Chemistry (Theory)

[*Time allowed: 3 hours*]   [*Maximum marks: 70*]

General Instructions:
(i) All questions are compulsory.
(ii) Marks for each question are indicated against it.
(iii) Question numbers **1** to **8** are very short-answer questions and carry **1** mark each.
(iv) Question numbers **9** to **18** are short-answer questions and carry **2** marks each.
(v) Question numbers **19** to **27** are also short-answer questions and carry **3** marks each.
(vi) Question numbers **28** to **30** are long-answer questions and carry **5** marks each.
(vii) Use Log Tables, if necessary. Use of calculators is not allowed.

1. Which point defect in crystals of a solid decreases the density of the solid?   **1**

Solution:
Vacancy defect decreases the density of a substance. Vacancy defect in ionic solids is known as Schottky defect.

2. Define 'rate of a reaction'.   **1**

Solution:
The **rate of reaction** is the change in the concentration of any one of the reactants or products per unit time.

$$\text{Rate of reaction} = \frac{\text{Decrease in concentration of reactants}}{\text{Time}}$$
$$= \frac{\text{Increase in concentration of products}}{\text{Time}}$$

3. Give an example of 'shape-selective catalyst'.   **1**

Solution:
Zeolites are shape-selective catalysts.

4. Draw the structure of O_3 molecule.   **1**

Solution:
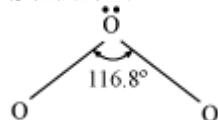
5. Give an example of ionization isomerism.   **1**

Solution:
$[CoBr(NH_3)_5]^{2+} SO_4^{2-}$ and $[CoSO_4(NH_3)_5]^{+} Br^{-}$ are examples of ionization isomerism.

6. Give the IUPAC name of $H_2N - CH_2 - CH_2 - CH = CH_2$.   **1**

Solution:
4-amino-but-1-ene

7. A solution of KOH hydrolyses $CH_3CHClCH_2CH_3$ and $CH_3CH_2CH_2Cl$. Which one of these is more easily hydrolysed?   **1**

Solution:
$CH_3CHClCH_2CH_3$ will undergo hydrolysis reaction with KOH more easily.

8. Draw the structural formula of 1-phenylpropan-1-one molecule

Solution:
The structural formula of 1-phenylpropan-1-one is

$$CH_3 - CH_2 - \overset{\overset{\displaystyle O}{\|}}{C} - \langle \circ \rangle$$
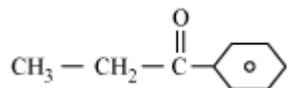
9. Draw the structures of white phosphorus and red phosphorus. Which one of these two types of phosphorus is more reactive and why?   **2**

Solution:
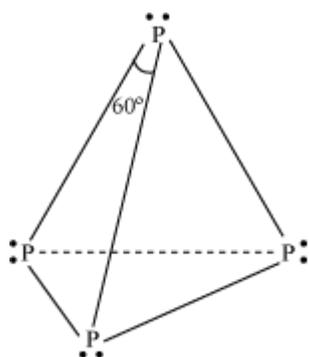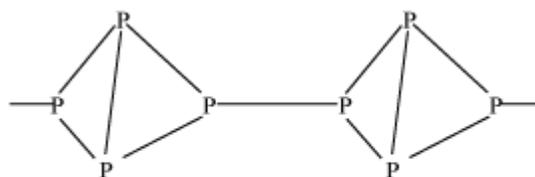
White phosphorus   Red phosphorus

White phosphorus is more reactive than red phosphorus.
The various P_4 molecules of white phosphorus are held together by weak Vander Waal's force of attraction, which makes it very reactive. On the other hand, molecules of red phosphorus are joined by covalent bonds to give a polymeric structure, which makes it very stable and less reactive.

10. The rate constant for a reaction of zero order in A is 0.0030 mol L^{-1} s^{-1}. How long will it take for the initial concentration of A to fall from 0.10 M to 0.075 M?   **2**

Solution:
For a first order reaction,

$$k = \frac{1}{t}\left[A_0 - A_t \right]$$

$$\therefore t = \frac{1}{k}\left[A_0 - A_t \right]$$

Given k = 0.0030 mol $L^{-1}S^{-1}$
A_0 = 0.10 M
A_t = 0.075 M
Substituting values

$$t = \frac{1}{0.0030} \ 0.10 - 0.075$$

$$= 8.33 \text{ s}$$

Hence, the concentration of A will fall from 0.10 M to 0.075 M in 8.33 seconds.

11. A reaction is of first order in reactant A and of second order in reactant B. How is the rate of this reaction affected when (i) the concentration of B alone is increased to three times (ii) the concentrations of A as well as B are doubled? **2**

Solution:
Let the concentration of the reactant A, [A] = a and
the concentration of the reactant B, [B] = b
So, Rate of reaction, R = k [A] [B]^2
$$= kab^2$$
(i) Case I
If the concentration of the reactant B is increased three times, then the rate of the reaction would be
R' = $ka(3b)^2$
$$= 9kab^2$$
$$= 9R$$
Therefore, the rate of the reaction would become 9 times the initial rate.

(ii) Case II:
If the concentration of both the reactants is doubled, then the rate of the reaction would be
R'' = $k(2a)(2b)^2$
$$= 8kab^2$$
$$= 8R$$
Therefore, the rate of the reaction would become 8 times the initial rate.

12. Non-ideal solutions exhibit either positive or negative deviations from Raoult's law. What are these deviations and why are they caused? Explain with one example for each type. **2**

Solution:
Positive deviations: In this type of deviations, the partial vapour pressure of each component (say 1 and 2) of a solution is greater than the vapour pressure as expected according to Raoult's law.
The plot of vapour pressure of two component solutions as a function of mole fraction is shown below.
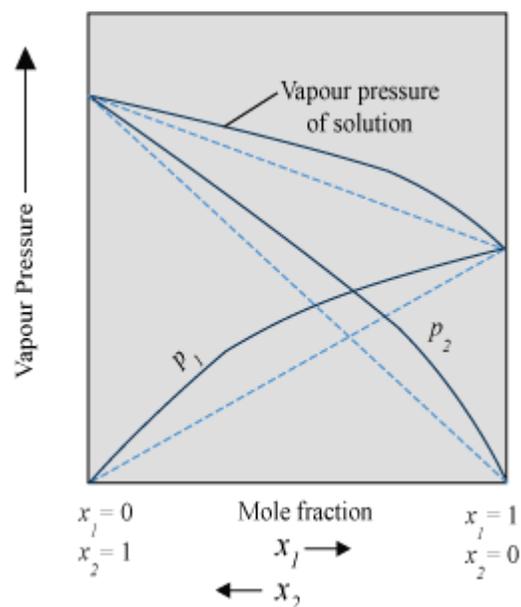
The intermolecular forces of attraction between solute-solvent molecules are weaker than those between solute-solute molecules and solvent-solvent molecules. Therefore, solvent molecules can easily escape, resulting in increase in vapour pressure.
Example: Ethanol and acetone mixture

Negative deviations: In this type of deviations, the partial vapour pressure of each component (say 1 and 2) of a solution is less than the vapour pressure as expected according to Raoult's law.
The plot of vapour pressure of two component solutions as a function of mole fraction is shown below.
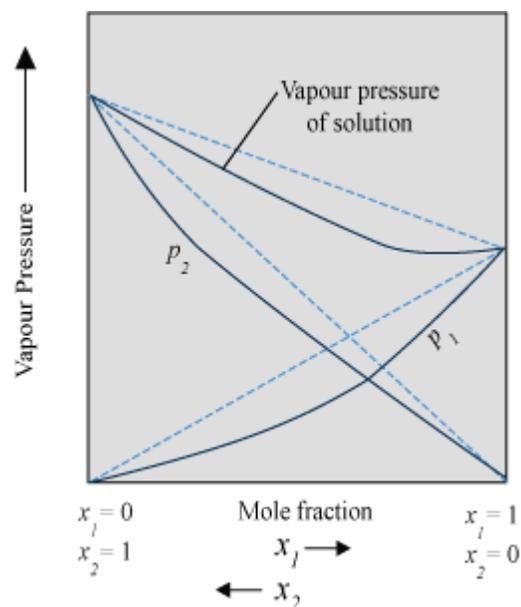
The intermolecular forces of attraction between solute-solute molecules and solvent-solvent molecules are weaker than those between solute-solvent molecules. This results in the decreasing of vapour pressure.
Example – Chloroform and acetone mixture
The intermolecular attractive forces between solute-solvent molecules increase due to the formation of H-bond.

Acetone   Chloroform
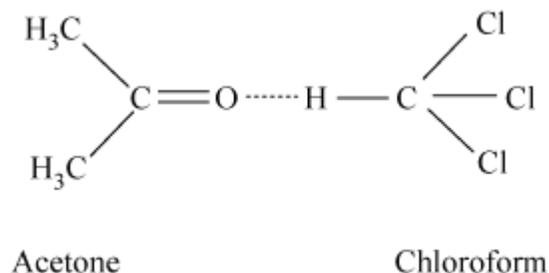
13. Explain the following observations:
(i) Transition elements generally form coloured compounds.
(ii) Zinc is not regarded as a transition element.   **2**

Solution:
(i) Most of the complexes of transition elements are coloured. This is because of the absorption of radiation from visible light region to promote an electron from one of the d–orbitals to another. In the presence of ligands, the d-orbitals split up into two sets of orbitals having different energies. Therefore, the transition of electrons can take place from one set to another. The energy required for these transitions is quite small and falls in the visible region of radiation. The ions of transition elements absorb the radiation of a particular wavelength and the rest is reflected, imparting colour to the solution.

(ii)
Electronic configuration of Zn = [Ar] $3d^{10}4s^2$
Hence, the d-subshell of zinc is completely occupied in both its ground state as well as in its common oxidation states.
Therefore, elements such as Zn cannot be classified as transition element because it has completely-filled d-subshell.

14. How are the following conversions carried out?
(i) Benzyl chloride to benzyl alcohol,
(ii) Methyl magnesium bromide to 2-methylpropan-2-ol   **2**

Solution:
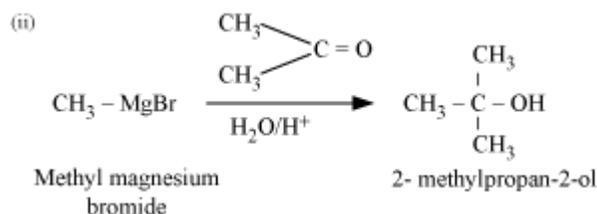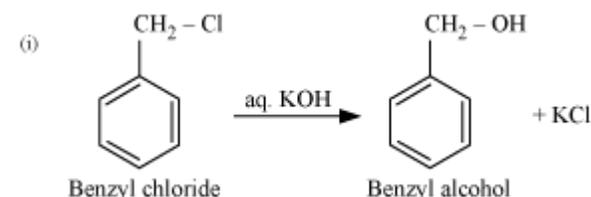
15. Illustrate the following reactions giving a chemical equation for each:
(i) Kolbe's reaction,
(ii) Williamson synthesis.   **2**

**Solution:**
(i) Kolbe's Reaction
It involves the reaction between sodium phenoxide and carbon dioxide under a pressure of $4 - 7$ atmospheres at 398 K to form sodium salicylate which on hydrolysis with minerals acids gives salicylic acid.
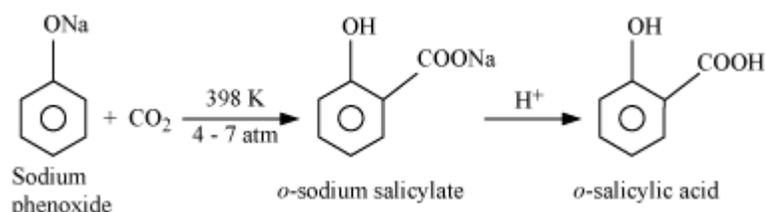
(ii) Williamson synthesis

This reaction is used to prepare both symmetrical as well as unsymmetrical ethers. It involves the treatment of alkyl halide with sodium alkoxide or sodium phenoxide.

$$CH_3I \quad + \quad NaOC_2H_5 \quad \longrightarrow \quad CH_3OC_2H_5 \quad + \quad NaI$$

Methyl	Sodium	Methoxy
iodide	ethoxide	ethane

16. Explain the following terms:
(i) Invert sugar
(ii) Polypeptides   **2**

OR

Name the products of hydrolysis of sucrose. Why is sucrose not a reducing sugar?

Solution:
(i)
The product formed on the hydrolysis of sucrose with dilute acids or enzyme invertase is   called invert sugar. These are known so because the sign of rotation changes from dextro (+)   to laevo (−).

(ii)
Two amino acids combine to form a peptide bond. When the number of combining amino acids is more than ten, the product obtained is known as polypeptide.

OR

On hydrolysis, sucrose gives one molecule of ∝-D glucose and one molecule of β- D-fructose.

α – D – glucose   β – D – fructose
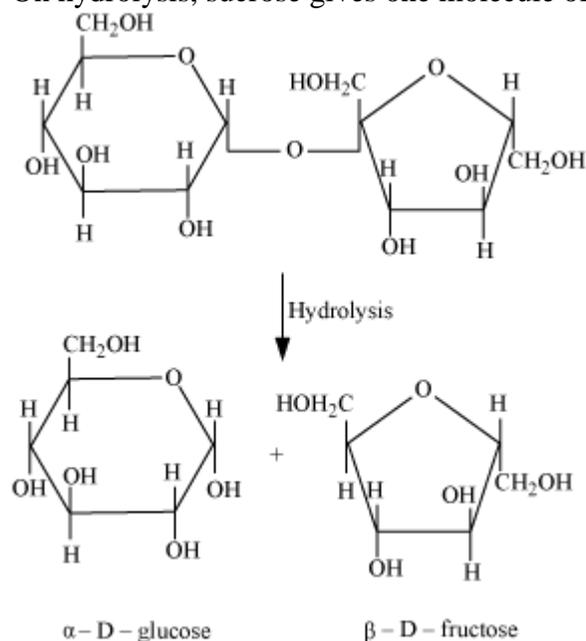
The two hexoses in sucrose are joined through a glycosidic linkage involving C-1 of glucose and C-2 of fructose. Thus, sucrose is non-reducing sugar.

17. Name the following coordination compounds according to IUPAC system of nomenclature:

(i) $[Co(NH_3)_4 (H_2O)Cl] Cl_2$

(ii) $[CrCl_2 (en)_2] Cl$, (en = ethane – 1, 2 – diamine) **2**

Solution:

(i) Tetraammineaquachlorocobalt(III) chloride

(ii) Dichlorobis(ethylenediamine)chromium(III) chloride

18. State clearly what are known as nucleosides and nucleotides. **2**

Solution:

A nucleoside is formed by the attachment of a base to $1'$ position of sugar.

Nucleoside = Sugar + Base

Structure of a nucleoside
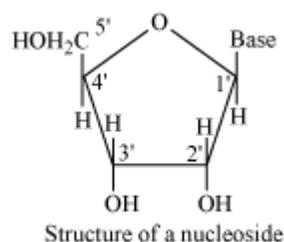
On the other hand, all the three basic components of nucleic acids (i.e., pentose sugar, phosphoric acid, and base) are present in a nucleotide.

Nucleotide = Sugar + Base + Phosphoric acid

Structure of a nucleotide
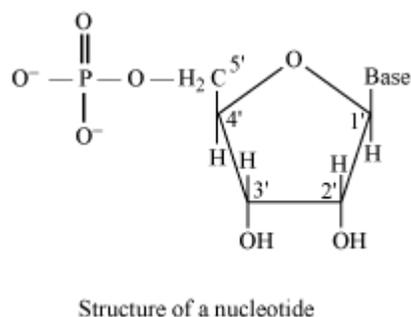
19. The density of copper metal is 8.95 g cm^{-3}. If the radius of copper atom is 127.8 pm, is the copper unit cell a simple cubic, a body-centred cubic or a face centred cubic structure? (Given: At. Mass of Cu = 63.54 g mol^{-1} and $N_A = 6.02 \times 10^{23}$ mol^{-1}) **3**

Solution:

It is given that density of copper metal, $d = 8.95$ g cm^{-3}

Molar mass, $M = 63.54$ g mol^{-1}

Edge length, $a = 127.8$ pm $= 127.8 \times 10^{-10}$ cm

Also, Avogadro's number, $N_A = 6.022 \times 10^{23}$ mol^{-1}

Applying the relation,

$$d = \frac{zM}{a^3 N_A}$$

$$\text{Or } 8.95 = \frac{z \times 63.54}{(127.8 \times 10^{-10})^3 \times (6.022 \times 10^{23})}$$

$$\text{Or } z = \frac{8.95 \times (127.8 \times 10^{-10})^3 \times (6.022 \times 10^{23})}{63.54}$$

$$0.17 \approx 2$$

Hence, the copper unit cell is bcc type.

20. How are the following colloids different from each other in respect of their dispersion medium and dispersed phase? Give one example of each.
(i) Aerosol
(ii) Emulsion
(iii) Hydrosol   **3**

Solution:
Colloidal solutions can be classified as aerosols, emulsions and hydrosols as given.

	Name of sol	Dispersed phase	Dispersion medium	Example
(i)	Aerosol	Solid/liquid	Gas	Smoke, cloud
(ii)	Emulsion	Liquid	Liquid	Milk
(iii)	Hydrosol	Solid	Water	Muddy water

21. A solution prepared by dissolving 1.25 g of oil of winter green (methyl salicylate) in 99.0 g of benzene has a boiling point of 80.31 °C. Determine the molar mass of this compound. (B.P. of pure benzene = 80.10 °C and K_b for benzene = 2.53 °C kg mol^{-1})   **3**

Solution:
Mass of solute (W_B) = 1.25 g
Mass of solvent (W_A) = 99 g
Elevation in boiling point (ΔT_b) = 80.31 – 80.10°C = 0.21°C
K_b = 2.53°C kg mol^{-1}

$$\text{Now, } \Delta T_b = K_b \frac{W_B \times 1000}{W_A \times M_B}$$

$$0.21 = \frac{2.53 \times 1.25 \times 1000}{99 \times M_B}$$

$$\text{Or } M_B = \frac{2.53 \times 1.25 \times 1000}{99 \times 0.21}$$

$$\text{Or } M_B = 152.116 \, g$$

22. Describe how the following changes are brought about:
(i) Pig iron into steel
(ii) Zinc oxide into metallic zinc
(iii) Impure titanium into pure titanium.

OR

Describe the role of
(i) NaCN in the extraction of gold from gold ore.
(ii) SiO$_2$ in the extraction of copper from copper matte.
(iii) Iodine in the refining of zirconium.
Write chemical equations for the involved reactions.

Solution:
(i)
Pig iron can be converted into steel by Bessemer process. It is done in iron vessels called converters. A strong blast of air is passed through molten pig iron. This blast is shut off before all the carbon has burnt out. The carbon concentration in various types of steel varies from 0.1% to 1.5%.

(ii)
Zinc is extracted from zinc oxide by the process of reduction. The reduction of zinc oxide is carried out by mixing it with powdered coke and then heating it at 673 K.

$$ZnO + C \xrightarrow{\text{coke, 673 K}} Zn + CO$$
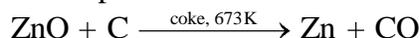
(iii)
Pure titanium can be obtained from impure titanium by Van Arkel method. In this method, first impure metal is converted to one of its unstable compounds. Pure metal is then obtained by heating the unstable compound at high temperature.

$$\underset{\substack{\text{Impure}\\\text{metal}}}{Ti} + 2\,I_2 \xrightarrow{50-250°C} \underset{\substack{\text{Titanium}\\\text{tetraiodide}}}{TiI_4} \xrightarrow{1400°C} \underset{\substack{\text{Pure}\\\text{metal}}}{Ti} + 2I_2$$
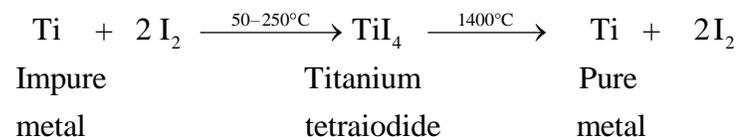
OR

(i)
The roasted ore of gold is leached with a solution of sodium cyanide in the presence of oxygen for many days. The role of NaCN in this process is to dissolve the gold to form an aurocyanide complex, from which the metal is obtained by displacement.

$$4\,Au + 8\,NaCN + 2\,H_2O + O_2 \longrightarrow 4\,Na\,Au(CN)_2 + 4\,KOH$$

$$2\,Na\,Au(CN)_2 + Zn \longrightarrow Na_2[Zn(CN)_4] + 2\,Au$$

(ii)
Copper *matte* contains Cu$_2$S and FeS. In the blast furnace, copper *matte* is added with powdered coke and silica. The oxidation of ore takes place in this process. As a result, cuprous oxide and ferrous oxide are produced. The role of silica in this process is to remove the iron oxide obtained as **'slag'**. FeO combines with silica (flux) to form iron silicate, FeSiO$_3$ (slag).
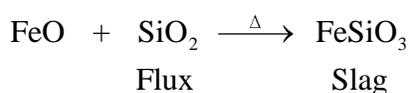
$$\underset{\text{Flux}}{FeO} + SiO_2 \xrightarrow{\Delta} \underset{\text{Slag}}{FeSiO_3}$$

(iii)
In Van Arkel method, iodine is added to zirconium to remove oxygen and nitrogen present in the form of impurities. The impure metal is heated in an empty vessel with iodine. The metal iodide formed in the process volatilises to give zirconium tetraiodide.
$Zr + 2 I_2 \rightarrow ZrI_4$
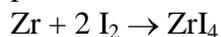
Zirconium tetraiodide is then decomposed on a tungsten filament, at a temperature of 1800 K, to obtain pure metal.
$ZrI_4 \rightarrow Zr + 2I_2$
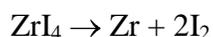
23. (i) State one use each of DDT and iodoform.
(ii) Which compound in the following couples will react faster in S_N2 displacement and why?
(a) 1-Bromopentane or 2-bromopentane
(b) 1-bromo-2-methylbutane or 2-bromo-2-methylbutane.   **3**

Solution:
(i)
Use of DDT:
DDT is widely used as an insecticide.
Use of iodoform:
Iodoform is used as an antiseptic.

(ii)
(a) 1-bromopentane will undergo S_N2 displacement reaction faster than 2-bromopentane.

Generally 1° alkyl halides react by S_N2 mechanisms, 2° alkyl halides by both S_N1 and S_N2 reactions and 3° alkyl halides by S_N2 reactions.
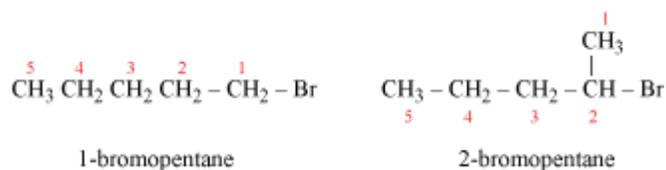
This is due to the fact that the electron density on α-carbon atom goes on increasing by inductive effect of the alkyl groups. This increased electron density on the α-carbon atom repels the direct attack of the nucleophile and thus retards S_N2 reaction. Moreover, the transition state of S_N2 reactions become over crowded as the size of the alkyl group increases. This also slows down the S_N2 reaction.

(b) 1-bromo-2-methylbutane will undergo S_N2 reaction faster than 2-bromo-2-methylbutane
Thus, the order of S_N2 reaction is

$$CH_3 - CH_3 - \underset{\underset{CH_3}{|}}{CH} - CH_2 - Br \quad > \quad CH_3 - CH_3 - \underset{\underset{Br}{|}}{\overset{\overset{CH_3}{|}}{C}} - CH_3$$
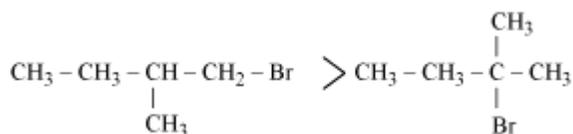
1- bromo-2-methyl butane proceeds by forming 1° carbocation while 2-bromo-2 methylbutane proceeds by forming 3° carbocation. The electron density on the α-carbon atom of the latter compound is more due to presence of more alkyl groups. This increased electron density on the α-carbon atom repels the direct attack of the nucleophile and thus retards S_N2 reaction. It rather proceeds by S_N1 reaction.

24. How would you account for the following?
(i) The atomic radii of the metals of the third (5d) series of transition elements are virtually the same as those of the corresponding members of the second (4d) 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 metal is exhibited in its oxide or fluoride.   **3**

Solution:
(i)
In the second transition series, the number of shells increases and so does the atomic size. However, in the third series (5d series), the atomic size is more or less the same. This is known as lanthanide contraction. This is due to the poor shielding effect by f-electrons.

(ii)
The large positive E˚ value for Mn^{3+}/Mn^{2+} shows that Mn^{2+} is much more stable than Mn^{3+}. This is because of the fact that Mn^{2+} has $3d^5$ configuration. This means that the d-orbital is half-filled. Half-filled and fully-filled configurations are very stable. Thus, the third ionization energy of Mn will be very high.

(iii)
Oxygen and fluorine act as strong oxidising agents because of their high electronegativities and small sizes. Hence, they bring out the highest oxidation states from various metals. In other words, a metal exhibits highest oxidation state in its oxides and fluorides. For example, in OsF_6 and V_2O_5, the oxidation states of Os and V are +6 and +5 respectively.

25. In the following cases rearrange the compounds as directed:
(i) In an increasing order of basic strength:
$C_6H_5NH_2, C_6H_5 N (CH_3)_2$, $(C_2H_5)_2 NH$ and CH_3NH_2
(ii) In a decreasing order of basic strength:
Aniline, p-nitroaniline and p-toluidine
(iii) In an increasing order of pK_b values:
$C_2H_5NH_2$, $C_6H_5 NHCH_3$, $(C_2H_5)_2 NH$ and $C_6H_5NH_2$ **3**

Solution:

(i) Basic strength:
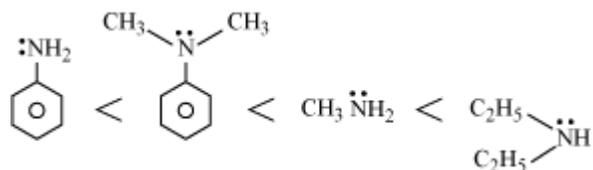
Aliphatic amines are stronger bases than aromatic amines due to the presence of lone pair of electrons on nitrogen atom. In case of aromatic amines the lone pair gets delocalised by resonance. Diethyl amine has greater + I effect. Hence, electron density over the nitrogen atom is more in this case. Similarly N, N – dimethyl aniline has greater + I effect than aniline.

(ii)

p-toluidine   aniline   *p*-nitro aniline
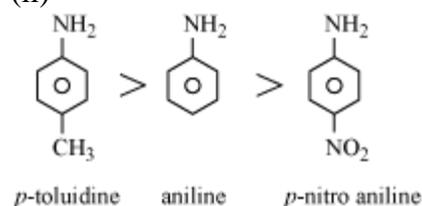
Methyl ($-CH_3$) is an electron donating group. It increases the electron density on the ring. Therefore, the lone pair of nitrogen is available for donation. Hence, it is most basic. On the other hand nitro ($-NO_2$) is an electron withdrawing group. It decreases the electron density of the ring. Therefore, the lone pair is more delocalized in this case and is less available for donation. Thus, it will be least basic among the three.

(iii)
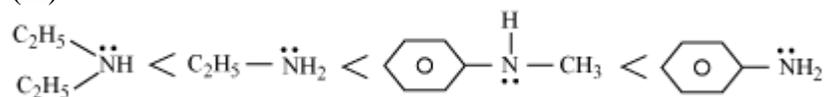
Stronger the base is lesser is the pK_b value. $(C_2H_5)_2NH$ is the strongest base due to two electron releasing group followed by $C_2H_5NH_2$ which has only one electron releasing group. $C_6H_5NHCH_3$ is the next stronger base because of the presence of one electron releasing alkyl group and electron delocalising phenyl group. $C_6H_5NH_2$ is the least basic wherein the electrons get delocalised by resonance.

26. Differentiate between thermoplastic and thermosetting polymers. Give one example of each.

Solution:

Thermoplastic polymers	Thermosetting polymers
Thermoplastic polymers are linear (slightly branched) long chain polymers, which can be repeatedly softened and hardened on heating and cooling. Hence, they can be modified again and again.	Thermosetting polymers are cross-linked or heavily branched polymers, which get hardened during the moulding process. These plastics cannot be softened again on heating.
Examples: Polythene, polystyrene.	Examples: Bakelite, urea-formaldehyde resins.

27. Explain the following terms with one suitable example in each case.
(i) Cationic detergents
(ii) Enzymes
(iii) Antifertility drugs   **3**

Solution:
(i) Cationic detergents: Cationic detergents are quaternary ammonium salts of acetates, chlorides, or bromides. These are called cationic detergents because the cationic part of these detergents contains a long hydrocarbon chain and a positive charge on the N atom.
Example: cetyltrimethylammonium bromide
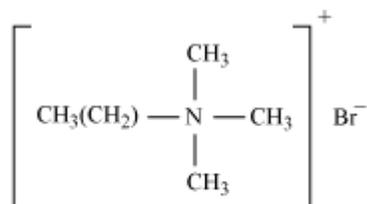
Cetyltrimethylammonium bromide

(ii) Enzymes: Biological catalysts are known as enzymes. They are made up of proteins. Enzymes are very specific for a particular reaction and for a particular substrate.
Example: Invertase, zymase

(iii) Antifertility drugs: These drugs are used to prevent pregnancy in women. They are also used for family planning. Antifertility drugs basically contain a mixture of synthetic estrogen and progesterone derivatives that prevent pregnancy by controlling the menstrual cycle.
Example: norethindrone, ethynylestradiol (novestrol)

28. (a) Explain the mechanism of a nuclophilic attack on the carbonyl group of an aldehyde or a ketone.
(b) An organic compound (A) (molecular formula $C_8H_{16}O_2$) was hydrolysed with dilute sulphuric acid to give a carboxylic acid (B) and an alcohol (C). Oxidation of (C) with chromic acid also produced (B). On dehydration (C) gives but-1-ene. Write the equations for the reactions involved.
5

OR

(a) Give chemical tests to distinguish between the following pairs of compounds:
(i) Ethanal and Propanal
(ii) Phenol and Benzoic acid

(b) How will you bring about the following conversions?
(i) Benzoic acid to benzaldehyde
(ii) Ethanal to but-2-enal
(iii) Propanone to propene
Give complete reaction in each case.

Solution:

(a)

The carbonyl group is polar due to the higher electronegativity of oxygen as compared to that of carbon. As a result, the shared pair of electrons is closer to oxygen atom. The following steps are involved in the reaction.

Step 1:

Nucleophile (Nu⁻) attacks the carbonyl group perpendicular to the plane of sp^2 hybridised orbitals of carbonyl carbon.

Step 2:

In the process, hybridisation of carbon changes from sp^2 to sp^3.

Step 3:

A tetrahedral alkoxide is formed as intermediate.
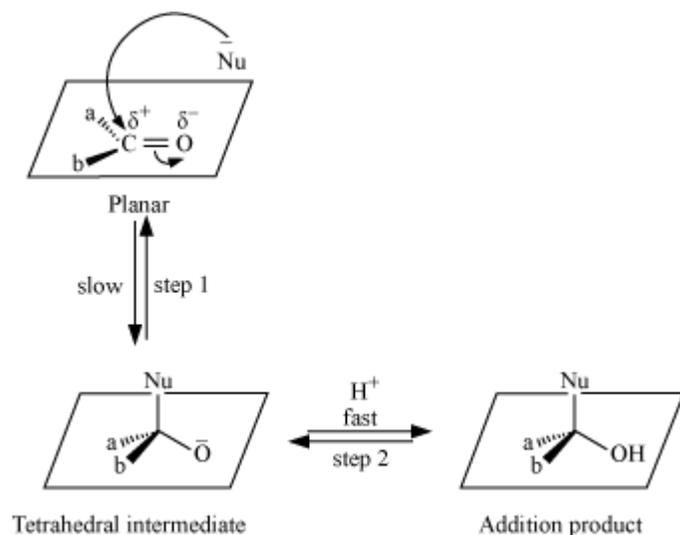
(b)

The organic compound A with molecular formula $C_8H_{16}O_2$ gives a carboxylic acid (B) and an alcohol (C) on hydrolysis with dilute sulphuric acid. Thus, compound A must be an ester. Further, alcohol C gives acid B on oxidation with chromic acid. Thus, B and C must contain equal number of carbon atoms.

Since compound A contains a total of 8 carbon atoms, each of B and C contain 4 carbon atoms.

Again, on dehydration, alcohol C gives but-1-ene. Therefore, C is of straight chain. Hence, it is butan-1-ol.

On oxidation, Butan-1-ol gives butanoic acid. Hence, acid B is butanoic acid.

Hence, the ester with molecular formula $C_8H_{16}O_2$ is butylbutanoate.

Butylbutanoate
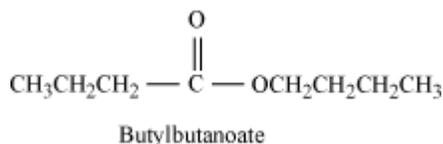
All the given reactions can be explained by the following equations.

$$CH_3CH_2CH_2 \overset{\overset{\displaystyle O}{\|}}{\underset{}{C}} OCH_2CH_2CH_2CH_3 \xrightarrow{\text{dil } H_2SO_4} CH_3CH_2CH_2 \overset{\overset{\displaystyle O}{\|}}{\underset{}{C}} OH + CH_3CH_2CH_2CH_2OH$$

Butylbutanoate   Butanoic acid   Butan – 1 – ol
(A)   (B)   (C)

$$CH_3CH_2CH_2CH_2 OH$$

CrO$_3$/CH$_3$COOH
Oxidation
$$\rightarrow CH_3CH_2CH_2 \overset{\overset{\displaystyle O}{\|}}{\underset{}{C}} OH$$
Butanoic acid
(B)

Dehydration
–H$_2$O
$$\rightarrow CH_3CH_2CH = CH_2$$
But – 1 – ene

OR

(a)
(i) Ethanal and propanal can be distinguished by iodoform test.

Iodoform test
Aldehydes and ketones having at least one methyl group linked to the carbonyl carbon atom responds to the iodoform test. Ethanal having one methyl group linked to the carbonyl carbon atom responds to this test. But propanal does not have a methyl group linked to the carbonyl carbon atom and thus, it does not respond to this state.

$$CH_3CHO + 3NaOI \longrightarrow HCOONa + CHI_3 + 2\,NaOH$$
Ethanal   Sodium   Iodoform
                           methanoate (yellow ppt)

(ii)
Phenol and benzoic acid can be distinguished by ferric chloride test.

Ferric chloride test:
Phenol reacts with neutral FeCl$_3$ to form ferric phenoxide complex giving violet colouration.

$$6\,C_6H_5OH + FeCl_3 \longrightarrow \left[Fe\,(OC_6H_5)_6 \right]^{3-} + 3H^+ + 3Cl^-$$
Phenol   Iron-phenol complex
                           (Violet colour)

But benzoic acid reacts with neutral FeCl$_3$ to give a buff coloured precipitate of ferric benzoate.

$$3\,C_6H_5OH + FeCl_3 \longrightarrow (C_6H_5COO)_3Fe + 3\,HCl$$
Benzoic acid   Ferric benzoate
                         (Buff coloured ppt)

(b)
(i)
Benzoic acid to benzaldehyde:

(ii) Ethanal to but-2-enal:

(iii) Propanone to propene:

29. (a) State Kohlrausch law of independent migration of ions. Write an expression for the molar conductivity of acetic acid at infinite dilution according to Kohlrausch law.

(b) Calcualte $\wedge_m^\circ$ for acetic acid.

Given that $\wedge_m^\circ$ (HCl) = 426 S cm^2 mol^{-1}

$\wedge_m^\circ$ (NaCl) = 126 S cm^2 mol^{-1}

$\wedge_m^\circ$ (CH$_3$COONa) = 91 S cm^2 mol^{-1} **5**

OR

(a) Write the anode and cathode reactions and the overall reaction occurring in a lead storage battery.
(b) A copper-silver cell is set up. The copper ion concentration is 0.10 M. The concentration of silver ion is not known. The cell potential when measured was 0.422 V. Determine the concentration of silver ions in the cell. (Given $E^\circ_{Ag^+/Ag}$ = +0.80V, $E^\circ_{Cu^{2+}/Cu}$ +0.34 V)

Solution:

(a)

Kohlrausch law of independent migration of ions: It states that the limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of its anions and cations.

Though acetic acid is a weak acid, it will dissociate completely at infinite dilution.

Now, if $\lambda^0_{H^+}$ = Limiting molar conductivity of H^+ ions

$\lambda^0_{CH_3COO^-}$ = Limiting molar conductivity of CH_3COO^- ions

$\Lambda^0_{m(CH_3COOH)}$ = Limiting molar conductivity of CH_3COOH

Then,

$\Lambda^0_{m(CH_3COOH)} = \lambda^0_{H^+} + \lambda^0_{CH_3COO^-}$

In general, if an electrolyte gives v_+ cations and v_- anions, then its limiting molar conductivity is given by

$\Lambda^0_m = v_+ \lambda^0_+ + v_- \lambda^0_-$

Where, λ^0_+, λ^0_- = Limiting molar concentration of cations and anions respectively

(b)

Λ^0_m (CH$_3$COOH)

$= \lambda^0_{CH_3COO^-} + \lambda^0_{H^+} + \lambda^0_{Na^+} - \lambda^0_{Na^+} + \lambda^0_{Cl^-} - \lambda^0_{Cl^-}$

$= [\lambda^0_{CH_3COO^-} + \lambda^0_{Na^+}] + [\lambda^0_{H^+} + \lambda^0_{Cl^-}] - [\lambda^0_{Na^+} + \lambda^0_{Cl^-}]$

$= \Lambda^0_m(CH_3COONa) + \Lambda^0_m(HCl) - \Lambda^0_m(NaCl)$

$= 91 + 426 - 126$

$= 391 \text{ S cm}^2 \text{ mol}^{-1}$

OR

(a)

A lead storage battery consists of a lead anode, a grid of lead packed with lead oxide (PbO_2) as the cathode, and a 38% solution of sulphuric acid (H_2SO_4) as an electrolyte.

When the battery is in use, the following cell reactions take place:

At anode: $Pb_s + SO_4^{2-}{}_{aq} \longrightarrow PbSO_{4\ s} + 2e^-$

At cathode: $PbO_{2\ s} + SO_4^{2-}{}_{aq} + 4H^+{}_{aq} + 2e^- \longrightarrow PbSO_{4\ s} + 2H_2O_l$
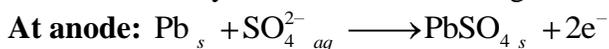
The overall cell reaction is given by,

$Pb_s + PbO_{2\ s} + 2H_2SO_{4\ aq} \longrightarrow 2PbSO_{4\ s} + 2H_2O_l$
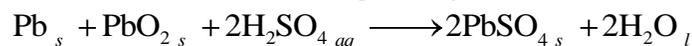
When a battery is charged, the reverse of all these reactions take place.

Hence, on charging, $PbSO_{4\ s}$ present at the anode and cathode is converted into Pb_s and

$PbO_{2\ s}$ respectively.

(b) The given cell is

$Cu\,|\,Cu^{2+}\,||\,Ag^+\,|\,Ag_{(s)}$

(Anode)   (Cathode)

The net cell reactions is

$$Cu_{(s)} + 2Ag^+_{(aq)} \longrightarrow 2Ag_{(s)} + Cu^{2+}_{(aq)}$$

This involves transfer of 2 electrons. Thus, $n = 2$

According to Nernst equation

$$E_{cell} = E^0_{cell} + \frac{0.059}{2} \log \frac{[Cu][Ag^+]^2}{[Cu^{2+}][Ag]^2} \qquad \text{...(i)}$$

$[Ag] = [Cu] = 1$ being solids

Also, $E^0_{cell} = E^0_{Ag^+|Ag} - E^0_{Cu^{2+}|Cu}$

$$= 0.80 - 0.34$$

$$= 0.46 \text{ V}$$

Substituting the value of E^0_{cell} in equation (i), we get

$$E_{cell} = 0.46 \text{ V} + \frac{0.059}{2} \log \frac{[Ag^+]^2}{[Cu^{2+}]}$$

$$0.422 = 0.46 + \frac{0.059}{2} \log \frac{[Ag^+]^2}{[0.10]}$$

$$-0.038 = \frac{0.059}{2} \log \frac{[Ag^+]^2}{[0.10]}$$

Or $\log \dfrac{[Ag^+]^2}{[0.10]} = -1.288$

$$\frac{[Ag^+]^2}{0.10} = 0.0515$$

$$[Ag^+]^2 = 0.005$$

$$Ag^+ = 0.07 \text{ M}$$

30. (a) Complete the following chemical equations:

(i) $NaOH_{(aq)} + Cl_{2(g)} \longrightarrow$

   (Hot and conc.)

(ii) $XeF_{6(s)} H_2O(l) \longrightarrow$
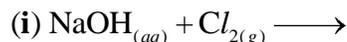
(b) How would you account for the following?
(i) The value of electron gain enthalpy with negative sign for sulphur is higher than that for oxygen.
(ii) NF_3 is an exothermic compound but NCl_3 is endothermic compound.
(iii) ClF_3 molecule has a T-shaped structure and not a trigonal planar one.   **5**

OR

(a) Complete the following chemical reaction equations:
(i) $P_4 + SO_2Cl_2 \rightarrow$
(ii) $XeF_4 + H_2O \rightarrow$
(b) Explain the following observations giving appropriate reasons:
(i) The stability of + 5 oxidation state decreases down the group in group 15 of the periodic table.
(ii) Solid phosphorus pentachloride behaves as an ionic compound.
(iii) Halogens are strong oxidizing agents.
Solution:
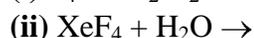
(a)
(i)
$$6NaOH_{(aq)} + 3Cl_{2(g)} \longrightarrow 5NaCl + NaClO_3 + 3H_2O$$
(Hot and conc.)

(ii) $XeF_{6(s)} + 3H_2O(l) \longrightarrow XeO_3 + 6HF$
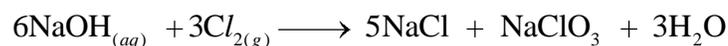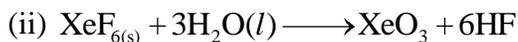
(b)
(i) The negative electron gain enthalpies are large for elements of group 16. However, the atomic size of oxygen is quite small. Because of this, the electron-electron repulsions in $2p$ sub-shell are quite high. Hence, the incoming electron is not accepted as easily in oxygen as it is in sulphur. Hence, the negative electron gain enthalpy for sulphur is higher than that of oxygen.

(ii) The instability of NCl_3 is due to the weak NCl bond. This is due to the large difference in the size of nitrogen and chlorine atoms. On the other hand, atoms of both nitrogen (75 pm) and fluorine (72 pm) are small sized. Thus, bonding in NF_3 is quite strong and it is an exothermic compound.

(iii) ClF_3 molecule involves a sp^3d hybridization of the central atom 'Cl'

Electronic structure of Cl (ground state)

Electronic structure of Cl (excited state)
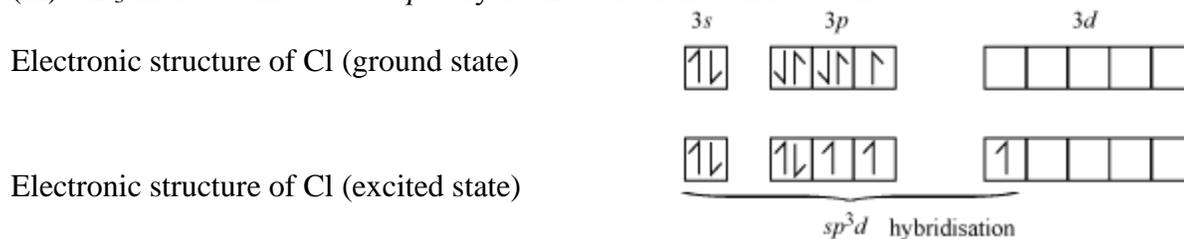
Thus, ClF_3 have trigonal bipyramidal geometries with two positions occupied by 2 lone pairs. Hence it is T-shaped.

OR
(a)
(1) $P_4 + 10 SO_2Cl_2 \rightarrow 4 PCl_5 + 10 SO_2$
(2) $6 XeF_4 + 12 H_2O \rightarrow 4 Xe + 2 XeO_3 + 24 HF + 3 O_2$
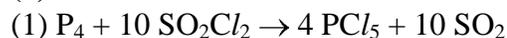
(b)
(i) On moving down the elements of group 15, the stability of +5 oxidation state decreases. This is due to the reluctances of s-electrons to participate in the bond formation. This is known as **inert pair effect.** It is the result of ineffective shielding of s-electrons of the valence shell by intervening d-and f-electrons.

(ii) PCl_5 is covalent in the vapour state but in the crystalline state, it exists as $[PCl_4]^+ [PCl_6]^-$. These ions have tetrahedral and octahedral geometry. Thus, solid phosphorous pentachloride behaves as ionic compounds.

(iii)
The general electronic configuration of halogens is np^5, where n = 2-6. Thus, halogens need only one more electron to complete their octet and to attain the stable noble gas configuration. Also, halogens are highly electronegative with low dissociation energies and high negative electron gain enthalpies. Therefore, they have a high tendency to gain an electron. Hence, they act as strong oxidizing agents.