SAMPLE QUESTION PAPER

BLUE PRINT

Time Allowed : 3 hours **Maximum Marks :** 70

S. No.	Chapter	Passage based/ MCQs/A & R (1 mark)	SA-I (2 marks)	SA-II (3 marks)	LA (5 marks)	Total
1.	The Solid State	1(1)	1(2)	1(3)	–	**10(23)**
2.	Solutions	1(1)	–	–	1(5)	
3.	Electrochemistry	1(1)	1(2)	–	–	
4.	Chemical Kinetics	1(4)	–	–	–	
5.	Surface Chemistry	1(1)	–	1(3)	–	
6.	The *p*-Block Elements	2(2)	2(4)	–	–	**10(19)**
7.	The *d*- and *f*-Block Elements	2(2)	–	–	1(5)	
8.	Coordination Compounds	1(1)	1(2)	1(3)	–	
9.	Haloalkanes and Haloarenes	1(1)	–	1(3)	–	**13(28)**
10.	Alcohols, Phenols and Ethers	2(2)	1(2)	–	–	
11.	Aldehydes, Ketones and Carboxylic Acids	1(1)	1(2)	–	1(5)	
12.	Amines	1(4)	1(2)	1(3)	–	
13.	Biomolecules	1(1)	1(2)	–	–	
	Total	**16(22)**	**9(18)**	**5(15)**	**3(15)**	**33(70)**

Subject Code : 043

CHEMISTRY

Time allowed : 3 hours **_Maximum marks : 70_**

General Instructions : Read the following instructions carefully.

(a) There are 33 questions in this question paper. All questions are compulsory.

(b) Section A : Q. No. 1 to 16 are objective type questions. Q. No. 1 and 2 are passage based questions carrying 4 marks each while Q. No. 3 to 16 carry 1 mark each.

(c) Section B : Q. No. 17 to 25 are short answer questions and carry 2 marks each.

(d) Section C : Q. No. 26 to 30 are short answer questions and carry 3 marks each.

(e) Section D : Q. No. 31 to 33 are long answer questions carrying 5 marks each.

(f) There is no overall choice. However, internal choices have been provided.

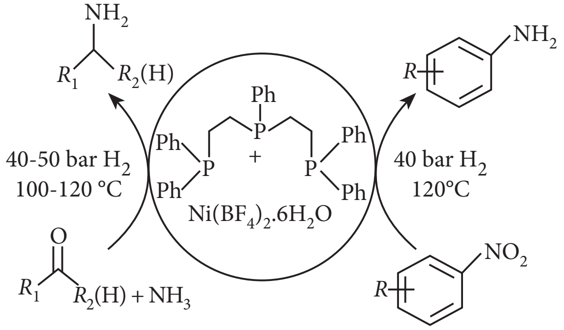
(g) Use of calculators and log tables is not permitted.

SECTION - A (OBJECTIVE TYPE)

1. Read the passage given below and answer the following questions :

The synthesis of primary amines is of central importance because these compounds serve as a key precursors and central intermediates to produce value added fine and bulk chemicals as well as pharmaceuticals, agrochemicals and materials.

Recently, a nickel-based homogeneous catalyst for both reductive amination of carbonyl compounds with ammonia and hydrogenation of nitroarenes to prepare all kinds of primary amines has been discovered.



Remarkably, this Ni–complex enabled the synthesis of functionalized and structurally diverse benzylic, heterocyclic and aliphatic linear and branched primary amines as well as aromatic primary amines starting from inexpensive carbonyl compounds (aldehydes and ketones) and nitroarenes using ammonia and molecular hydrogen.

The following questions are multiple choice questions. Choose the most appropriate answer :

(i) The nickel-based homogeneous complex mention in the study above can be used to convert

(a) nitrobenzene to aniline (b) nitrobenzene to benzylamine

(c) benzamine to acetanilide (d) nitrite salt to nitrosoamine.

(ii) The primary amine formed during reductive amination of acetaldehyde with ammonia can also be obtained by reduction of

(a) acetamide
(b) *N*–methylacetamide
(c) methyl isocyanide
(d) acetone.

OR

Which of the following is a primary amine?

(a) Phenylaminomethane
(b) *N*-methylaminobenzene
(c) *N*-methyl-2-aminopropane
(d) Triethylamine

(iii) Nitrobenzene on treatment with this Ni-based homogeneous catalyst gives a compound, *X* which on reaction with warmed chloroform and alcoholic solution of KOH, forms a compound, *Y*.
Compound *Y* on treatment with $LiAlH_4$ gives compound, *Z*. Compounds *X*, *Y* and *Z* respectively are

(a) aniline, *N*-methylaniline, Phenyl isocyanide
(b) aniline, phenyl isocyanide *N*-methylaniline
(c) benzylamine, phenyl isocyanide *N*-methylaniline
(d) N-methylaniline, benzylamine, phenyl isocyanide.

(iv) An organic compound '*X*' with molecular formula, C_2H_4O with this Ni-based homogeneous catalyst in presence of ammonia gives compound '*Y*'. Compound '*Y*' on reaction with nitrous acid gives compound '*Z*' with evolution of N_2. What is the product of reaction of '*Z*' with phosphorus bromide?

(a) CH_3Br
(b) CH_3CH_2Br
(c) $CH_2 = CHBr$
(d) $BrCH = CHBr$

2. Read the passage given below and answer the following questions:

Chemical reactions require varying lengths of time for completion, depending upon the characteristics of the reactants and products and the conditions under which the reaction is taking place. Chemical kinetics is the study of reaction rates, how reaction rates change under varying conditions and by which mechanism the reaction proceeds.

There are five general properties that can affect the rate of a reaction (i) Concentration of the reactant : The more concentrated the faster the rate; (ii) Temperature : usually reaction speed up with increasing temperature; (iii) Physical state of reactants: powder reacts faster than blocks as they have greater surface area and since the reaction occurs at the surface, we get a faster rate; (iv) Catalyst : A catalyst speeds up a reaction; (v) Light : Light of a particular wavelength may also speed up a reaction.

Mathematically, rate of a reaction is defined as the change in concentration of reactant or product over time.

In these questions (Q. No. i- iv), a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

(a) Assertion and reason both are correct statements, and reason is the correct explanation of the assertion.
(b) Assertion and reason both are correct statements, but reason is not the correct explanation of the assertion.
(c) Assertion is correct, but reason is wrong statement.
(d) Assertion is wrong, but reason is correct statement.

(i) **Assertion :** A catalyst increases the rate of a reaction.
Reason : A catalyst forms an activated complex of lower potential energy.

(ii) **Assertion :** Rate of reaction increases with increase in temperature.
Reason : Number of collisions increases with increase in temperature.

(iii) **Assertion :** Rate of reaction always decreases with time.
Reason : The amount of reactant remaining always decreases with time in chemical reaction.

(iv) **Assertion :** In rate law, unlike in the expression for equilibrium constants, the exponents for concentrations do not necessarily match the stoichiometric coefficients.
Reason : It is the mechanism and not the balanced chemical equation for the overall change that governs the reaction rate.

OR

Assertion : A piece of wood burns slowly in air but rapidly burns in pure oxygen.
Reason : Concentration of oxygen is less in air.

Following questions (Q. No. 3-11) are multiple choice questions carrying 1 mark each :

3. In orthorhombic crystal, the values of *a*, *b* and *c* are respectively 4.2 Å, 8.6 Å and 8.3 Å. The molecular mass of the solute is 155 g mol^{-1} and density is 3.3 g/cc. The number of formula units per unit cell is

(a) 2 (b) 3 (c) 4 (d) 6

OR

A binary solid (A^+B^-) has a zinc blende structure with B^- ions constituting the lattice and A^+ ions occupying 25% tetrahedral holes. The formula of solids is

(a) AB (b) A_2B (c) AB_2 (d) AB_4

4. XeF_6 on hydrolysis gives

(a) XeO_3 (b) XeO (c) XeO_2 (d) Xe

5. One kilogram of water contains 4 g of NaOH. The concentration of the solution is best expressed as

(a) 0.1 molal (b) 0.1 molar (c) decinormal (d) about 0.1 mole.

6. Within the list shown below, the correct pair of structures of alanine in pH ranges 2-4 and 9-11 is respectively.

I. $H_3N^+—CH(CH_3)CO_2H$
II. $H_2N—CH(CH_3)CO_2^-$
III. $H_3N^+—CH(CH_3)CO_2^-$
IV. $H_2N—CH(CH_3)CO_2H$

(a) I, II (b) I, III (c) II, III (d) III, IV

OR

The primary structure of a protein refers to

(a) whether the protein is fibrous or globular
(b) the amino acid sequence in the polypeptide
(c) the orientation of the amino acid side chains in space
(d) the presence or absence of an α-helix.

7. An ether (*A*) $C_5H_{12}O$ when heated with excess HI produced two alkyl iodide which on alkaline hydrolysis forms compound (*B*) and (*C*). Oxidation of (*B*) gives acid and oxidation of (*C*) gives ketone. What is compound (*A*)?

(a) $CH_3OCH_2CH_2CH_2CH_3$ (b) $C_2H_5OCH_2CH_2CH_3$
(c) $C_2H_5OCH(CH_3)_2$ (d) All of these

8. Consider the following complex, $Na[Cr(NH_3)_2(ox)_2].3H_2O$
The coordination number, oxidation number, number of *d*-electrons, number of unpaired electrons on the metal and magnetic moment are respectively

(a) 6, +2, 4, 0, 0 (b) 4, +3, 3, 3, 3.87
(c) 6, +3, 3, 3, 3.87 (d) 4, +2, 4, 0, 0

OR

Which of the following statements are correct?

(i) In octahedral complexes, $d_{z^2}, d_{x^2-y^2}$ orbitals have higher energy than d_{xy}, d_{yz} and d_{zx} orbitals.

(ii) In tetrahedral complexes d_{xy}, d_{yz}, d_{zx} orbitals have higher energy than d_{z^2} and $d_{x^2-y^2}$ orbitals.

(iii) The colours of complexes are due to electronic transitions from one set of *d*-orbitals to another set of orbitals.

(iv) $\Delta_{\text{tetrahedral}} = \frac{9}{4} \times \Delta_{\text{octahedral}}$

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

9. On adding few drops of dilute HCl or $FeCl_3$ to freshly precipitated ferric hydroxide a red coloured colloidal solution is obtained. The phenomenon is known as

(a) peptisation
(b) dialysis
(c) protective action
(d) dissolution.

10. The lanthanoids contraction is responsible for the fact that

(a) Zr and Y have about the same radius
(b) Zr and Nb have similar oxidation state
(c) Zr and Hf have about the same radius
(d) Zr and Zn have same oxidation state.

11. The e.m.f. of the following galvanic cells :

(i) $Zn|Zn^{2+}$ (1 M) || Cu^{2+} (1 M) | Cu
(ii) $Zn|Zn^{2+}$ (0.1 M) || Cu^{2+} (1 M) | Cu
(iii) $Zn|Zn^{2+}$ (1 M) || Cu^{2+} (0.1 M) | Cu
(iv) $Zn|Zn^{2+}$ (0.1 M) || Cu^{2+} (0.1 M) | Cu

are represented by E_1, E_2, E_3 and E_4 respectively. Which of the following orders is correct?

(a) $E_1 > E_2 > E_3 > E_4$
(b) $E_3 > E_2 > E_1 > E_4$
(c) $E_3 > E_1 = E_4 > E_2$
(d) $E_2 > E_1 = E_4 > E_3$

OR

If the conductivity and conductance of a solution is same then its cell constant is equal to

(a) 1
(b) 0
(c) 10
(d) 1000

In the following questions (Q. No. 12 - 16) a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
(c) Assertion is correct statement but reason is wrong statement.
(d) Assertion is wrong statement but reason is correct statement.

12. **Assertion :** Fluorine has a less negative electron affinity than chlorine.
Reason : There is relatively greater effectiveness of 2*p*-electrons in the small F atom to repel the additional electron entering the atom than to 3*p*-electrons in the larger Cl atom.

13. **Assertion :** Addition reaction of water to but-1-ene in acidic medium yields butan-1-ol.
Reason : Addition of water in acidic medium proceeds through the formation of secondary carbocation.

14. **Assertion :** Mn^{2+} is more stable than Mn^{3+}.

Reason : Mn^{2+} has half-filled configuration.

15. **Assertion :** Formaldehyde cannot be prepared by Rosenmund's reduction.
Reason : Acid chlorides can be reduced into aldehydes with hydrogen in boiling xylene using palladium or platinum as a catalyst supported on barium sulphate. This is known as Rosenmund's reduction.

OR

Assertion : Benzaldehyde is more reactive than ethanal towards nucleophilic attack.
Reason : The overall effect of $-I$ and $+R$ effect of phenyl group decreases the electron density on the carbon atom of $> C = O$ group in benzaldehyde.

16. **Assertion :** The presence of nitro group facilitates nucleophilic substitution reactions in aryl halides.
Reason : The intermediate carbanion is stabilised due to the presence of nitro group.

SECTION - B

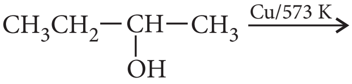
The following questions, Q. No. 17-25 are short answer type and carry 2 marks each.

17. What happens when

(i) Nitroethane is treated with $LiAlH_4$?

(ii) Ethanamine reacts with AgCl?

18. Write the final product(s) in each of the following reactions :

(a) 

$CH_3CH_2-\underset{OH}{\underset{|}{C}}H-CH_3 \xrightarrow{Cu/573\ K}$

(b) $C_6H_5-OH \xrightarrow[(ii)\ H^+]{(i)\ CHCl_3 + aq.\ NaOH}$

19. Distinguish between :

(i) Essential and non-essential amino acids.

(ii) α-Glucose and β-glucose.

OR

What is DNA finger printing? What are the areas of its application?

20. Using crystal field theory, draw energy level diagram, write electronic configuration of the central metal atom/ion and determine the magnetic moment value for the following :
$[FeF_6]^{3-}$, $[Fe(H_2O)_6]^{2+}$.

OR

What will be the correct order of absorption of wavelength of light in the visible region for the complexes $[Co(NH_3)_6]^{3+}$, $[Co(CN)_6]^{3-}$ and $[Co(H_2O)_6]^{3+}$?

21. (i) Tendency to show – 2 oxidation state diminishes from sulphur to polonium in group 16. Why?

(ii) Only higher members of group-18 of the periodic table are expected to form compounds. Why?

22. An element with density 2.8 g cm^{-3} forms a *fcc* unit cell with edge length 4×10^{-8} cm. Calculate the molar mass of the element. (Given : $N_A = 6.022 \times 10^{23}\ mol^{-1}$)

23. The $E°$ values corresponding to the following two reduction electrode processes are :
$Cu^+/Cu = +\ 0.52$ V, $Cu^{2+}/Cu^+ = +\ 0.16$ V
Formulate the galvanic cell for their combination. What will be the standard cell potential for it? Calculate $\Delta_r G°$ for the cell reaction. ($F = 96500\ C\ mol^{-1}$)

OR

Determine the value of equilibrium constant (K_c) and $\Delta G°$ for the following reaction :
$Ni_{(s)} + 2Ag^+_{(aq)} \rightarrow Ni^{2+}_{(aq)} + 2Ag_{(s)}$, $E° = 1.05$ V
($1\ F = 96500\ C\ mol^{-1}$)

24. How will you bring about the following conversions?

(i) Ethanal to but-2-enal

(ii) Propanone to propene

25. (a) Arrange halogens in increasing order of electron affinity.

(b) Why does fluorine show abnormal behaviour?

SECTION - C

Q. No. 26-30 are short answer type II carrying 3 marks each.

26. (i) A compound forms hexagonal close-packed structure. What is the total number of voids in 0.5 mol of it? How many of these are tetrahedral voids?

(ii) Why is Frenkel defect not found in pure alkali metal halides?

27. Write the chemical equations for the following conversions :

(i) Aniline to *N*-phenylethanamide. (ii) Aniline to *p*-nitroaniline.

OR

Identify *A*, *B* and *C* in the following reactions :

(a) $CH_3Br \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow[273\ K]{HNO_2} C$

(b) $CH_3COOH \xrightarrow[\Delta]{NH_3} A \xrightarrow{Br_2 + KOH} B \xrightarrow{CHCl_3 + NaOH} C$

28. Explain the following terms with a suitable example in each case :

(i) Zeta potential

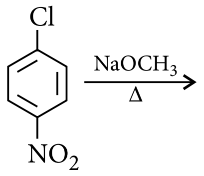
(ii) Tanning

(iii) Multimolecular colloids

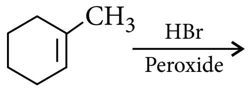
29. (i) Allyl chloride is more reactive than *n*-propyl chloride towards nucleophilic substitution reaction. Explain why.

(ii) What are the major products of the following reactions?

(a)



(b)



OR

(i) Which of the two compounds, $CH_3CH{=}CHCH_2Br$ or $CH_3CH(Br)CH{=}CH_2$ is achiral and which is chiral?

(ii) Arrange each set of compounds in order of increasing boiling points :

(a) Bromomethane, bromoform, chloromethane, dibromomethane

(b) 1-Chloropropane, *iso*-propyl chloride, 1-chlorobutane.

30. Write the name, the structure and the magnetic behaviour of each one of the following complexes :

(i) $[Pt(NH_3)_2Cl(NO_2)]$ (ii) $[Co(NH_3)_4Cl_2]Cl$

(iii) $Ni(CO)_4$

(At. nos. Co = 27, Ni = 28, Pt = 78)

SECTION - D

Q No. 31-33 are long answer type carrying 5 marks each.

31. (i) Give one chemical test to distinguish between the following pairs of compounds :

(a) Ethanal and propanal

(b) Benzoic acid and ethyl benzoate

(ii) How will you bring about the following conversions in not more than two steps?

(a) Benzene to *m*-nitroacetophenone

(b) 2-Methylpropanol to 2-methylpropene

(iii) There are two —NH_2 groups in semicarbazide. However, only one is involved in the formation of semicarbazone. Explain.

OR

An organic compound contains 69.77% carbon, 11.63% hydrogen and rest, oxygen. The molecular mass of the compound is 86. It does not reduce Tollens' reagent but forms an addition compound with sodium hydrogen sulphite and give positive iodoform test. On vigorous oxidation it gives ethanoic and propanoic acid. Write the possible structure of the compound and give reactions involved also.

32. (i) At 300 K, 36 g of glucose present per litre in its solution has an osmotic pressure of 4.98 bar. If osmotic pressure of solution is 1.52 bar at the same temperature, what would be its concentration?

(ii) Osmotic pressure is more useful to calculate molecular mass than other colligative properties. Why?

(iii) If N_2 gas is bubbled through water at 293 K, how many millimoles of N_2 gas would dissolve in 1 litre of water? Assume that N_2 exerts a partial pressure of 0.987 bar. Given that Henry's law constant for N_2 at 293 K is 76.48 kbar.

OR

The vapour pressure of two pure liquids, *A* and *B* that form an ideal solution are 300 and 800 torr respectively, at temperature *T*. A mixture of the vapours of *A* and *B* for which the mole fraction of *A* is 0.25 is slowly compressed at temperature *T*. Calculate

(a) the composition of the first drop of the condensate,
(b) the total pressure when this drop is formed,
(c) the composition of the solution whose normal boiling point is *T*,
(d) the pressure when only the last bubble of vapour remains, and
(e) the composition of the last bubble.

33. (a) Assign reason for the following :

(i) The enthalpies of atomisation of transition elements are high.

(ii) Scandium ($Z = 21$) does not exhibit variable oxidation states and yet it is regarded as transition element.

(b) What may be the possible oxidation states of the transition metals with the following *d* electronic configurations in the ground state of their atoms :
$3d^3 4s^2$, $3d^5 4s^2$ and $3d^6 4s^2$. Indicate relative stability of oxidation states in each case.

OR

(a) How would you account for the following :

(i) The atomic radii of the metals of the third (5*d*) series of transition elements are virtually the same as those of the corresponding members of the second (4*d*) series.

(ii) The $E°$ value for the Mn^{3+}/Mn^{2+} couple is much more positive than that for Cr^{3+}/Cr^{2+} couple or Fe^{3+}/Fe^{2+} couple.

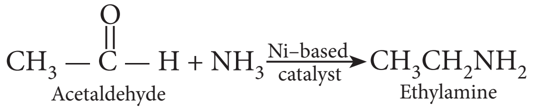
(iii) The highest oxidation state of a Mn metal is exhibited in its oxide or fluoride.

(b) Which of following cations are coloured in aqueous solutions and why?
Sc^{3+}, V^{3+}, Ti^{4+}, Mn^{2+} (At. Nos. Sc = 21, V = 23, Ti = 22, Mn = 25)

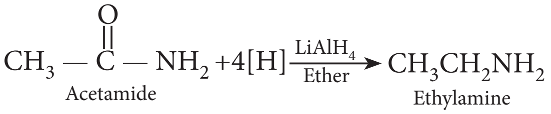
SOLUTIONS

1. (i) (a)

(ii) (a) :



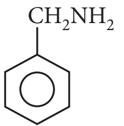
$$\underset{\text{Acetaldehyde}}{CH_3-\overset{O}{\overset{\|}{C}}-H} + NH_3 \xrightarrow[\text{catalyst}]{\text{Ni–based}} \underset{\text{Ethylamine}}{CH_3CH_2NH_2}$$



$$\underset{\text{Acetamide}}{CH_3-\overset{O}{\overset{\|}{C}}-NH_2} + 4[H] \xrightarrow[\text{Ether}]{LiAlH_4} \underset{\text{Ethylamine}}{CH_3CH_2NH_2}$$

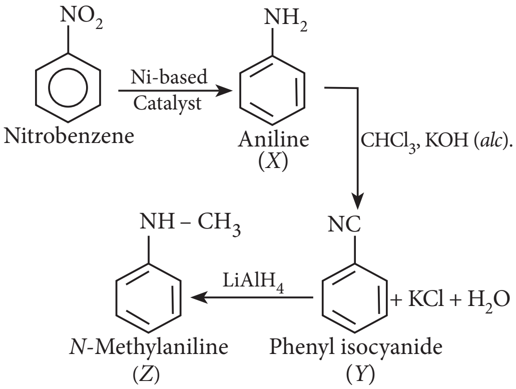
OR

(a) :

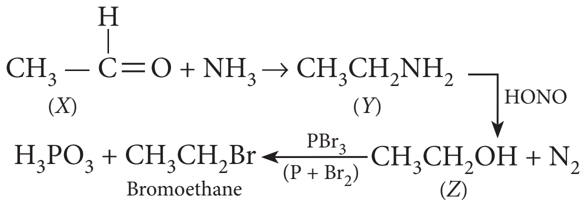


Phenylaminomethane

(iii) (b) :



(iv) (b) :



$$\underset{(X)}{CH_3-\overset{H}{\overset{|}{C}}=O} + NH_3 \rightarrow \underset{(Y)}{CH_3CH_2NH_2} \xrightarrow{\text{HONO}}$$

$$H_3PO_3 + \underset{\text{Bromoethane}}{CH_3CH_2Br} \xleftarrow[(P + Br_2)]{PBr_3} \underset{(Z)}{CH_3CH_2OH} + N_2$$

2. (i) (a)

(ii) (b) : An increase in temperature will raise the kinetic energy of the reactant molecules. Therefore, a greater proportion of reactant molecules will have minimum energy necessary for an effective collision. Therefore by increase in number of collisions, the rate of reaction gets increased.

(iii) (d) : Rate of reaction not always decreases with time. In zero order reaction, rate of reaction is independent of concentration.

(iv) (a)

OR

(a) Rate of reaction is directly proportional to concentration of oxygen.

3. (c) : $Z = \dfrac{V \times N_0 \times d}{M}$

$$= \frac{4.2 \times 8.6 \times 8.3 \times 10^{-24} \times 6.023 \times 10^{23} \times 3.3}{155} = 3.84 \approx 4$$

OR

(c) : No. of B^- (*fcc*) ions in unit cell

$$= 8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$$

Now A^+ ion occupies 25% of tetrahedral holes $= \dfrac{8 \times 25}{100} = 2$

Thus, ratio of B^- to A^+ is 2 : 1 and formula is AB_2.

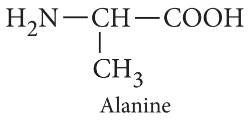
4. (a) : $XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$

5. (a) : Mole of NaOH $= \dfrac{4}{40} = 0.1$ mol

Mass of water = 1 kg

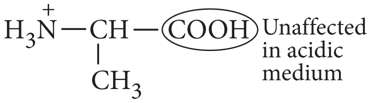
Molality $= \dfrac{0.1}{1} = 0.1\,\text{m}$

6. (a) :



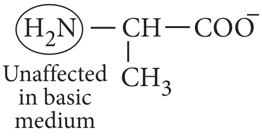
$$\underset{\text{Alanine}}{H_2N-\underset{CH_3}{\underset{|}{CH}}-COOH}$$

Acidic medium :



$$H_3\overset{+}{N}-\underset{CH_3}{\underset{|}{CH}}-\boxed{COOH}\ \text{Unaffected in acidic medium}$$

Basic medium :



$$\underset{\text{Unaffected in basic medium}}{\boxed{H_2N}}-\underset{CH_3}{\underset{|}{CH}}-COO^-$$

OR

(b)

7. (c) : $\underset{(A)}{C_2H_5OCH(CH_3)_2} + 2HI \xrightarrow{\text{Heat}}$

$$C_2H_5I + (CH_3)_2CHI + H_2O$$

$$C_2H_5I + KOH \xrightarrow{aq.} \underset{(B)}{C_2H_5OH} + KI$$

$$\underset{(B)}{C_2H_5OH} \xrightarrow{\text{oxidation}} CH_3COOH$$

$$(CH_3)_2CHI + KOH \xrightarrow{aq.} \underset{(C)}{(CH_3)_2CHOH} + KI$$

$$\underset{(C)}{(CH_3)_2CHOH} \xrightarrow{\text{oxidation}} CH_3COCH_3$$

8. (c) : NH_3 is monodentate while *ox* is a bidentate ligand. Thus, coordination number of metal is

$= 2 \times 1 + 2 \times 2 = 6$

Oxidation number of metal = +3

Cr = [Ar] $3d^5, 4s^1$; $Cr^{3+} = 3d^3$
All the three electrons are unpaired.

Magnetic moment $= \sqrt{n(n+2)} = \sqrt{3\times5} = \sqrt{15} = 3.87$ B.M.

OR

(a) : $\Delta_{\text{tetrahedral}} = \frac{4}{9}\times\Delta_{\text{octahedral}}$

9. (a)

10. (c) : It is a fact developed due to lanthanoid contraction, otherwise size of Hf should have been greater than Zr.

11. (d) : $E = E^\circ - \frac{0.0591}{2}\log\frac{[Zn^{2+}]}{[Cu^{2+}]}$

As $Q\downarrow, E\uparrow$
$Q_1 = 1, Q_2 = 0.1, Q_3 = 10, Q_4 = 1$
$E_2 > E_1 = E_4 > E_3$

OR

(a) κ = conductance × cell constant
since κ = conductance
$\therefore$ cell constant = 1

12. (a)

13. (d) : Addition of water to but-1-ene in acidic medium yields butan-2-ol because this reaction proceeds through the formation of secondary carbocation.

14. (a) : A half-filled or fully-filled orbital is more stable than incompletely filled orbital.

15. (b)

OR

(a)

16. (a)

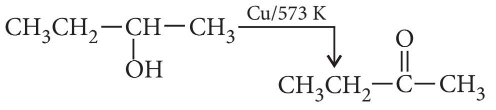
17. (i) Ethylamine is formed.

$$\underset{\text{Nitroethane}}{C_2H_5NO_2} \xrightarrow[\text{dry ether}]{LiAlH_4} \underset{\text{Ethylamine}}{C_2H_5-NH_2} + 2H_2O$$

(ii) Silver chloride dissolves in aqueous ethylamine due to the formation of the complex

$$C_2H_5NH_2 \xrightarrow{AgCl} [Ag(C_2H_5NH_2)_2]^+ Cl^-$$

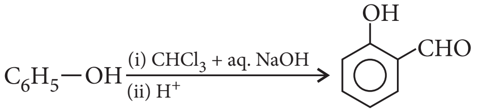
18. (a)



$$CH_3CH_2-\underset{OH}{CH}-CH_3 \xrightarrow{Cu/573\ K} CH_3CH_2-\overset{O}{\overset{\|}{C}}-CH_3$$

Butan-2-one

(b)



Salicylaldehyde

19. (i) The amino acids which can be synthesised in our body are called non-essential amino acids.

While the amino acids which cannot be synthesised in our body and must be taken through diet are called essential amino acids.

(ii) α-Glucose and β-glucose differ in configuration of –OH group on the anomeric carbon (C_1). In α-glucose, the –OH group at C_1 is towards right while in β-glucose, the –OH group at C_1 is towards left.

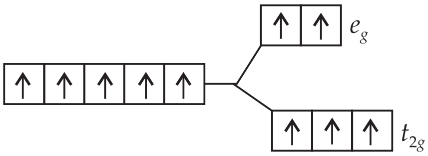
OR

A sequence of bases on DNA is unique for a person and information regarding this is called DNA finger printing.

Applications :

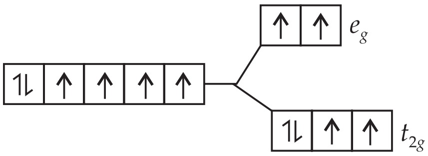
(i) In forensic lab for identifying criminals.
(ii) To determine paternity of an individual.
(iii) To identify the dead bodies in any accident by comparing the DNA's of parents or children.

20. $[FeF_6]^{3-}$: $Fe^{3+} = 3d^5$



Number of unpaired electrons = 5
Magnetic moment $= \sqrt{5(5+2)} = 5.92$ B.M.

$[Fe(H_2O)_6]^{2+}$: $Fe^{2+} = 3d^6$



Number of unpaired electrons = 4
Magnetic moment $= \sqrt{4(4+2)} = 4.9$ B.M.

OR

As strength of ligand increases crystal field splitting energy (CFSE) increases.
Order of strength of ligands :
$I^- < Br^- < Cl^- < NO_3^- < F^- < OH^- < ox < H_2O < py = NH_3 < en <$ dipy $< o$-phen $< NO_2^- < CN^- <$ CO.

Now, $\Delta E = \frac{hc}{\lambda}$.

So, as CFSE increases, λ decreases.
Thus, the correct order of absorption of wavelength of light in the visible region is :
$[Co(H_2O)_6]^{3+} > [Co(NH_3)_6]^{3+} > [Co(CN)_6]^{3-}$.

21. (i) From sulphur to polonium electronegativity decreases hence tendency to show negative oxidation state decreases.

(ii) Higher members have smaller ionisation enthalpy than lower members and hence they are expected to form compounds.

22. Given, density of solid, $d = 2.8$ g cm^{-3}
For *fcc* unit cell, $Z = 4$

Edge length, $a = 4 \times 10^{-8}$ cm,
Molar mass, $M = ?$
$N_A = 6.022 \times 10^{23}\ \text{mol}^{-1}$

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

Substituting these values, we get

$$M = \frac{2.8\ \text{g cm}^{-3} \times 6.022 \times 10^{23}\ \text{mol}^{-1} \times (4 \times 10^{-8}\ \text{cm})^3}{4}$$

or $M = \dfrac{2.8 \times 6.022 \times 6.4}{4} = 26.98\ \text{g mol}^{-1}$

23. At cathode : $Cu^+ + e^- \longrightarrow Cu$; $E° = +0.52$ V
At anode : $Cu^+ \longrightarrow Cu^{2+} + e^-$; $E° = +0.16$ V
Cell reaction : $2Cu^+ \longrightarrow Cu + Cu^{2+}$

Cell representation is

$Cu^+ \mid Cu^{2+} \parallel Cu^+ \mid Cu$

$E°_{\text{cell}} = E°_{\text{cathode}} - E°_{\text{anode}} = 0.52 - 0.16 = 0.36$ V

$\Delta_r G° = -nE°F = -1 \times 0.36 \times 96500$
$= -34740\ \text{J mol}^{-1}$

OR

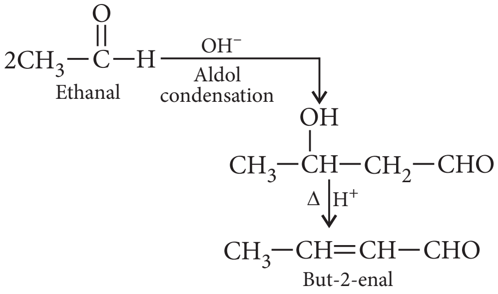
$Ni_{(s)} + 2Ag^+_{(aq)} \rightarrow Ni^{2+}_{(aq)} + 2Ag_{(s)}$, $E° = 1.05$ V
Here, $n = 2$

Using formula, $\log K_c = \dfrac{nE°_{\text{cell}}}{0.059}$

or $\log K_c = \dfrac{2 \times 1.05}{0.059} = 35.5932$

$K_c = \text{antilog } 35.5932$ or $K_c = 3.92 \times 10^{35}$
Again, $\Delta G° = -nFE°_{\text{cell}}$
$\Delta G° = -2 \times 96500 \times 1.05 = -202650$ J
$\Delta G° = -202.65$ kJ

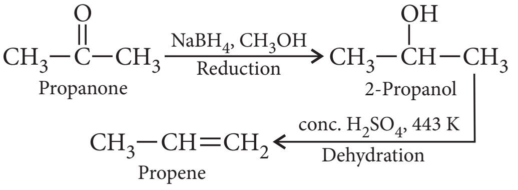
24. (i)



$$2CH_3-\overset{\overset{O}{\|}}{C}-H \xrightarrow[\text{Aldol condensation}]{OH^-} CH_3-\overset{\overset{OH}{|}}{CH}-CH_2-CHO \xrightarrow[\Delta]{H^+} CH_3-CH=CH-CHO$$

Ethanal; But-2-enal

(ii) Propanone to propene



$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow[\text{Reduction}]{NaBH_4,\ CH_3OH} CH_3-\overset{\overset{OH}{|}}{CH}-CH_3 \xrightarrow[\text{Dehydration}]{\text{conc. } H_2SO_4,\ 443\ K} CH_3-CH=CH_2$$

Propanone; 2-Propanol; Propene

25. (a) $I_2 < Br_2 < F_2 < Cl_2$ - electron affinity.
(b) (i) Due to small size.
(ii) Due to absence of vacant *d*-orbitals.
(iii) Due to high electronegativity.

26. (i) No. of atoms in the close packing = 0.5 mol $= 0.5 \times 6.022 \times 10^{23} = 3.011 \times 10^{23}$

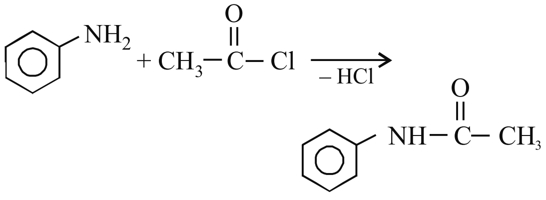
No. of octahedral voids = 1 × No. of atoms in the packing $= 3.011 \times 10^{23}$

No. of tetrahedral voids = 2 × No. of atoms in the packing $= 2 \times 3.011 \times 10^{23} = 6.022 \times 10^{23}$

Total no. of voids $= 3.011 \times 10^{23} + 6.022 \times 10^{23}$
$= 9.033 \times 10^{23}$

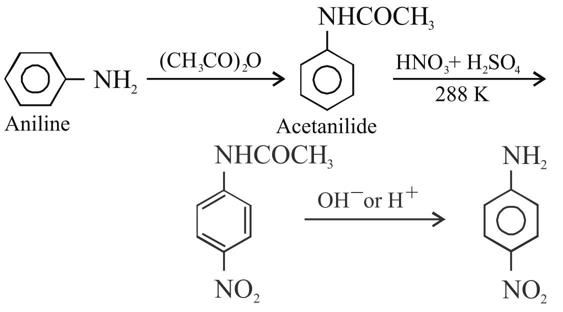
(ii) Frenkel defect is not found in pure alkali metal halides because alkali metal ions cannot fit into the interstitial sites.

27. (i)



N-Phenylethanamide

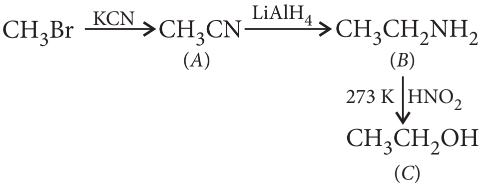
(ii)



p-Nitroaniline

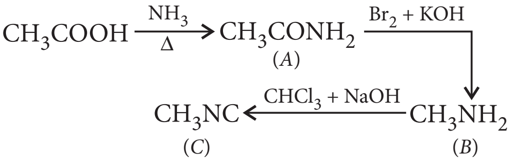
OR

(a)



$$CH_3Br \xrightarrow{KCN} \underset{(A)}{CH_3CN} \xrightarrow{LiAlH_4} \underset{(B)}{CH_3CH_2NH_2} \xrightarrow[273\ K]{HNO_2} \underset{(C)}{CH_3CH_2OH}$$

(b)



$$CH_3COOH \xrightarrow[\Delta]{NH_3} \underset{(A)}{CH_3CONH_2} \xrightarrow{Br_2 + KOH} \underset{(B)}{CH_3NH_2} \xrightarrow{CHCl_3 + NaOH} \underset{(C)}{CH_3NC}$$

28. (i) The potential difference between the fixed layer and the diffused layer of opposite charge of colloidal system is called Zeta potential.

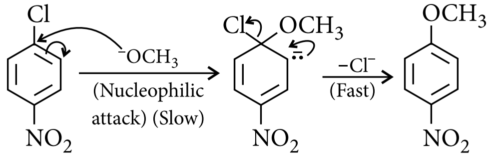
(ii) Animal hides are colloidal in nature. When a hide which has positively charged particles is soaked in tannin, which contains negatively charged colloidal particles, mutual coagulation takes place. This results in the hardening of leather. This process is termed as tanning.

(iii) A large number of atoms or smaller molecules of a substance on dissolution aggregate together to form species having size (diameter < 1 nm) in the colloidal range (1–1000 nm). Such species are known as multimolecular colloids. For example, a sulphur sol consists of particles containing a thousand or more of S_8 sulphur molecules.

29. (i) Allyl chloride is more reactive than *n*-propyl chloride towards nucleophilic substitution reaction due to the greater stabilisation of allylic carbocation intermediate formed by resonance.

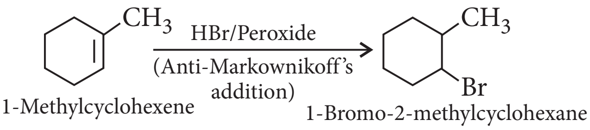
$$H_2C{=}CH{-}H_2\overset{+}{C} \longleftrightarrow H_2\overset{+}{C}{-}CH{=}CH_2$$

(ii) (a)



p-Nitroanisole

(b)



OR

(i) $CH_3CH{=}CHCH_2Br$ is achiral because it does not contain chiral carbon atom whereas $CH_3\overset{*}{C}H(Br)CH{=}CH_2$ is chiral because it contains chiral carbon atom.

(ii) (a) Boiling point increases with increase in molecular mass. It also depends on the size and number of halogen atoms. Therefore, the arrangement of the given compounds in order of increasing boiling points is as follows :

$CH_3Cl < CH_3Br < CH_2Br_2 < CHBr_3$

(b) For the same halogen, boiling point increases with increase in size of the alkyl group. Further the boiling point decreases as the branching increases. Therefore, the arrangement of the given compounds in the order of increasing boiling points is as follows :

$(CH_3)_2CHCl < ClCH_2CH_2CH_3 < ClCH_2CH_2CH_2CH_3$

30. (i) $[Pt(NH_3)_2Cl(NO_2)]$:
Diamminechloridonitrito-N-platinum(II)
It is square planar and diamagnetic.

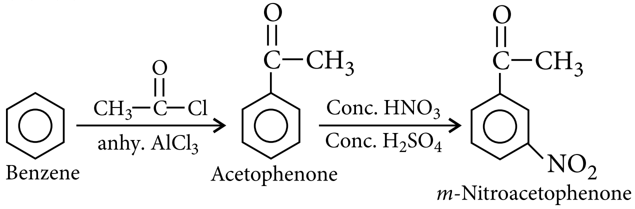
(ii) $[Co(NH_3)_4Cl_2]Cl$:
Tetraamminedichloridocobalt (III) chloride
It is octahedral and diamagnetic.

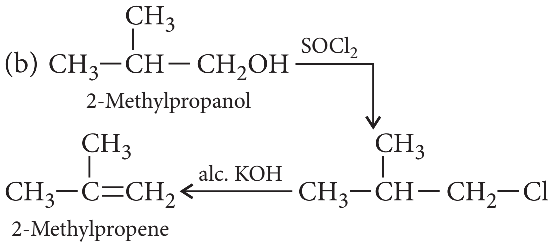
(iii) $Ni(CO)_4$: Tetracarbonylnickel(0)
It is tetrahedral and diamagnetic.

31. (i) (a) Ethanal and propanal can be distinguished by iodoform test. Yellow precipitate of iodoform will be formed from ethanal on heating with iodine and sodium hydroxide solution whereas propanal does not give iodoform test.

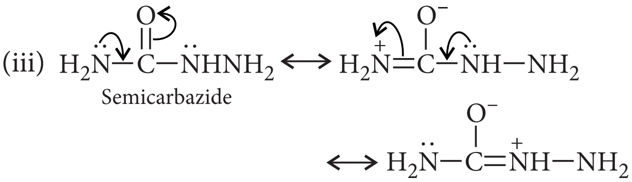
(b) Benzoic acid and ethyl benzoate can be distinguished by their reactions with sodium bicarbonate solution. Benzoic acid will give effervescence with $NaHCO_3$ whereas ethyl benzoate does not react.

(ii) (a)





(iii)



As electron density on one $—NH_2$ group decreases due to resonance it does not act as a nucleophile while the lone pair of electrons on the other NH_2 group (*i.e.*, attached to NH) is not involved in resonance and hence is available for nucleophilic attack on the $>C{=}O$ group of aldehydes and ketones.

OR

(I) The given compound does not reduce Tollens' reagent which implies that it is not an aldehyde.

(II) Positive iodoform test proves that it has a $CH_3{-}\overset{O}{\overset{\|}{C}}{-}$ group.

(III) The oxidation products are indicative of the presence of 5 carbon atoms.

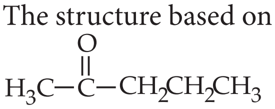
To find the exact molecular formula

%C = 69.77%, %H = 11.63%

%O = 100 – (69.77 + 11.63) = 18.6 %

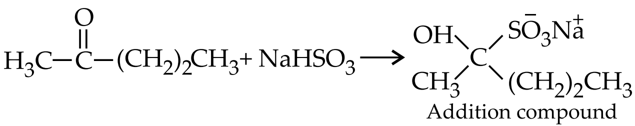
$$C:H:O = \frac{69.77}{12} : \frac{11.63}{1} : \frac{18.6}{16}$$

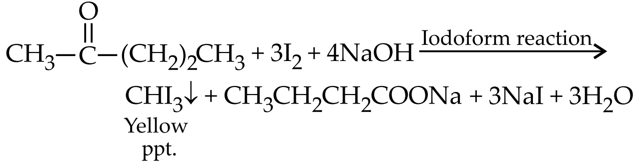
The structure based on inferences (I), (II) and (III) is



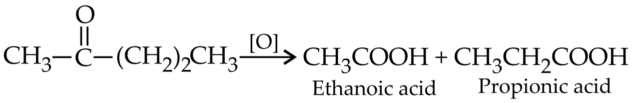
$$H_3C{-}\overset{O}{\overset{\|}{C}}{-}CH_2CH_2CH_3$$

Reactions involved are :





$$CH_3{-}\overset{O}{\overset{\|}{C}}{-}(CH_2)_2CH_3 + 3I_2 + 4NaOH \xrightarrow{\text{Iodoform reaction}} \underset{\substack{\text{Yellow}\\\text{ppt.}}}{CHI_3\downarrow} + CH_3CH_2CH_2COONa + 3NaI + 3H_2O$$



$$CH_3-\overset{\overset{O}{\|}}{C}-(CH_2)_2CH_3 \xrightarrow{[O]} \underset{\text{Ethanoic acid}}{CH_3COOH} + \underset{\text{Propionic acid}}{CH_3CH_2COOH}$$

32. (i) $\pi = CRT$

R and T are same in both cases hence

$$\frac{\pi_1}{\pi_2} = \frac{C_1}{C_2} \text{ or, } C_2 = \frac{\pi_2 C_1}{\pi_1}$$

Molarity of first solution

$$C_1 = \frac{36}{180} = 0.2 \text{ mol L}^{-1}$$

$$C_2 = \frac{\pi_2 C_1}{\pi_1} = \frac{1.52 \times 0.2}{4.98} = 0.0610\,\text{M}$$

(ii) Magnitude of osmotic pressure is large even for very dilute solutions and it can be measured at room temperature hence it is more useful for the calculation of molecular mass.

(iii) According to Henry's law, $p_{N_2} = K_H \times x_{N_2}$

$$x_{N_2} = \frac{p_{N_2}}{K_H} = \frac{0.987 \text{ bar}}{76480 \text{ bar}} = 1.29 \times 10^{-5}$$

If n moles of N_2 are present in 1 L (*i.e.*, 55.55 moles),

$$x_{N_2} = \frac{n}{n + 55.55} \simeq \frac{n}{55.55}$$

$$\therefore \quad \frac{n}{55.55} = 1.29 \times 10^{-5}$$

or $n = 1.29 \times 10^{-5} \times 55.55$ moles

$= 71.659 \times 10^{-5}$ moles $= 0.716$ millimoles

OR

(a) Let y_A and y_B be the mole fraction of A and B in the vapour phase, respectively.

$$y_A = \frac{P_A}{P_{\text{Total}}} = \frac{P_A^\circ x_A}{P_A^\circ x_A + P_B^\circ x_B} = \frac{P_A^\circ x_A}{P_B^\circ + (P_A^\circ - P_B^\circ) x_A}$$

where, x_A is the mole fraction of A in the first drop of the condensate.

$$\therefore \quad x_A = \frac{y_A P_B^\circ}{P_A^\circ - (P_A^\circ - P_B^\circ) y_A}$$

Substituting the given values,

$$x_A = \frac{0.25 \times 800}{300 - [(300 - 800) \times 0.25]} = 0.47$$

(b) The total pressure when this drop is formed is given by

$$P_{\text{Total}} = P_A + P_B = P^\circ_A x_A + P^\circ_B x_B$$

$$\therefore \quad P_{\text{Total}} = (300 \times 0.47) + (800 \times 0.53)$$

$$= 141 + 424 = 565 \text{ Torr}$$

(c) Normal boiling point implies that the solution boils at a temperature when vapour pressure of the solution becomes equal to the atmospheric pressure (1 atm or 760 Torr).

Thus, $P_{\text{Total}} = 760 = P^\circ_A x_A + P^\circ_B (1 - x_A)$

$$x_A = \frac{760 - P^\circ_B}{P^\circ_A - P^\circ_B} = \frac{760 - 800}{300 - 800} = 0.08 \text{ and } x_B = 0.92$$

(d) Now when the entire vapours are condensed and only last bubble of vapour remains, then we can assume that the mole fraction of A, which was in the vapour phase originally, will now be in the liquid phase and the mole fraction of A remaining in the vapour phase x'_A and P'_T be the total pressure when last bubble of vapour remains.

$P'_T = P^\circ_A y_A + P^\circ_B y_B = (300 \times 0.25) + (800 \times 0.75)$

$P'_T = 75 + 600 = 675$ Torr.

(e) According to Raoult's law and Dalton's law of partial pressures,

$$P'_T x'_A = P^\circ_A y_A$$

$$\therefore \quad x'_A = \frac{P^\circ_A y_A}{P'_T} = \frac{300 \times 0.25}{675} = 0.11 \text{ and } x'_B = 0.89$$

33. (a) (i) As transition metals have a large number of unpaired electrons in the *d*-orbitals of their atoms they have strong interatomic attractions or metallic bonds. Hence they have high enthalpy of atomization.

(ii) Scandium ($Z = 21$) has incompletely filled 3*d*-orbitals in the ground state ($3d^1$). Hence it is considered as a transition element.

(b) The possible oxidation states for $3d^3 4s^2$ = +5, +4, +3, +2.

The possible oxidation states for $3d^5 4s^2$ = +7, +6, +5, +4, +3, +2

The possible oxidation states for $3d^6 4s^2$ = +6, +4, +3, +2.

In a transition series the oxidation states which lead to exactly half filled or completely filled *d*-orbitals are more stable.

OR

(a) (i) This is due to lanthanoid contraction.

(ii) Much larger third ionisation energy of Mn(where change is d^5 to d^4) is mainly responsible for this. This also explains that +3 state of Mn is of little importance and from the relation, $\Delta G^\circ = -nFE^\circ$.

More positive is the value of E°, reaction will be feasible.

$$\underset{3d^4}{Mn^{3+}} \xrightarrow{+e^-} \underset{\substack{3d^5 \\ \text{more stable} \\ \text{(half filled)}}}{Mn^{2+}}; \qquad \underset{\substack{3d^5 \\ \text{more stable} \\ \text{(half filled)}}}{Fe^{3+}} \xrightarrow{+e^-} \underset{3d^6}{Fe^{2+}}$$

Hence, E°_{value} for Mn^{3+}/Mn^{+2} couple is much more positive than that for Fe^{3+}/Fe^{2+}.

(iii) Manganese can form $p\pi$ - $d\pi$ bond with oxygen by utilising 2*p*-orbital of oxygen and 3*d*-orbital of manganese due to which it can show highest oxidation state of +7. While with fluorine it cannot form such $p\pi$ - $d\pi$ bond thus, it can show a maximum of +4 oxidation state.

(b) Only those ions will be coloured which have partially filled *d*-orbitals facilitating *d*-*d* transition. Ions with d^0 and d^{10} will be colourless.

From electronic configuration of the ions, $V^{3+}(3d^2)$ and $Mn^{2+}(3d^5)$ are coloured while $Ti^{4+}(3d^0)$ and $Sc^{3+}(3d^0)$ are colourless.

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