cm⁻³ For *fcc* lattice, Z = 4, Atomic mass M = ?

Using formula,
$$d = \frac{Z \times M}{N_A \times a^3}$$

or, $M = \frac{d \times N_A \times a^3}{Z}$

or
$$M = \frac{10.5 \times 6.022 \times 10^{23} \times (4.077 \times 10^{-8})^3}{4}$$

or
$$M = 107.12 \text{ g mol}^{-1}$$

33. (i) CH₃COOH
$$\xrightarrow{\text{PCl}_5}$$
 CH₃ $\xrightarrow{\text{C}}$ C-Cl $\xrightarrow{\text{NH}_3}$
Ethanoic acid
(Acetic acid)

$$CH_{3} - C - NH_{2} \xrightarrow{Br_{2}/KOH} CH_{3} - NH_{2}$$

$$Methanamine$$

 \sim

(ii) $CH_3-CH_2-NH_2 \xrightarrow{NaNO_2/HCl} CH_3-CH_2-OH$ Ethanamine CH_3-CH_2-OH

$$\xrightarrow{K_2Cr_2O_7 - /H^+} CH_3 - COOH \xrightarrow{PCl_5} CH_3 - COCI \xrightarrow{NH_3}$$

$$CH_3 - CONH_2 \xrightarrow{Br_2/KOH} CH_3 - NH_2$$

Methanamine

(iii) $CH_3 - NO_2 \xrightarrow{Sn / HCl} CH_3 - NH_2 \xrightarrow{CHCl_3 / KOH}$ Nitromethane

$$CH_3$$
-NC $\xrightarrow{Na/C_2H_3OH}$ CH_3 -NH-CH₃
Dimethylamine

34. (a) The electron gain enthalpy of oxygen is least negative in this group, due to its small size.

(b) Nitrogen does not form pentahalide, due to the absence of *d*-orbitals in its valence shell.

(c) The strength of an acid depends upon its bond strength. Since bond dissociation energy of HCl is greater than HI therefore, HI is stronger acid than HCl.

35. (a) (i) The sum of powers of the concentration of the reactants in the rate law expression is called the order of that chemical reaction. If rate $= kC_A^m \cdot C_B^n$

Then order of reaction = m + n

(ii) Let initial concentration be $[R]_0$. For a first order reaction, $t = \frac{2.303}{k} \log \frac{[R]_0}{[R]}$ At time t, $[R] = \frac{[R]_0}{4}$, $k = 2.4 \times 10^{-3} \text{ s}^{-1}$ Thus, $2.4 \times 10^{-3} = \frac{2.303}{t} \log \frac{[R]_0}{[R]_0/4}$ $t = \frac{2.303}{2.4 \times 10^{-3}} \log 4 = \frac{2.303}{2.4 \times 10^{-3}} \times 0.6021 = 5.77 \times 10^2 \text{ s}$

(b) Given,
$$\frac{d[\text{NO}_2]}{dt} = 2.8 \times 10^{-3} \,\text{M s}^{-1}$$

According to rate law expression,

$$-\frac{1}{2} \frac{d[N_2O_5]}{dt} = \frac{1}{4} \frac{d[NO_2]}{dt} = \frac{d[O_2]}{dt}$$

$$\therefore -\frac{1}{2} \frac{d[N_2O_5]}{dt} = \frac{1}{4} \times 2.8 \times 10^{-3}$$

$$\frac{-d[N_2O_5]}{dt} = \frac{1}{2} \times 2.8 \times 10^{-3} = 1.4 \times 10^{-3} \,\mathrm{M \, s^{-1}}$$

OR

The given reaction is

$$P_o + 2x = P_o + P_o \times \frac{40}{100}$$
; $\frac{2x}{1} = \frac{P_o}{2.5}$ or $P_o = 5x$
 $\therefore \quad x = \frac{P_o}{5}$

Now, $[R]_0 = P_o$

$$[R] = P_o - x = P_o - \frac{P_o}{5} = 0.8 P_o$$

Using formula, $k = \frac{2.303}{t} \log_{10} \frac{[R]_0}{[R]}$

or,
$$k = \frac{2.303}{20 \text{ min}} \log_{10} \frac{P_o}{0.8P_o}$$

or, $k = \frac{2.303}{20 \text{ min}} \log 1.25$ or, $k = \frac{2.303 \times 0.0969}{20 \text{ min}}$
 $k = 1.115 \times 10^{-2} \text{ min}^{-1}$

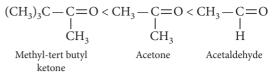
36. (a) (i)

$$\bigcirc = O + H_2 N - OH \xrightarrow{H^+} \bigcirc = N - OH \\Oxime$$

(ii)
$$2C_6H_5CHO + \text{conc. NaOH}$$

 $\rightarrow C_6H_5COONa + C_6H_5CH_2OH$
(iii) $CH_3COOH \xrightarrow[]{Cl_2/P} CH_2COOH$
 Cl

(b) (i) Greater the number of alkyl groups attached to the carbonyl group, lower is the reactivity towards nucleophilic addition reactions.



(ii) We know that + *I*-effect decreases while -I-effect increases the acid strength of carboxylic acids. The overall acid strength increases in the order :

$$\label{eq:ch3} \begin{split} (\mathrm{CH}_3)_2 \mathrm{CHCOOH} &< \mathrm{CH}_3 \mathrm{CH}(\mathrm{Br}) \mathrm{CH}_2 \mathrm{COOH} \\ &< \mathrm{CH}_3 \mathrm{CH}_2 \mathrm{CH}(\mathrm{Br}) \mathrm{COOH} \end{split}$$

OR

(i) (a)
$$C_6H_5COOH + NaHCO_3 \longrightarrow C_6H_5COONa + H_2O + CO_2 \uparrow$$

(effervescence)

 $C_6H_5COOC_2H_5 + NaHCO_3 \longrightarrow No reaction$ (b) Acetophenone with $I_2/NaOH$ gives yellow precipitate of iodoform but benzophenone does not.

$$C_{6}H_{5}COCH_{3} + 3I_{2} + 4NaOH \longrightarrow C_{6}H_{5}COONa + CHI_{3} + 3NaI + 3H_{2}OC_{6}H_{5}COC_{6}H_{5} + I_{2} + NaOH \longrightarrow No reaction$$

$$(ii) \bigcirc COOH \xrightarrow{COOH} OCCI_{COOH} OCCI_{COO} OCCI_{COOH} OCCI_{C$$

37. (a) (i) The transition metals and their compounds, are known for their catalytic activity. This activity is ascribed to their ability to adopt multiple oxidation states, ability to adsorb the reactant on its surface and to form complexes. Vanadium (V) oxide (in Contact Process), finely divided iron (in Haber's Process), and nickel (in catalytic hydrogenation) are some of the examples. (ii) This is because due to lanthanoid contraction the expected increase in size does not occur hence

they have very high value of ionisation enthalpy.

(b) (i) In 3*d* series atomic radius decreases from ${}_{21}$ Sc to ${}_{25}$ Mn and then becomes almost constant for next five elements *i.e.*, ${}_{26}$ Fe to ${}_{30}$ Zn. This is due to the combined effect of increasing effective nuclear charge and increasing inter electronic repulsions when pairing of electron starts along the period.

(ii) 3d-series elements show variable oxidation states due to the participation of 4s and 3d-electrons in bonding because the energies of 4sand 3d-subshells are almost equal. Oxidation state increases with the increase in number of unpaired electrons in 3d-subshell, reaches a maximum value in the middle and then starts decreasing when pairing of electrons in 3d-subshell starts. For example, Mn shows a maximum oxidation state of +7 in 3d-series.

(iii) Except Zn^{2+} , 3*d*-series transition metal ions possess incomplete *d*-orbitals which undergo *d*-*d*

transition and impart colour to them.

Some of the ions may impart colour due to charge transfer when metal ion has high +ve charge and anions are polarisable *e.g.*, $KMnO_4$, $K_2Cr_2O_7$.

OR

(i) As the size decreases covalent character increases. Therefore La_2O_3 is more ionic and Lu_2O_3 is more covalent.

(ii) As the size decreases from La to Lu, stability of oxosalts also decreases.

(iii) Stability of complexes increases as the size decreases.

(iv) Radii of 4d and 5d block elements will be almost same. It is associated with intervention of the 4f orbitals which must be filled before 5dseries of elements begins. The filling of 4f before 5d results in lanthanoids contraction hence 4dand 5d series have almost same size.

(v) Acidic character of oxides increases from La to Lu.