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(3)	–	**10(23)**
2.	Solutions	1(4)	1(2)	–	–	
3.	Electrochemistry	3(3)	1(2)	–	–	
4.	Chemical Kinetics	–	–	–	1(5)	
5.	Surface Chemistry	–	–	1(3)	–	
6.	The *p*-Block Elements	2(5)	1(2)	–	–	**8(19)**
7.	The *d*- and *f*-Block Elements	1(1)	1(2)	1(3)	–	
8.	Coordination Compounds	1(1)	–	–	1(5)	
9.	Haloalkanes and Haloarenes	2(2)	–	–	–	**15(28)**
10.	Alcohols, Phenols and Ethers	2(2)	2(4)	–	–	
11.	Aldehydes, Ketones and Carboxylic Acids	2(2)	1(2)	–	1(5)	
12.	Amines	1(1)	1(2)	1(3)	–	
13.	Biomolecules	–	1(2)	1(3)	–	
	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:

In March 1962, Bartlett prepared world's first noble gas compound, *i.e.*, $XePtF_6$. Within months, other scientist successfully repeated the experiment. Bartlett's experiment opened the door to a better understanding of the oxidation states of atoms and their possible reactions.

More than 100 noble gas compounds are known today. Noble gases and their compounds have already made an impact on our daily lives.

XeF_2 has been used to convert uracil to 5-fluorouracil, one of the first anti-tumor agents. Excimers losers use compounds of argon, krypton or xenon to produce precise beam of UV light that are used to perform eye surgery for vision pair. Helium gas is used as a heat transfer agent in gas nuclear reactors and it is also used by deep sea divers as a helium oxygen mixture. Researchers recently succeed combining noble gases with hydrocarbons, a development that could lead to new and better synthetic approach to some organic materials.

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

(i) Which one of the following elements is most reactive?

(a) He (b) Ne (c) Xe (d) Kr

(ii) The idea which prompted Bartlett to prepare first ever compound of noble gas was

(a) high bond energy of Xe–F (b) low bond energy of F–F in F_2

(c) ionization energy of O_2 and xenon were almost similar

(d) none of these.

(iii) Helium is suitable for low temperature gas thermometry because of its

(a) high transition temperature (b) real behaviour

(c) low boiling point and near ideal behaviour (d) high boiling point and high polarizability.

OR

Helium-oxygen mixture is used by deep sea divers in preference to nitrogen-oxygen mixture because

(a) helium is much less soluble in blood than nitrogen

(b) nitrogen is much less soluble in blood than helium

(c) due to high pressure deep under the sea, nitrogen and oxygen react to give poisonous nitric oxide

(d) nitrogen is highly soluble in water.

(iv) Which of the following noble gases form maximum compound?

(a) Xe (b) Ne (c) Ar (d) Kr

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

Fractional distillation is the process employed to separate miscible volatile liquids having different boiling points. The possibility of separating the two liquids by fractional distillation depends on the effect each has on the vapour pressure at the other. The vapour pressure of the mixture (completely miscible binary mixture) is a function of the composition as well as the vapour. Pressure of the two pure compounds in an ideal solution where the relation of vapour pressure and composition is given by Rault's law the partial vapour pressure of each volatile component is equal the vapour pressure of the pure component multiplied by its mole fraction. Thus, for a mixture of A and B:

$$p_A = p_A^\circ x_A$$
$$p_B = p_B^\circ x_B$$

Total vapour pressure of the system is equal to sum of vapour pressure of A and B, *e.g.*, $p_A + p_B$. Binary mixtures that follows Raoult's law are those where the attraction between A and B molecules is the same as those for pure components, *e.g.*, benzene/toluene and paraffin mixtures. Thus, for binary mixture ΔH_{mix} and ΔV_{mix} are zero. When the interaction of A and B molecules is not same as those for pure components, the mixture becomes non-ideal. Non-ideal solutions show positive or negative deviation from Rault's law. Non-ideal solutions showing positive deviation have $A–B$ interactions weaker than the $A – A$ and $B – B$ interactions and non-ideal solutions showing negative deviations have $A – B$ interactions stronger than the $A – A$ and $B – B$ interactions.

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 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.

(i) Assertion : An ideal solution obeys Raoult's law.

Reason : In an ideal solution, solute-solute as well as solvent-solvent interactions are similar to solute-solvent interactions.

(ii) Assertion : Acetone and aniline show negative deviations.

Reason : H–bonding between acetone and aniline is stronger than that between acetone-acetone and aniline-aniline.

(iii) Assertion : Two misicible liquids, *i.e.*, ethanol and water can be seperated by fractional distillation.

Reason : Both the liquids have same boiling points.

(iv) Assertion : ΔH_{mix} and ΔV_{mix} are zero for binary mixture.

Reason : The interactions between the particles of the components of a solution are almost identicle as between particles in the liquids.

OR

Assertion : A solution of *n*-hexane and *n*-heptane obeys Rault's law.

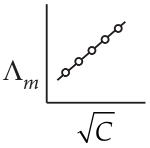
Reason : Solution of *n*-hexane and *n*-heptane is ideal liquid solution.

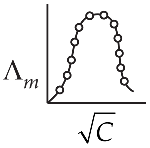
Following questions (No. 3 -11) are multiple choice questions carrying 1 mark each:

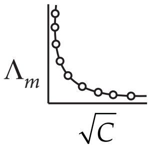
3. In a face-centred cubic cell, an atom at the face contributes to the unit cell is

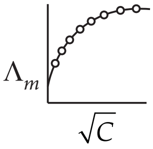
(a) 2 (b) $\frac{1}{2}$ (c) 3 (d) 1

4. The variation of Λ_m of acetic acid with concentration is correctly represented by

(a) 

(b) 

(c) 

(d) 

OR

The free energy change is related to equilibrium constant as

(a) $\Delta G = RT \ln K$ (b) $-\Delta G = RT \log K$

(c) $-\Delta G = 2.303\ RT \log K$ (d) $-\Delta G = (RT \log K)/2.303$

5. Which one of the following alcohol undergoes acid–catalysed dehydration to alkenes most readily?

(a) $(CH_3)_2CHCH_2OH$ (b) $(CH_3)_3COH$ (c) $CH_3CHOHCH_3$ (d) $CH_3CH_2CH_2OH$

6. Which of the following reactions is most suitable for the preparation of *n*-propylbenzene?

(a) Friedel-Crafts alkylation (b) Wurtz reaction

(c) Wurtz-Fittig reaction (d) Grignard reaction

OR

The reactivity of the compounds (i)MeBr (ii) $PhCH_2Br$ (iii) MeCl (iv) *p*-$MeOC_6H_4Br$ decreases as

(a) (i) > (ii) > (iii) > (iv) (b) (iv) > (ii) > (i) > (iii)

(c) (iv) > (iii) > (i) > (ii) (d) (ii) > (i) > (iii) > (iv)

7. The molar conductance of 0.001 M acetic acid is 50 $\text{ohm}^{-1}\ \text{cm}^2\ \text{mol}^{-1}$. The maximum value of molar conductance of acetic acid is 250 $\text{ohm}^{-1}\ \text{cm}^2\ \text{mol}^{-1}$. What is the degree of dissociation (α) of acetic acid?

(a) 0.5 (b) 0.2 (c) 0.3 (d) 0.4

8. Elements of group 16 (except polonium) are called chalcogens because

(a) these elements, particularly sulphur and oxygen, are present in many metallic ores, mainly as oxides and sulphides

(b) a large number of acids contain these elements, particularly sulphur and oxygen

(c) these elements mainly form anions

(d) these elements exist in different allotropic forms.

OR

Which statement is correct about halogens?

(a) They are all diatomic and form univalent ions.

(b) They are all capable of exhibiting several oxidation states.

(c) They are all diatomic and form divalent ions.

(d) They can mutually displace each other from the solution of their compounds with metals.

9. Propene, $CH_3CH = CH_2$ can be converted into propan-l-ol by oxidation. Indicate which set of reagents amongst the following is ideal for the above conversion?

(a) $KMnO_4$ (alkaline) (b) Osmium tetroxide (OsO_4/CH_2Cl_2)

(c) B_2H_6 and alk. H_2O_2 (d) O_3/Zn

10. When ethanal is treated with Fehling's solution, it gives a precipitate of

(a) Cu_2O (b) Cu (c) Cu_3O (d) CuO

OR

The conversion of phenyl glyoxal (C_6H_5COCHO) to $C_6H_5CHOHCOONa$ is an example of

(a) self-oxidation
(b) aldol condensation
(c) internal crossed Cannizzaro reaction
(d) auto-reduction.

11. Which of the following compounds is not coloured?

(a) $Na_2[CuCl_4]$
(b) $Na_2[CdCl_4]$
(c) $K_4[Fe(CN)_6]$
(d) $K_3[Fe(CN)_6]$

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 :** Zinc displaces copper from copper sulphate solution.
Reason : The $E°$at 298 K of Zn is –0.76 volts and that of Cu is +0.34 volts.

13. **Assertion :** In transition elements, *ns* orbital is filled up first and $(n - 1)d$ afterwards, during ionization *ns* electrons are lost prior to $(n - 1)d$ electrons.
Reason : The effective nuclear charge felt by $(n - 1)d$ electrons is higher as compared to that by *ns* electrons.

14. **Assertion :** Anilinium chloride is less acidic than ammonium chloride.
Reason : Anilinium ion is resonance stabilised.

OR

Assertion : Benzyl amine is less basic than ethyl amine.
Reason : Benzene shows $+I$-effect.

15. **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.

16. **Assertion :** Aldol condensation can be catalysed both by acids and bases.
Reason : β-Hydroxy aldehydes or ketones readily undergo acid catalysed dehydration.

SECTION - B

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

17. Calculate the mole fraction of ethylene glycol ($C_2H_6O_2$) in a solution containing 20% of $C_2H_6O_2$ by mass.

OR

State Raoult's law. How is it formulated for solutions of non-volatile solutes?

18. Give reasons for the following :

(a) Sulphur has a greater tendency for catenation than oxygen.
(b) HCl is a stronger acid than HF though fluorine is more electronegative than chlorine.

19. What is the basic difference between the electronic configuration of the transition and inner transition elements?

OR

Explain the following observations :

(i) Transition metals form alloys.

(ii) There is a general increase in density from titanium ($Z = 22$) to copper ($Z = 29$).

20. Depict the electrochemical cell and calculate the $E°$ for each cell.

(i) $2Ag^+ + Cd \longrightarrow Ag + Cd^{2+}$

(ii) $Cl_{2(g)} + 2I^- \longrightarrow 2Cl^- + I_{2(s)}$

Given : $E^\circ_{Ag^+/Ag} = 0.80$ V, $E^\circ_{Cd^{2+}/Cd} = -0.40$ V, $E^\circ_{Cl_2/Cl^-} = 1.36$ V, $E^\circ_{I_2/I^-} = 0.54$ V

21. Draw the structures of all the isomeric alcohols of molecular formula $C_5H_{12}O$, give their IUPAC names.

22. Account for the following :

(i) Tertiary amines do not undergo acylation reaction.

(ii) Amines are more basic than comparable alcohols.

OR

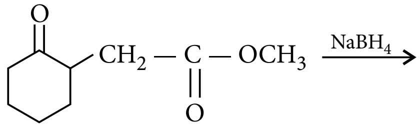
(i) Aromatic 1°-amines cannot be prepared by Gabriel phthalimide reaction. Explain.

(ii) Select the amine which is most reactive towards dil. HCl among the following :

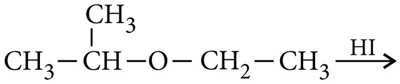
CH_3NH_2, $(CH_3)_2NH$,$(CH_3)_3N$, $C_6H_5NH_2$

23. Write the structures of the products formed in the following reactions :

(i)



(ii)



$CH_3-\overset{\overset{CH_3}{|}}{C}H-O-CH_2-CH_3 \xrightarrow{HI}$

24. Account for the following :

$Cl-CH_2COOH$ is a stronger acid than CH_3COOH.

25. State the significance of primary and secondary structures of proteins.

SECTION - C

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

26. Write the differences between physisorption and chemisorption with respect to the following :

(i) Specificity

(ii) Temperature dependence

(iii) Enthalpy change

OR

Explain what is observed when

(i) an electrolyte is added to ferric hydroxide solution

(ii) persistent dialysis of a colloidal solution is carried out

(iii) direct current is passed through a colloidal solution.

27. For M^{2+}/M and M^{3+}/M^{2+} systems, the $E°$ values for some metals are as follows :

Cr^{2+}/Cr : −0.9 V; Cr^{3+}/Cr^{2+}: −0.4 V

Mn^{2+}/Mn : −1.2 V; Mn^{3+}/Mn^{2+}: +1.5 V

Fe^{2+}/Fe : −0.4 V; Fe^{3+}/Fe^{2+} : +0.8 V

Use this data to comment upon :

(i) The stability of Fe^{3+} in acid solution as compared to Cr^{3+} or Mn^{3+}.

(ii) The ease with which iron can be oxidised as compared to a similar process for either chromium or manganese metal.

OR

$$\underset{\text{(Colourless liquid)}}{MCl_4} \xrightarrow[H_2O]{Zn,\ \Delta} \underset{\text{Purple coloured compound}}{(A)}$$

$$MCl_4 \xrightarrow{\text{Moist air}} \underset{\text{White fumes}}{(B)}$$

Identify (A), (B) and MCl_4. Also explain colour difference between MCl_4 and (A).

28. (a) State differences between the following pairs :

(i) α-helix structure and β-pleated sheet structure

(ii) Primary and secondary structure of proteins

(b) What is the difference between acidic amino acids and basic amino acids?

29. How will you distinguish between the following pairs of terms :

(i) Hexagonal close packing and cubic close packing

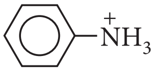
(ii) Crystal lattice and unit cell

(iii) Tetrahedral void and octahedral void

30. (i) *t*-Butylamine cannot be prepared by the action of ammonia on *t*-butyl bromide. Why?

(ii) Sulphanilic acid is soluble in dil. NaOH but not in dil. HCl. Explain.

(iii) Which is more acidic and why?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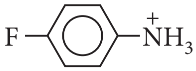


SECTION - D

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

31. (a) The decomposition of a compound is found to follow a first order rate law. If it takes 15 minutes for 20 percent of original material to react, calculate (i) the specific rate constant (ii) the time at which 10 percent of the original material remains unreacted, (iii) the time it takes for the next 20 percent of the reactant left after the first 15 minutes.

(b) Following data are obtained for the reaction :

$$N_2O_5 \longrightarrow 2NO_2 + \frac{1}{2}O_2$$

t/s	0	300	600
$[N_2O_5]$/mol L^{-1}	1.6×10^{-2}	0.8×10^{-2}	0.4×10^{-2}

(i) Show that it follows first order kinetics.

(ii) Calculate the half-life.

(Given : log 2 = 0.3010, log 4 = 0.6021)

OR

(a) A first order reaction takes 160 minutes time for 20% completion. Calculate time required for half completion of reaction.

(b) (i) For a reaction, $A + B \rightarrow$ Product, the rate law is given by, Rate = $k[A]^1[B]^2$. What is the order of the reaction?

(ii) Write the unit of rate constant 'k' for the first order reaction.

(iii) For the reaction $A \rightarrow B$, the rate of reaction becomes twenty seven times when the concentration of A is increased three times. What is the order of reaction?

32. (i) How will you convert acetic acid to

(a) malonic acid

(b) *tert*-butyl alcohol?

(ii) Give chemical tests to distinguish between the following pairs of compounds :

(a) Methyl acetate and ethyl acetate

(b) Benzaldehyde and benzoic acid

(c) Phenol and benzoic acid

OR

(i) State reasons for the following :

(a) Monochloroethanoic acid has a higher pK_a value than dichloroethanoic acid.

(b) Ethanoic acid is a weaker acid than benzoic acid.

(ii) How will you convert acetic acid to

(a) glycine

(b) acetylene

(c) ethylamine?

33. (i) Using valence bond theory, explain the following in relation to the complexes given below :
$[Mn(CN)_6]^{3-}$, $[Co(NH_3)_6]^{3+}$, $[Cr(H_2O)_6]^{3+}$

(a) Type of hybridisation

(b) Inner or outer orbital complex

(c) Magnetic behaviour

(d) Spin only magnetic moment value

(ii) $[Mn(CN)_6]^{3-}$ has two unpaired electrons whereas $[MnCl_6]^{3-}$ has four unpaired electrons. Why?

OR

Explain why :

(i) $[Cr(NH_3)_6]^{3+}$ is paramagnetic while $[Ni(CN)_4]^{2-}$ is diamagnetic.

(ii) A solution of $[Ni(H_2O)_6]^{2+}$ is green but $[Ni(CN)_4]^{2-}$ is colourless.

(iii) The low spin tetrahedral complexes are rarely observed.

SOLUTIONS

1. **(i) (c) :** Xe due to its lowest ionisation energy amongst the mentioned noble gases, is most reactive.

(ii) (c) : On the assumption of similar ionisation energy of O_2 and xenon, Bartlett prepared first noble gas compound $Xe[PtF_6]$.

(iii) (a) : Xenon forms maximum noble gases compounds because of its low ionisation energy amongst the noble gases.

OR

(a) : He-O_2 mixture is used by deep sea divers in preference to nitrogen-O_2 mixture because helium is much less soluble in blood than nitrogen.

(iv) (a) : Xenon forms maximum noble gases compounds because of its low ionisation energy amongst the noble gases.

2. **(i) (a)**

(ii) (a)

(iii) (c) : Fractional distillation is used to separate miscible liquids having different boiling points. Boiling points of ethanol and water are 78°C and 100°C respectively.

(iv)(a)

OR

(a) : Those solutions which obey Rault's law are called ideal liquid solutions.

3. **(b) :** In *fcc,* an atom at the face contributes to the unit cell = 1/2.

4. **(c) :** For weak electrolyte (CH_3COOH), Λ_m first increases slowly and then rapidly with dilution but does not become constant.

OR

(c) : $-\Delta G = 2.303\, RT \log K$

5. **(b) :** The order of dehydration of alcohols is 3° > 2° > 1°.

6. **(c) :** Friedel-Crafts alkylation of benzene with *n*-propyl bromide will give isopropylbenzene as the major product. Therefore, Wurtz-Fittig reaction is the right choice.

OR

(d) : The order of reactivity follows the sequence : benzyl halides > alkyl halides > aryl halides.

Out of chloride and bromides, bromides are more reactive. Therefore, the correct order of reactivity is $PhCH_2Br$ (ii) > MeBr (i) > MeCl (iii) > *p*-$MeOC_6H_4Br$ (iv).

7. **(b) :** Degree of dissociation $= \alpha = \dfrac{\Lambda_c}{\Lambda_\infty} = \dfrac{50}{250} = 0.2$

8. **(a) :** Elements of group-16 (except Po) are called chalcogens, *i.e.*, ore forming elements since these elements are present in many metallic ores in the form of oxides and sulphides.

OR

(a) : All halogens are diatomic and form univalent ion.

9. **(c) :**

$$3CH_3-CH=CH_2 \xrightarrow[\text{Hydroboration}]{BH_3,\ THF} \underset{\text{Tripropyl borane}}{(CH_3CH_2CH_2)_3B}$$

$$\xrightarrow[OH^-]{H_2O_2} \underset{\text{Propan-1-ol}}{3CH_3CH_2CH_2OH}$$

10. **(a) :** $CH_3CHO + 2Cu^{2+} + 5OH^-$

$$\rightarrow CH_3COO^- + \underset{\text{(Red ppt)}}{Cu_2O\downarrow} + 3H_2O$$

Thus in this reaction, precipitate of copper oxide (Cu_2O) is formed. Fehling's solution is an alkaline solution of cupric ion complexed with sodium potassium tartrate.

OR

(c) : When two $>C=O$ groups are present in a single molecule then in presence of base one of the $>C=O$ groups undergoes oxidation and another undergoes reduction, this is known as internal crossed Cannizzaro reaction.

11. **(b)**

12. **(a) :** $Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$

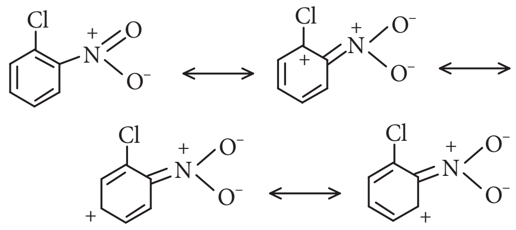
13. **(a)**

14. **(d)**

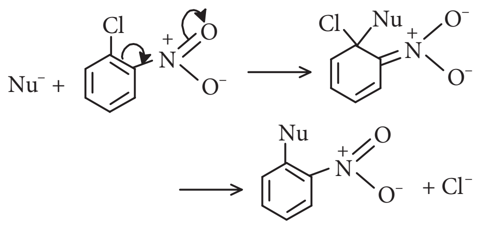
OR

(c) : $PhCH_2NH_2$ (Benzyl amine) has –*I*-effect of phenyl group while $CH_3CH_2NH_2$ has +*I*-effect of ethyl group.

15. **(a) :** The C-atom of C – Cl in chloronitrobenzene carries a small +ve charge.



Because of the positive charge, attack at this carbon atom by the nucleophile is facilitated.



16. **(b) :** Both carbanions (formed in presence of base) and enol form (formed in presence of an acid) act as nucleophiles and hence add on the carbonyl group of aldehydes and ketones to give aldols.

17. Let total mass of solution = 100 g

$\therefore$ Mass of ethylene glycol $w_2 = 20$ g

and mass of solvent (water) = $w_1 = 80$ g

Molar mass of $C_2H_6O_2$, $(M_2) = 62\text{ g mol}^{-1}$

Molar mass of H_2O, $(M_1) = 18\text{ g mol}^{-1}$

Moles of H_2O; $n_1 = \dfrac{w_1}{M_1} = \dfrac{80}{18} = 4.444$ mol

Moles of $C_2H_6O_2$; $n_2 = \dfrac{w_2}{M_2} = \dfrac{20}{62} = 0.322$ mol

Mole fraction of $C_2H_6O_2 = \dfrac{n_2}{n_1 + n_2}$

$$= \frac{0.322}{4.44 + 0.322} = \frac{0.322}{4.762} = 0.068$$

OR

Raoult's law : For a solution of volatile liquids, the partial pressure of each component in the solution is directly proportional to its mole fraction. Thus, for any component, partial vapour pressure, $p \propto x \Rightarrow p = p°.\,x$

where, $p°$ = vapour pressure of pure component

x = mole fraction of that component

Raoult's law for solution containing non-volatile solute : It states that partial vapour pressure of a solution of non-volatile solute, p_{solution} is directly proportional to the mole fraction of the solvent in the solution.

Mathematically,

$p_{\text{solution}} = p°_{\text{solvent}} \times x_{\text{solvent}}$

where, $p°_{\text{solvent}}$ = vapour pressure of the pure solvent at the given temperature.

or, $\dfrac{p° - p_{\text{solution}}}{p°} = x_2$

18. (a) The property of catenation depends upon $E - E$ bond strength of the element. As S – S bond is much stronger (213 kJ mol^{-1}) than O – O bond (138 kJ mol^{-1}) therefore, sulphur has greater tendency for catenation than oxygen.

(b) HF a the weaker acid than HCl because of its high bond dissociation energy due to small size of fluorine atom.

19. Transition elements are those elements in which the last electron enters the *d*-orbital of penultimate shell. Their general electronic configuration is [Noble gas] $(n-1)\,d^{1-10}\,ns^{1-2}$.

Inner transition elements are those elements in which the last electron enters the *f*-orbital of anti-penultimate shell. Their general outer configuration is,

[Noble gas] $4f^{1-14}\,5d^{0-1}\,6s^2$ or [Noble gas] $5f^{1-14}\,6d^{0-1}\,7s^2$.

OR

(i) Transition metals form alloys because they have similar atomic radii.

(ii) As we move along transition metal series from left to right (*i.e.,* Ti to Cu), the atomic radii decrease due to increase in nuclear charge. Hence, the atomic volume decreases. At the same time, atomic mass increases. Hence, the density from titanium to copper increases.

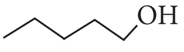
20. (i) $Cd|Cd^{2+}||Ag^+|Ag$

$E°_{\text{cell}} = E°_{\text{cathode}} - E°_{\text{anode}} = (0.80) - (-0.40) = 1.20$ V

(ii) $Pt, I^-_{(aq)}|I_{2(s)}||\,Cl_{2(g)}|Cl^-_{(aq)}, Pt$

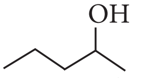
$E°_{\text{cell}} = E°_{\text{cathode}} - E°_{\text{anode}} = (1.36) - (0.54) = 0.82$ V

21. (a)



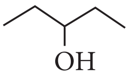
Pentan-1-ol

(b)



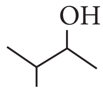
Pentan-2-ol

(c)



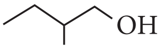
Pentan-3-ol

(d)



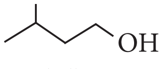
3-Methylbutan-2-ol

(e)

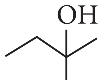


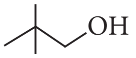
2-Methylbutan-1-ol

(f)



3-Methylbutan-1-ol

(g)  2-Methylbutan-2-ol

(h)  2, 2-Dimethylpropan-1-ol

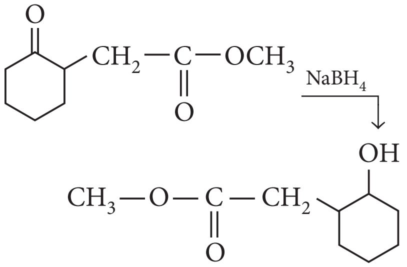
22. (i) In tertiary amines there are no acidic hydrogen due to which they do not undergo acylation reaction.

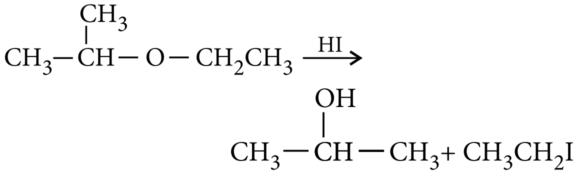
(ii) N being less electronegative than O, gives lone pair of electron more easily than O atom. Therefore amines are more basic than alcohols.

OR

(i) Aromatic 1°-amines cannot be prepared by Gabriel phthalimide reaction because aryl halides do not undergo nucleophilic substitution reactions with potassium phthalimide under mild conditions.

(ii) $(CH_3)_2NH$ is most basic amongst the given amines. Thus, it is most reactive amine towards HCl.

23. (i) 

(ii) 

$$CH_3-\underset{CH_3}{CH}-O-CH_2CH_3 \xrightarrow{HI} CH_3-\overset{OH}{CH}-CH_3+CH_3CH_2I$$

24. Chloroacetic acid has lower pK_a value than acetic acid. 'Cl' in chloroacetic acid shows $-I$ effect, it creates less electron density on oxygen of carboxylic acid. Thus, release of proton becomes easier than acetic acid. Hence, chloroacetic acid is stronger than acetic acid.

25. The significance of primary structure of proteins is that the amino acid sequence of a protein determines its function and is critical to its biological activity. Even a change of just one amino acid can drastically alter the properties of the entire protein molecule. For example change of glutamic amino acid by valine amino acid in the protein sequence causes sickle cell anaemia.

Secondary structure of proteins provide mechanical movement of muscles, bind substrates to modify them chemically. Antibody proteins bind foreign proteins.

26.

S. No.	Criteria	Physisorption	Chemisorption
(i)	Specificity	It is not specific in nature.	It is highly specific in nature.
(ii)	Temperature dependence	It decreases with increase in temperature. Thus, low temperature is favourable for physisorption.	It increases with increase in temperature. Thus, high temperature is favourable for chemisorption.
(iii)	Enthalpy change	Low enthalpy of adsorption.	High enthalpy of adsorption.

OR

(i) When an electrolyte like NaCl is added to ferric hydroxide solution, the Cl^- ions of NaCl neutralise the positive charge of ferric hydroxide solution particles, and coagulation of the solution takes place.

(ii) When dialysis is persistent and prolonged, the traces of electrolyte are also removed. These electrolytes stabilise the colloid and when removed completely, make the colloid unstable and the colloid gets coagulated.

(iii) When an electric current is passed through a colloidal solution its colloidal particles move towards oppositely charged electrode, where they lose their charge and get coagulated.

27. (i) As $E^\circ_{Cr^{3+}/Cr^{2+}}$ is negative (–0.4 V), this means Cr^{3+} ions in solution cannot be reduced to Cr^{2+} easily, *i.e.*, Cr^{3+} ions are very stable. As $E^\circ_{Mn^{3+}/Mn^{2+}}$ is more positive (+1.5 V) as compared to $E^\circ_{Fe^{3+}/Fe^{2+}}$ (+0.8 V), Mn^{3+} ions can easily be reduced to Mn^{2+} ions in comparison to Fe^{3+} ions. Thus, the relative stability of these ions is : $Mn^{3+} < Fe^{3+} < Cr^{3+}$

(ii) Oxidation potentials for Cr, Mn and Fe will be +0.9 V, +1.2 V and +0.4 V. Thus, the ease of getting oxidised will be in the order, Mn > Cr > Fe.

OR

M = Ti; A = $[Ti(H_2O)_6]Cl_3$; B = HCl

$$TiCl_4 \xrightarrow{\text{Zn, heat}} TiCl_3 \xrightarrow{H_2O} \underset{\substack{A \\ \text{(Purple coloured)}}}{[Ti(H_2O)_6]Cl_3}$$

$$TiCl_4 + \underset{\substack{\text{From moist} \\ \text{air}}}{H_2O} \rightarrow TiOCl_2 + \underset{\substack{B \\ \text{(White fumes)}}}{2HCl}$$

$TiCl_4$ is colourless because in $Ti^{4+}(3d^0)$ *d*-*d* transition is not possible. In $TiCl_3$ *i.e.*, Ti^{3+} $(3d^1)$ *d*-*d* transition is possible. Ti^{3+} absorbs greenish yellow component of white light and in its aqueous solution its colour is purple.

28. (a) (i) α - helix structure : In this type of structure, the long peptide chains undergo formation of H-bonding between the $-\overset{\overset{O}{\|}}{C}-$ and $-\overset{\overset{H}{|}}{N}-$ bonds of different peptide groups within the same chain. As a result the polypeptide chain gets coiled up to form a right handed helix.

β-pleated sheet : In this structure, the long peptide chains lie side by side to form a flat sheet. Each chain is held by the two neighbouring chains by H-bonds (N – H .... OC).

(ii) Primary structure of protein refers to the arrangement of α-amino acids in the polypeptide chain. Secondary structure of protein is the arrangement of polypeptide chains.

(b) Acidic amino acids are those which contain more number of carboxyl groups as compared to amino groups whereas basic amino acids are those which contains more number of amino groups than carboxyl groups.

29. (i) In hexagonal close packing, the sphere of third layer lie directly above those in first layer. This leads to a pattern of the type *AB AB AB*... .

In the cubic close packing, the spheres of fourth layer will corresponds to those in first layer. This leads to a pattern of the type *ABC ABC ABC*... .

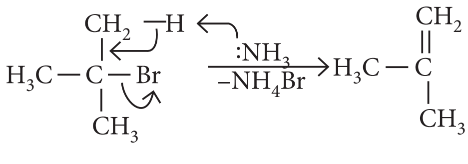
(ii) A regular arrangement of points (each representing an atom, ion or a molecule), in three dimensions is called a crystal lattice.

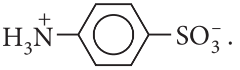
A unit cell is the smallest, but complete unit in a crystal lattice which when repeated in three dimensions generates the crystal lattice.

(iii) A tetrahedral void is formed when one sphere (or particle) is placed in the depression formed by three particles placed in a plane.

An octahedral void is formed when three close-packed spheres forming an equilateral triangle are placed over another similar set of three spheres, in opposite direction. Thus, the empty space at the centre of six spheres placed octahedrally is the octahedral void.

30. (i) *t*-Butyl bromide is a 3° alkyl halide. Therefore, it prefers to undergo elimination reaction rather than substitution reaction when treated with NH_3 (a base). Therefore, the product is isobutylene instead of *tert*-butylamine.



(ii) Sulphanilic acid exists as Zwitter ion, . In the presence of dil. NaOH, the weakly acidic group transfers its proton to OH^- to form soluble p-$NH_2C_6H_4SO^-{}_3Na^+$. On the other hand, $—SO_3^-$ group is a very weak base and therefore, it does not accept H^+ ion from dil. HCl to form p-$\overset{+}{N}H_3C_6H_4SO_3H$ and hence, it does not dissolve in dil. HCl.

(iii) Due to its powerful –*I* effect, the F-atom withdraws electrons from $—NH_3$ group. As a result, electron density on $\overset{+}{N}H_3$ of p-fluoroanilinium ion decreases and hence, release of proton from p-fluoroanilinium ion is much easier than from the anilinium ion. Therefore, p-fluoroanilinium ion is more acidic than anilinium ion.

31. (a) (i) For a first order reaction, $k = \dfrac{2.303}{t}\log\dfrac{[R]_0}{[R]}$

Given : $t = 15$ min, $R = 0.8[R]_0$

$$\text{or,}\quad k = \frac{2.303}{15}\log\frac{[R]_0}{0.8\,[R]_0}$$

$$\text{or,}\quad k = \frac{2.303}{15}\log\frac{10}{8} \qquad \text{... (1)}$$

$$\text{or,}\quad k = 0.015\ \text{min}^{-1}$$

(ii) When $[R] = 0.1\ [R]_0$, $t = ?$

$$k = \frac{2.303}{t_1}\log\frac{[R]_0}{0.1\,[R]_0} = \frac{2.303}{t_1}\log 10 \qquad \text{... (2)}$$

$$\text{or,}\quad 0.015\ \text{min}^{-1} = \frac{2.303}{t_1}\ \text{or,}\ t_1 = \frac{2.303}{0.015\ \text{min}^{-1}}$$

$$t_1 = 153.53\ \text{min}$$

∴ After 153.53 min, 10% of the original material remains unreacted.

(iii) Also,

$$k = \frac{2.303}{t_2}\log\frac{0.8\,[R]_0}{0.64\,[R]_0} = \frac{2.303}{t_2}\log\frac{10}{8} \qquad \text{...(3)}$$

From (1) and (3)

$$\frac{2.303}{15}\log\frac{10}{8} = \frac{2.303}{t_2}\log\frac{10}{8}$$

∴ $t_2 = 15$ min

(b) (i) The formula of rate constant for first order reaction is

$$k = \frac{2.303}{t}\log\frac{[R]_0}{[R]}$$

$$k_1 = \frac{2.303}{300\ \text{s}}\log\frac{(1.6\times10^{-2})\ \text{mol L}^{-1}}{(0.8\times10^{-2})\ \text{mol L}^{-1}} = 2.3\times10^{-3}\ \text{s}^{-1}$$

Similarly, $k_2 = \frac{2.303}{600\text{ s}}\log\frac{(1.6\times10^{-2})\text{ mol L}^{-1}}{(0.4\times10^{-2})\text{ mol L}^{-1}}$

$= 2.3\times10^{-3}\text{ s}^{-1}$

Unit and magnitude of rate constant shows the given reaction is of first order.

(ii) The formula for half-life for first order reaction is

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{2.3\times10^{-3}\text{ s}^{-1}} = 301.30\text{ s}$$

OR

(a) Given : $[R]_0 = 1$, $[R] = 0.80$, $t = 160$ min

$t_{1/2} = ?$

For first order reaction $k = \frac{2.303}{t}\log_{10}\frac{[R]_0}{[R]}$

or, $k = \frac{2.303}{160\text{ min}}\log_{10}\frac{1}{0.8}$

or, $k = \frac{2.303}{160\text{ min}}\times\log 1.25$

or, $k = \frac{2.303\times0.0969}{160\text{ min}} = 1.39\times10^{-3}\text{ min}^{-1}$

Again $t_{1/2} = \frac{0.693}{k} = \frac{0.693}{1.39\times10^{-3}}\text{ min} = 498\text{ min}$

(b) (i) Order of reaction is sum of powers of concentration terms,

∴ Order of reaction = 1 + 2 = 3

(ii) Unit of rate constant for first order reaction is s^{-1}.

(iii) Let $r = k[A]^n$

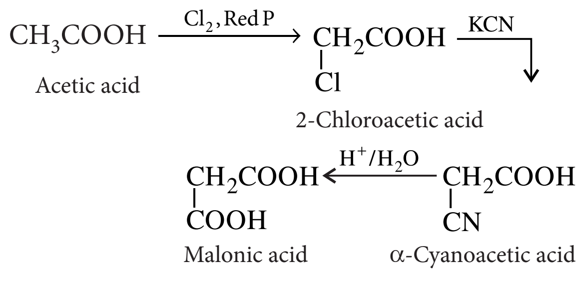
Then, $27r = k[3A]^n$

$\frac{27r}{r} = \frac{k[3A]^n}{k[A]^n}$ or $3^3 = 3^n$

$n = 3$

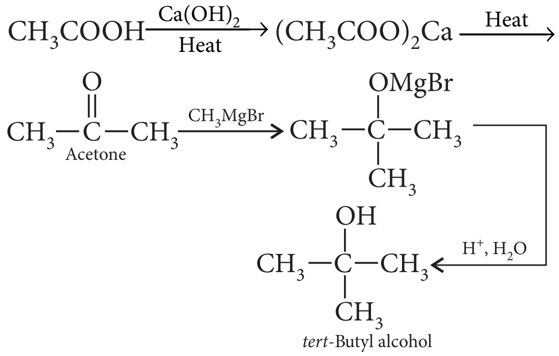
∴ Thus, order = 3

32. (i) (a) Acetic acid to malonic acid :



$$\underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow{Cl_2,\text{ Red P}} \underset{\text{2-Chloroacetic acid}}{\underset{|\;Cl}{CH_2COOH}} \xrightarrow{KCN} \underset{\alpha\text{-Cyanoacetic acid}}{\underset{|\;CN}{CH_2COOH}} \xrightarrow{H^+/H_2O} \underset{\text{Malonic acid}}{\underset{|\;COOH}{CH_2COOH}}$$

(b) Acetic acid to *tert*-butyl alcohol :



$$CH_3COOH \xrightarrow[\text{Heat}]{Ca(OH)_2} (CH_3COO)_2Ca \xrightarrow{\text{Heat}} \underset{\text{Acetone}}{CH_3-\overset{O}{\overset{\|}{C}}-CH_3} \xrightarrow{CH_3MgBr} CH_3-\overset{OMgBr}{\underset{CH_3}{C}}-CH_3 \xrightarrow{H^+,\,H_2O} \underset{tert\text{-Butyl alcohol}}{CH_3-\overset{OH}{\underset{CH_3}{C}}-CH_3}$$

(ii) (a) Ethyl acetate is hydrolysed slowly by water to form ethyl alcohol while methyl acetate gives methyl alcohol.

$$\underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + H_2O \longrightarrow CH_3COOH + \underset{\text{Ethyl alcohol}}{C_2H_5OH}$$

$$\underset{\text{Methyl acetate}}{CH_3COOCH_3} + H_2O \longrightarrow CH_3COOH + \underset{\text{Methyl alcohol}}{CH_3OH}$$

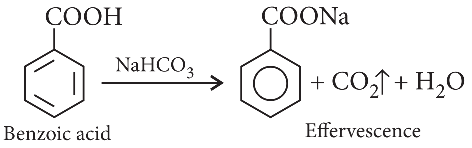
The hydrolysis product of ethyl acetate *i.e.*, ethanol undergoes iodoform test with iodine and alkali.

(b) Benzaldehyde when treated with ammoniacal silver nitrate gives silver mirror.

$$C_6H_5CHO + 2[Ag(NH_3)_2]^+OH^- \longrightarrow C_6H_5COO^- + \underset{\text{Silver mirror}}{2Ag} + 4NH_3 + 2H_2O$$

Benzoic acid does not give silver mirror test.

(c) Phenol and benzoic acid can be distinguished by their reactions with sodium bicarbonate solution. Benzoic acid will give effervescence with $NaHCO_3$ but phenol will not react.



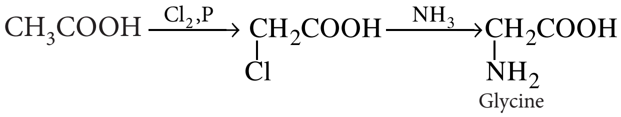
OR

(i) (a) The strength of an acid is indicated by pK_a value, where, $pK_a = -\log K_a$

Since, monochloroethanoic acid is weaker acid than dichloroethanoic acid so, it has lower value of dissociation constant K_a. Therefore, it has higher value of pK_a.

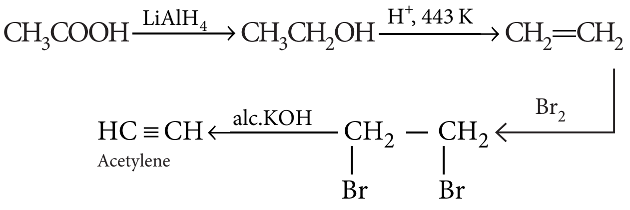
(b) —COOH group in benzoic acid is attached to sp^2-carbon of the phenyl ring and is more acidic than ethanoic acid in which —COOH group is attached to sp^3-carbon atom of $—CH_3$ group.

(ii) (a) Acetic acid to glycine :



$$CH_3COOH \xrightarrow{Cl_2,P} \underset{|\;Cl}{CH_2COOH} \xrightarrow{NH_3} \underset{\text{Glycine}}{\underset{|\;NH_2}{CH_2COOH}}$$

(b) Acetic acid to acetylene :



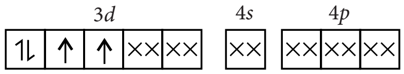
$$CH_3COOH \xrightarrow{LiAlH_4} CH_3CH_2OH \xrightarrow{H^+, 443\text{ K}} CH_2{=}CH_2 \xrightarrow{Br_2} \underset{Br}{CH_2} - \underset{Br}{CH_2} \xrightarrow{alc.KOH} \underset{\text{Acetylene}}{HC \equiv CH}$$

(c) Acetic acid to ethylamine :

$$CH_3COOH \xrightarrow{LiAlH_4} CH_3CH_2OH \xrightarrow{PCl_5} \underset{\text{Ethyl chloride}}{CH_3CH_2Cl} \xrightarrow{NH_3} \underset{\text{Ethylamine}}{CH_3CH_2NH_2}$$

33. (i) $[Mn(CN)_6]^{3-}$:

$Mn^{3+}(3d^4)$:



(a) Hybridisation - d^2sp^3

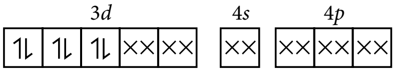
(b) Inner orbital complex

(c) Paramagnetic

(d) $\mu = \sqrt{2(2+2)} = 2.83$ B.M.

$[Co(NH_3)_6]^{3+}$:

$Co^{3+}(3d^6)$:



(a) Hybridisation - d^2sp^3

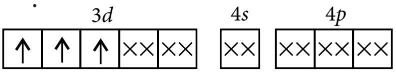
(b) Inner orbital complex

(c) Diamagnetic

(d) Magnetic moment = 0

$[Cr(H_2O)_6]^{3+}$:

$Cr^{3+}(3d^3)$:



(a) Hybridisation - d^2sp^3

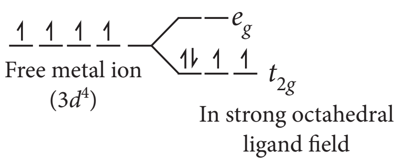
(b) Inner orbital complex

(c) Paramagnetic

(d) $\mu = \sqrt{3(3+2)} = 3.87$ B.M.

(ii) In $[Mn(CN)_6]^{3-}$, Mn is in +3 oxidation state so, it has configuration of $3d^4$.

Since CN^- is a strong field ligand hence pairing of electrons in 3*d*-orbital takes place.



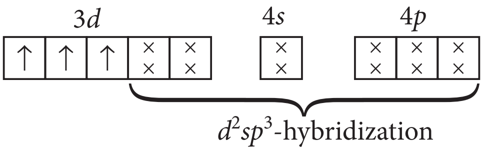
So, $[Mn(CN)_6]^{3-}$ has two unpaired electrons. But in $[MnCl_6]^{3-}$, Cl^- is a weak field ligand, so no pairing takes place and it has 4 unpaired electrons.

OR

(i) The oxidation state of Cr in the compelx is +3.

Cr^{3+} : $Ar[3d]^3$

$[Cr(NH_3)_6]^{3+}$:

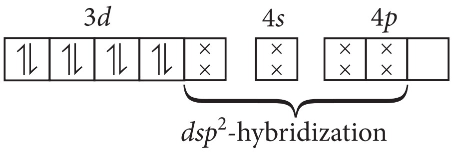


Three unpaired electrons are present, hence it is paramagnetic.

The oxidation state of Ni in the complex is +2.

Ni^{2+} : $[Ar]3d^8$

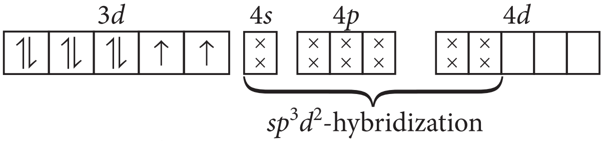
$[Ni(CN)_4]^{2-}$:



As CN^- is a strong ligand, unpaired electrons are paired up, hence it is diamagnetic.

(ii) H_2O is a weak ligand hence, $[Ni(H_2O)_6]^{2+}$ is a outer-orbital complex. The complex has two unpaired electrons. The *d-d* transition is possible. Hence, the compound is coloured.

$[Ni(H_2O)_6]^{2+}$:



In $[Ni(CN)_4]^{2-}$: CN^- is a strong ligand. The unpaired electrons are paired up. No unpaired electrons are present, *i.e.*, *d-d* transition is not possible, hence the complex is colourless.

(iii) In tetrahedral coordination entity formation, the *d*-orbital splitting is smaller. Consequently, the orbital splitting energies are not sufficiently large to force pairing and therefore, low spin configurations are rarely observed.

☺ ☺ ☺