# SAMPLE PAPER 2
## CHEMISTRY THEORY (043)

**Max.Marks:70**                                                                    **Time: 3 Hours**

**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:

   Only the surface atoms in an adsorbent, play an active role in adsorption, these atoms possess some residual forces like van der Waals 'forces and chemical forces.

   In the process of adsorption, weak adsorbate is substituted by strong adsorbate activated charcoal used in gas mask is already exposed to the atmospheric air so the gases and water vapours in air are adsorbed on its surface. when the mask is exposed to chlorine atmosphere, the gases are displaced by chlorine, Porous and finely powdered solids, e,g., charcoal and Fuller s earth adsorb more as compared to the hard non-porous material. It is due to this property that the powdered charcoal is used in gas masks. In general, easily that the powdered charcoal is used in gas masks. In general, easily liquefiable gases like $CO_2$, $NH_3$, $Cl_2$ and $SO_2$, etc., are adsorbed to greater extent than the elemental gases, e.g., $H_2$, $N_2$, $O_2$ and He etc.,

    (i) Gas masks work on the principle of:

       (a) physical adsorption                         (b) chemical adsorption

       **(c) both physical and chemical adsorptions**     (d) absorption

   (ii) Which of the following gases will be most easily adsorbed by the charcoal in the gas mask?

       (a)$H_2$         (b)$O_2$         (C)$N_2$         **(d)$SO_2$**

   (iii) Gas mask contains:

       (a) charcoal granules                 **(b) powdered charcoal**

       (c) calcium carbonate                 (d) Fuller's earth

   (iv) Which of the following gas molecules has maximum value of enthalpy of physisorption in a gas mask?

       (a) $C_2H_6$         (b) Ne         **(c) $H_2O$**         (d) H2

                                    (Or)

   Which of the following gases will substitute $O_2$ from adsorbed charcoal?

       (a)$H_2$         (b)$N_2$         (c)Ar         **(d)$Cl_2$**

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

   The high reactivity of alkyl halides can be explained in terms of nature of C-X bond which is highly polarised covalent bond due to large difference in the electronegativities of carbon and halogen atom. This polarity is responsible for the nucleophilic substitution reactions of alkyl halides which mostly occur by $S_N1$ and $S_N2$ mechanisms. $S_N1$ reaction is a twostep process and in the first step, R-X ionises to give carbocation (slow process). In the second step, the nucleophile attacks the carbocation from either side to form the product (fast process). In $S_N1$ reaction, there can be racemization and inversion. $S_N1$ reaction is favoured by heavy (bulky) groups on the carbon atom attached to halogens. i.e., $R_3C-X > R_2CH-X > R-CH_2X > CH_3X$, In $S_N2$ reaction, the strong nucleophile OH⁻ attacks from the opposite side of the chlorine atom to give an intermediate (transition state). which breaks to yield the

product (alcohol) and leaving (X⁻) group. The alcohol has a configuration opposite to that of the bromide and is said to proceed with inversion of configuration. $S_N2$ reaction is favoured by small groups on the carbon atom attached to halogen i.e., $CH_3-X > R-CH_2X > R_2CHX > R_3C- X$.

In these questions (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 incorrect statement.

(d Assertion is incorrect statement but Reason correct statement.

(i) Assertion: $S_N2$ reaction takes place in single step.

   Reason: $S_N2$ reaction involves the reactivity order of alkyl halides as 1° > 2° > 3° halides.

   **Ans: (a)**

(ii) Assertion: Nucleophilic substitution of iodoethane, is easier than chloroethane.

   Reason: Bond energy of C-I bond is less than that of C-Cl bond.

   **Ans: (a)**

(Or)

   Assertion: Tert-butyl methyl ether is not prepared by the reaction of tert-butyl bromide with sodium methoxide.

   Reason: Sodium methoxide is a strong nucleophile.

   **Ans: (b)**

(iii) Assertion: Ethyl chloride is more reactive than vinyl chloride towards nucleophilic substitution reactions.

   Reason: In vinyl chloride, the-Cl is bonded to sp-hybridized carbon of an alkene.

   **Ans: (c)**

(iv) Assertion: 2-Bromobutane, on reaction with sodium ethoxide in ethanol gives 1-butene as a major product.

   Reason: 2-Butene is less stable than 2-butene.

   **Ans: (d)**

3. In a crystalline solid, atoms of X form fcc packing and the atoms of Y occupy all octahedral voids. If all the atoms along one body diagonal are removed then the simplest formula of the crystalline solid will be:

   (a) XY  (b) $X_4Y_3$  **(c) $X_5Y_4$**  (d) $X_4Y_5$

4. Ideal solution is formed when its components:

   (a) have zero heat of mixing only

   (b) have zero volume change on mixing only

   (c) can be converted into gases

   **(d) have zero heat of mixing and Zero volume change**

(Or)

Mole fraction of $C_3H_5(OH)_3$ in a solution of 36 g of water and 46 g of glycerine is:

   (a) 0.46  **(b) 0.20**  (c) 0.26  (d) 0.36

5. In a reaction, $2A_2 + B_2 \rightarrow 2A_2B$, the reactant A will disappear at:

   (a) half the rate that B will decrease  (b) the same rate that B will decrease

   (c) double the rate that $A_2B$ will form  **(d) twice the rate that B will decrease**

6. Which is in the decreasing order of boiling points of V group hydrides?

   (a) $NH_3 > PH_3 > AsH_3 > SbH_3$  (b) $SbH_3 > AsH_3 > PH_3 > NH_3$

   (c) $PH_3 > NH_3 > AsH_3 > SbH_3$  **(d) $SbH_3 > NH_3 > AsH_3 > PH_3$**

7. Lanthanide contraction is caused due to:
   (a) the appreciable shielding on outer electrons by 4f electrons from the nuclear charge
   (b) the appreciable shielding on outer 'electrons by 5d electrons from the nuclear charge
   (c) the same effective nuclear charge from Ce to Lu.
   **(d) the imperfect shielding on outer electrons by 4f electrons from the nuclear charge**

8. The donor sites of EDTA ligand are:
   (a) O atoms only                    (b) N atoms only
   **(c) two N atoms and four O atoms**  (d) three N atoms and three O atoms

9. Formaldehyde forms an addition product with $CH_3MgI$ which on hydrolysis gives:
   (a) ethyl iodide                    **(b) ethyl alcohol**
   (c) methyl alcohol                  (d) methyl iodide

10. When dihydroxy acetone reacts with $HIO_4$ the product is/are:
    (a) HCHO    **(b) HCHO and HCOOH**    (c) HCHO and $CO_2$    (d) HCOOH

11. Glucose has difference from fructose in that it:
    (a) does not undergo hydrolysis              (b) Is a monosaccharide
    **(c) gives silver mirror with Tollens's reagent**    (d) none of the above

In the following questions (Q. no. 12-16) a statement of assertion followed by a statement of reason by given. Choose the correct answer out of the following choices.
   (a) Assertion and Reason both are correct explanation for Assertion.
   (b) Assertion and reason both are correct statement but reason is not correct explanation for Assertion.
   (c) Assertion is correct statement but Reason is incorrect statement.
   (d) Assertion is incorrect statement but reason is correct statement.

12. Assertion: White tin is an example of tetragonal system.
    Reason: For tetragonal system a=b=c and $\alpha = \beta = \gamma \neq 90$
    **Ans: (c)**

13. Assertion: Nitrogen is unreactive at room temperature but becomes reactive at elevated temperatures or in presence of a catalyst.
    Reason: In nitrogen molecule, there is extensive delocalization of electrons.
    **Ans: (c)**

14. Assertion: Ethyl acetate is more reactive than acetamide towards nucleophilic substitution
    Reason: $-OC_2H_5$ is more electron attracting than $-NH_2$ group
    **Ans: (a)**

15. Assertion: Uracil occurs in DNA.
    Reason: RNA undergoes replication.
    **Ans: (d)**

16. Assertion: In strongly acidic solutions; aniline becomes more reactive towards electrophilic reagents.
    Reason: The amino group being completely protonated in strongly acidic solution, the lone pair of electrons on the nitrogen is no longer available for resonance.
    **Ans: (d)**

## SECTION B

17. A compound forms hcp structure. What is the total number of voids in 0.5 mol of it? How many of these are tetrahedral voids?
    Number of atoms in 0.5 mol *hcp* lattice $= 0.5 \times 6.022 \times 10^{23} = 3.011 \times 10^{23}$
    Number of octahedral voids = Number of atoms
    $$= 3.011 \times 10^{23}$$
    Number of tetrahedral voids $= 2 \times$ Number of atoms
    $$= 2 \times 3.011 \times 10^{23} = 6.022 \times 10^{23}$$
    Total number of voids = Number of octahedral voids + Number of tetrahedral voids
    $$= 3.011 \times 10^{23} + 6.022 \times 10^{23} = 9.033 \times 10^{23} \text{ voids}$$

18. State Henry's law and mention two of its important applications.

Henry's law states that, the partial pressure of the gas in vapour phase (p) is proportional to the mole fraction of the gas (x) in the solution.

$$p = K_H \cdot x \text{ where, } K_H = \text{Henry's law constant.}$$

Different gases have different $K_H$ values at the same temperature.

Applications of Henry's law:

(i) To increase the solubility of $CO_2$ in soft drinks and soda water, the bottle is sealed under high pressure.

(ii) To minimise the painful effects of decompression sickness in deep sea divers, oxygen diluted with less soluble helium gas is used as breathing gas.

19. Define the term molar conductivity. How is it related to conductivity of the related solution?

Molar conductivity of a solution at a dilution V is the conductance of all the ions produced from one mole of the electrolyte dissolved in V cm3 of the solution when the electrodes are one cm apart and the area of the electrodes is so large that the whole solution is contained between them.

$$\Lambda_m = kV$$

It units is S cm$^2$ mol$^{-1}$

$$\Lambda_m = k \, X \frac{1000}{M} \text{ in CGS units}$$

$\Lambda_m = k \times 10^{-3}$ M in SI units

where k is the conductivity, M is the molar concentration and $\Lambda_m$ is molar conductivity.

20. Calculate the emf of following cell at 298 K :

$$Mg_{(s)} \mid Mg^{2+}(0.1 \text{ M}) \parallel Cu^{2+}(0.01 \text{ M}) \mid Cu_{(s)}$$
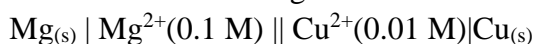
[Given: E°cell = + 2.71 V, 1 F = 96500 C mol$^{-1}$]

The cell reaction can be represented as :

$$Mg_{(s)} + Cu^{2+}_{(aq)} \rightarrow Mg^{2+}_{(aq)} + Cu_{(s)}$$
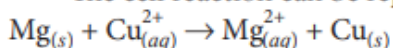
Given: $E^{o}_{cell} = +2.71$ V, $T = 298$ K

According to the Nernst equation :

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0591}{n} \log \frac{[Mg^{2+}_{(aq)}]}{[Cu^{2+}_{(aq)}]}$$

$$= 2.71 - \frac{0.0591}{2} \log \frac{0.1}{0.01} = 2.6805 \text{ V}$$

21. Account for the following:

(i) $H_2S$ has lower boiling point than $H_2O$.

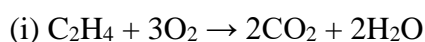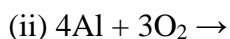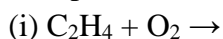(ii) Reducing character decreases from $SO_2$ to $TeO_2$.

(i)                    $H_2O$    $H_2S$
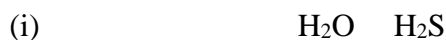
Boiling point 373 K > 213 K

The abnormally high boiling point of $H_2O$ is due to strong intermolecular H-bonding. Since, all other elements have much lower electronegativity than oxygen, they do not undergo H-bonding.
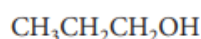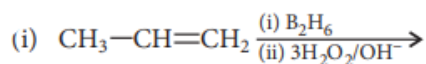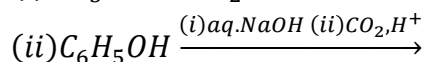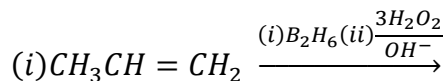
(ii) The +6 oxidation state of S is more stable than +4 therefore, $SO_2$ acts as a reducing agent. Further, since the stability of +6 oxidation decreases from S to Te therefore, the reducing character of the dioxides decreases while their oxidising character increases. Thus, $TeO_2$ acts as an oxidising agent
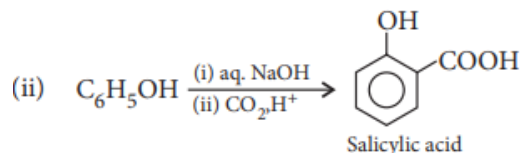
(Or)

Complete the following reactions:

(i) $C_2H_4 + O_2 \rightarrow$

(ii) $4Al + 3O_2 \rightarrow$

(i) $C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$

(ii) $4Al + 3O_2 \rightarrow 2Al_2O_3$

22. Write the main product(s) in each of the following reactions:

$(i) CH_3CH = CH_2 \xrightarrow{(i)B_2H_6 (ii)\frac{3H_2O_2}{OH^-}}$

$(ii) C_6H_5OH \xrightarrow{(i)aq.NaOH\ (ii)CO_2,H^+}$

(i) $CH_3-CH=CH_2 \xrightarrow[\text{(ii) 3H}_2\text{O}_2/\text{OH}^-]{\text{(i) B}_2\text{H}_6}$

$CH_3CH_2CH_2OH$

Propanol

(ii) $C_6H_5OH \xrightarrow[\text{(ii) CO}_2,\text{H}^+]{\text{(i) aq. NaOH}}$ 
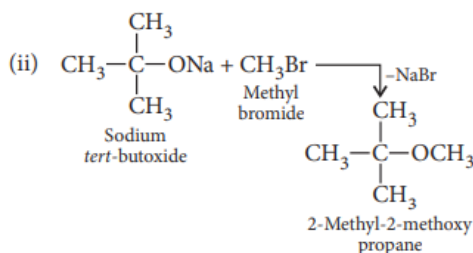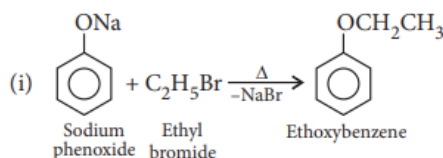
OH
—COOH

Salicylic acid

(Or)

Name the reagents and write the chemical equations for the preparation of the following compounds by Williamson's synthesis:
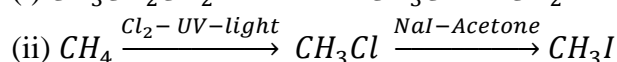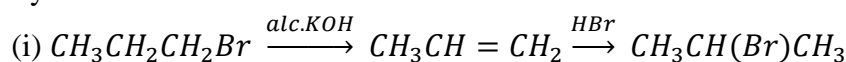
(i) Ethoxybenzene    (ii) 2-Methyl-2-methoxypropane

(i)
ONa
+ $C_2H_5Br \xrightarrow[-\text{NaBr}]{\Delta}$
OCH$_2$CH$_3$

Sodium    Ethyl        Ethoxybenzene
phenoxide  bromide

(ii) $CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-ONa + CH_3Br$

Sodium
tert-butoxide

Methyl
bromide

$\xrightarrow{-NaBr}$

$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OCH_3$

2-Methyl-2-methoxy
propane

23. How will you synthesise?
    (i) Isopropyl bromide from n-propyl bromide.
    (ii) Methyl iodide from methane.

    (i) $CH_3CH_2CH_2Br \xrightarrow{alc.KOH} CH_3CH = CH_2 \xrightarrow{HBr} CH_3CH(Br)CH_3$

    (ii) $CH_4 \xrightarrow{Cl_2-UV-light} CH_3Cl \xrightarrow{NaI-Acetone} CH_3I$
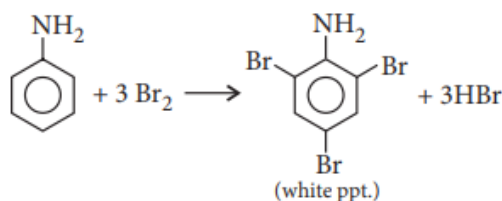
24. Give one chemical test each to distinguish between the following pairs of compounds:
    (i) Ethylamine and aniline    (ii) Aniline and N-methylaniline

        (i) Aniline gives white or brown precipitate with bromine water. Ethylamine does not react with bromine water.

NH$_2$
+ 3 Br$_2 \longrightarrow$
NH$_2$
Br—⬡—Br
Br
(white ppt.)
+ 3HBr

        (ii) Aniline gives carbylamine test, i.e., on treatment with alc. KOH and chloroform followed by heating it gives offensive odour of phenylisocyanide but N-methylaniline being secondary amine, does not show this test.

25. Explain the following observations:

(i) Among the divalent cations in the -rst series of transition elements, manganese exhibits the maximum paramagnetic.

(ii) $Cu^+$ ion is not known in aqueous solutions.

(i) it is due to presence of maximum number of unpaired electrons in $Mn^{2+}$ in ($3d^5$).

(ii) In aqueous solutions, $Cu^+$ undergoes disproportionation to form a more stable $Cu^{2+}$ ion.

$$2Cu^+_{(aq)} \rightarrow Cu^{2+}(aq) + Cu(s)$$
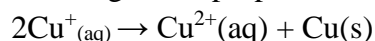
$Cu^{2+}$ in aqueous solutions is more stable than $Cu^+$ ion because hydration enthalpy of $Cu^{2+}$ is higher than that of $Cu^+$. It compensates the second ionisation enthalpy of Cu involved in the formation of $Cu^{2+}$ ions

## SECTION C

26. Account the following:

a. Calculate the temperature at which a solution containing 54 g of glucose, $(C_6H_{12}O_6)$, in 250 g of water will freeze. ($K_f$ for water = 1.86 K mol$^{-1}$ kg)

b. Define the following term: Osmotic pressure

$$M_2 \text{ (glucose, } C_6H_{12}O_6) = 180 \text{ g mol}^{-1}$$
$$w_2 = 54 \text{ g}, W_1 = 250 \text{ g}, K_f = 1.86 \text{ K kg mol}^{-1}$$
$$\Delta T_f = \frac{K_f \times W_2 \times 1000}{M_2 \times W_1}$$
$$= \frac{1.86 \times 54 \times 1000}{180 \times 250} = 2.23 \text{ K}$$

Freezing point of solution, $T_f = T_f^\circ - \Delta T_f$
$$= 273 \text{ K} - 2.23 \text{ K} = 270.77 \text{ K}$$

Osmotic pressure is the extra pressure which is applied on the solution to just prevent the low of solvent into the solution through a semi-permeable membrane.

27. Give reasons for the following:

(i) The third ionization enthalpy of manganese (Z = 25) is exceptionally high.

(ii) The variation in oxidation states of transition metals is of dierent type from that of the non-transition metals.

(iii) Europium (II) more stable than cerium (II)?

(i) Third ionization enthalpy of Mn is very high because the third electron has to be removed from the stable half-filled 3d-orbitals [$Mn^{2+}$ (Z = 25) = $3d^5$].

(ii) The variability in oxidation states of transition metals is due to the incomplete filling of d-orbitals. Their oxidation states differ from each other by unity. For example, $Fe^{3+}$ and $Fe^{2+}$, $Cu^{2+}$ and $Cu^+$, etc.

In case of non-transition elements, the oxidation states normally differ by units of two. For example, $Pb^{2+}$ and $Pb^{4+}$, $Sn^{2+}$ and $Sn^{4+}$, etc. It arises due to expansion of octet and inert pair effect.

(iii) Europium (II) has electronic configuration [Xe]$4f^7 5d^0$ while cerium (II) has electronic configuration [Xe] $4f^1 5d^1$. In $Eu^{2+}$, 4f subshell is half-filled and 5d-subshell is empty. Since half-filled and completely filled electronic configurations are more stable, $Eu^{2+}$ ions is more stable than $Ce^{2+}$ in which neither 4f subshell nor 5d subshell is half-filled or completely -filled.

28. Explain the following situations:

(i) $XeF_2$ has a straight linear structure and not a bent angular structure.

(ii) Write balanced chemical equations for the following reaction: XeF6 is hydrolysed
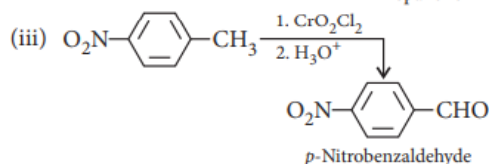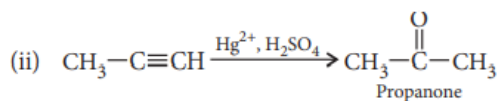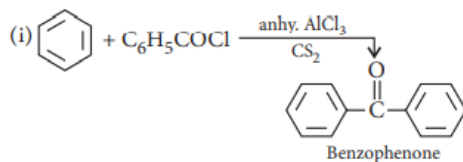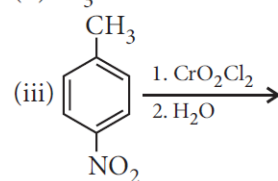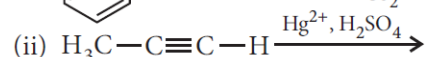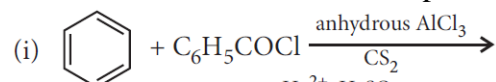
(iii) Why is ICl more reactive than $I_2$?

      (i) Since there are two Xe—F covalent bonds and three lone pairs in $XeF_2$. According to VSEPR theory, the shape of $XeF_2$ is linear.

      (ii) $XeF_6 + H_2O \rightarrow XeOF_4 + 2HF$

      (iii) Interhalogen compounds are more reactive than halogens (except flourine) because X — X′ bond (I—Cl bond) in interhalogens is weaker than X—X bond (I—I bond) in halogens except F — F bond. In other words, I —Cl bond is weaker than I — I bond. at's why ICl is more reactive than $I_2$.

29. Write the structures of the main products of the following reactions:

(i)  $+ C_6H_5COCl \xrightarrow[\text{CS}_2]{\text{anhydrous AlCl}_3}$

(ii) $H_3C-C\equiv C-H \xrightarrow{Hg^{2+},\ H_2SO_4}$

(iii)  $\xrightarrow[\text{2. H}_2\text{O}]{\text{1. CrO}_2\text{Cl}_2}$

(i)  $+ C_6H_5COCl \xrightarrow[\text{CS}_2]{\text{anhy. AlCl}_3}$


Benzophenone

(ii) $CH_3-C\equiv CH \xrightarrow{Hg^{2+},\ H_2SO_4} CH_3-\overset{\overset{\displaystyle O}{||}}{C}-CH_3$
Propanone

(iii) $O_2N-\!\!\bigcirc\!\!-CH_3 \xrightarrow[\text{2. H}_3\text{O}^+]{\text{1. CrO}_2\text{Cl}_2}$

$O_2N-\!\!\bigcirc\!\!-CHO$
p-Nitrobenzaldehyde

30. Answer the following:

(a) Give two differences between globular and fibrous proteins.

(b) What change occurs in the nature of egg protein on boiling?

      (a) Characteristic differences between globular and fibrous proteins can be given as :

      Globular proteins

            These are cross-linked proteins and are condensation product of acidic and basic amino acids.

            These are soluble in water, mineral acids and bases.

            These are stabilised by internal hydrogen bonding. e.g., egg albumin, enzymes.

      Fibrous proteins

            These are linear condensation polymer.

            These are insoluble in water but soluble in strong acids and bases.

            These proteins have three-dimensional folded structure.

            These are linear polymers held together by intermolecular hydrogen bonds. e.g., hair, silk.

      (b) Protein is denatured and its biological activity is lost.

31. The elements of 3d transition series are given as Sc Ti V Cr Mn Fe Co Ni Cu Zn

Answer the following:

(i) Write the element which shows maximum number of oxidation states. Given reason.

(ii) Which element has the highest melting point?

(iii) Which element shows only +3 oxidation state?

(iv) Which element is a strong oxidising agent in +3 oxidation state and why?

(v) In general, the atomic radii of transition elements decrease with atomic number in a given series.

(i) Mn shows maximum no. of oxidation states from +2 to +7 because Mn has maximum number of unpaired electrons in 3d sub-shell.

(ii) Cr has maximum melting point, because it has 6 unpaired electrons in the valence shell, hence it has strong interatomic interaction.

(iii) Sc shows only +3 oxidation state because after losing 3 electrons, it has noble gas electronic configuration.

(iv) Mn is strong oxidising agent in +3 oxidation state because change of $Mn^{3+}$ to $Mn^{2+}$ give stable half-filled (d5) electronic configuration, $E°(Mn^{3+}/Mn^{2+}) = 1.5$ V.

(v) The atomic radii of transition elements decrease with the increase in atomic number as the effective nuclear charge increases because shielding effect of d-electron is small.

(Or)

Account for the following:

(i) Zn is not considered as a transition element.

(ii) Transition metals show variable oxidation states.

(iii) Many of the transition elements are known to form interstitial compounds.

(iv) With the same d-orbital configuration ($d^4$) $Cr^{2+}$ is a reducing agent while $Mn^{3+}$ is an oxidising agent.

(v) Cobalt (II) is very stable in aqueous solutions but gets easily oxidised in the presence of strong ligands.

(i) In the electronic configuration of Zn, Cd and Hg the d-orbitals are completely -filled in the ground state as well as in their common oxidation state. So, they are not regarded as transition metals.

(ii) Transition elements can use their ns and (n – 1) d orbital electrons for bond formation therefore, they show variable oxidation states.

For example - Sc has $4s^2 3d^1$ electronic configuration.

It utilizes two electrons from its ns subshell then its oxidation state = +2. When it utilizes both the electrons then its oxidation state = +3.

(iii) Transition metals form a large number of interstitial compounds because small atoms of certain non-metallic elements (H, B, C, N, etc.) get trapped in voids or vacant spaces of lattices of the transition metals. As a result of filling up of the interstitial spaces such interstitial compounds are hard and rigid.

(iv) $E°$ values for the $Cr^{3+}/Cr^{2+}$ and $Mn^{3+}/Mn^{2+}$ couples are

$Cr^{3+}_{(aq)} + e^- \rightarrow Cr^{2+}_{(aq)}$; $E° = -0.41$ V  $Mn^{3+}_{(aq)} + e- \rightarrow Mn^{2+}_{(aq)}$ ; $E° = +1.551$ V

These $E°$ values indicate that $Cr^{2+}$ is strongly reducing while $Mn^{3+}$ is strongly oxidising.

(v) The tendency to form complexes is high for Co (III) as compared to Co (II). $Co^{2+}$ ions are very stable and are difficult to oxidise. $Co^{3+}$ ions are less stable and are reduced by water. In contrast many Co (II) complexes are readily oxidised to Co (III) complexes and Co (III) complexes are very stable, e.g.,

$[Co(NH_3)_6]^{2+}$(air) $\rightarrow [Co(NH_3)_6]^{3+}$

It is happens because the crystal field stabilisation energy of Co(III) with a $d^6$ ($t2g^6$) configuration is higher than for Co(II) with a $d^7$ ($t_2g^6 eg^1$) arrangement

32. Answer the following:
- (a) Hydrogen peroxide, $H_2O_{2(aq)}$ decomposes to $H_2O_{(l)}$ and $O_{2(g)}$ in a reaction that is first order in $H_2O_2$ and has a rate constant $k = 1.06 \times 10^{-3}$ min$^{-1}$.
  - (i) How long will it take for 15% of a sample of $H_2O_2$ to decompose?
  - (ii) How long will it take for 85% of the sample to decompose?
- (b) Define the half-life period of reaction
  - (a)

$$(i) \; t = \frac{2.303}{k} \log \frac{[A]_0}{[A]}$$

Given $k = 1.06 \times 10^{-3}$ min$^{-1}$, $\dfrac{[A]_0}{[A]} = \dfrac{100}{85}$

$$t = \frac{2.303}{1.06 \times 10^{-3} \, \text{min}^{-1}} \log \frac{100}{85}$$

$$t = \frac{2303}{1.06} [2 \log 10 - \log 85] \text{min}$$

$$t = \frac{2303}{1.06} [2 \times 1 - 1.9294] = \frac{2303 \times 0.0706}{1.06}$$

$$t = 153.39 \text{ min} = 153.4 \text{ min}.$$

(ii) Given $k = 1.06 \times 10^{-3}$ min$^{-1}$, $\dfrac{[A]_0}{[A]} = \dfrac{100}{15}$

$$t = \frac{2.303}{1.06 \times 10^{-3} \, \text{min}^{-1}}, \log \frac{100}{15}$$

$$= \frac{2303}{1.06} [2 \log 10 - \log 15] \text{min}$$

$$= \frac{2303}{1.06} [2 \times 1 - 1.1761] = \frac{2303 \times 0.8231}{1.06} \text{min} = 1788 \text{ min}$$

- (b) The time taken for half of the reaction to complete, i.e., the time in which the concentration of a reactant is reduced to half of its original value Is called half-life period of the reaction.

(Or)

- (c) For a chemical reaction R P, the variation in the concentration, ln [R] vs. time (s) plot is given as
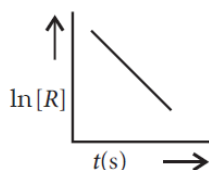


  - (i) Predict the order of the reaction.
  - (ii) What is the slope of the curve?
  - (iii) Write the unit of the rate constant for this reaction.
- (d) A first order decomposition reaction takes 40 minutes for 30% decomposition. Calculate its $t_{1/2}$ value.

  - (c) (i) The reaction is of 1st order.
  - (ii) For -first order reaction

$$\ln[R] = -kt + \ln [R]_0$$

comparing eqn. $y = m \times x + c$

we get a straight line with slope $= -k$ and intercept equal to $\ln[R]_0$.

  - (iii) Unit of rate constant for first order reaction

$$\frac{mol \; L^{-1}}{s} \; X \; \frac{1}{(mol \; L^{-1})^1} = s^{-1}$$
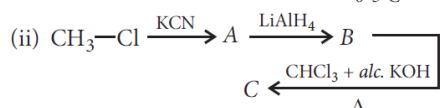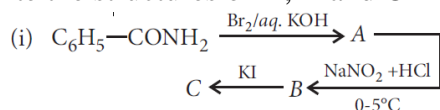
(d)

Let $a = 100$ $\therefore$ $x = 30\%$ of $100 = 30$

Using the formula,

$$t = \frac{2.303}{k}\log\frac{a}{a-x}$$

$$40 = \frac{2.303}{k}\log\frac{100}{100-30}$$

$$40 = \frac{2.303}{k}\log\frac{100}{70}$$

$$40 = \frac{2.303}{k}(\log 10 - \log 7)$$

$$40 = \frac{2.303}{k}(1 - 0.8451)$$

$$40 = \frac{2.303}{k}\times 0.1549 \Rightarrow k = \frac{0.357}{40} = 0.0089 \text{ min}^{-1}$$

$$\therefore \quad t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.0089} = 77.86 \text{ min.}$$

33. (a) Account for the following:

(i) Aniline does not undergo Friedel-Crafts reaction.

(ii) Aliphatic amines are stronger bases than aromatic amines.

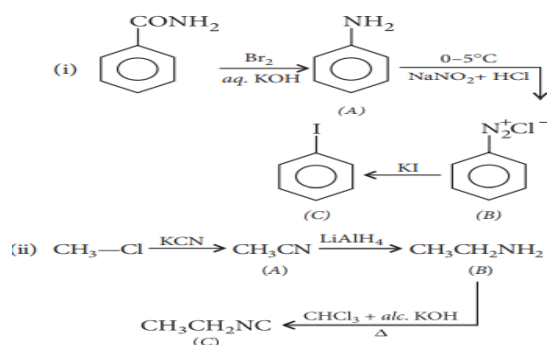(b) Write the structures of A, B and C in the following:

(i) $C_6H_5-CONH_2 \xrightarrow{Br_2/aq.\ KOH} A$

$C \xleftarrow{KI} B \xleftarrow[0\text{-}5°C]{NaNO_2 +HCl}$

(ii) $CH_3-Cl \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B$

$C \xleftarrow[\Delta]{CHCl_3 + alc.\ KOH}$

(a) (i) In Friedel - Crafts reaction, $AlCl_3$ is added as a catalyst which is a Lewis acid. It forms a salt with aniline due to which the nitrogen of aniline acquires positive charge. this positively charged nitrogen acts as a strong deactivating group, hence aniline does not undergo Friedel - Craft reaction.
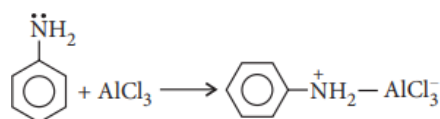


(ii) In aromatic amines, the lone pair of electrons present on nitrogen takes part in resonance and hence, not available for donation. However, in aliphatic amines, the lone pair is available for donation. -That's why aliphatic amines are more basic than aromatic amines.

(b)



(ii) $CH_3-Cl \xrightarrow{KCN} CH_3CN \xrightarrow{LiAlH_4} CH_3CH_2NH_2$
(A)        (B)

$CH_3CH_2NC \xleftarrow[\Delta]{CHCl_3 + alc.\ KOH}$
(C)

(Or)

(c) How do you convert the following:

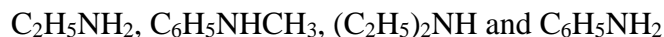(i) $C_6H_5CONH_2$ to $C_6H_5NH_2$

(ii) Aniline to phenol

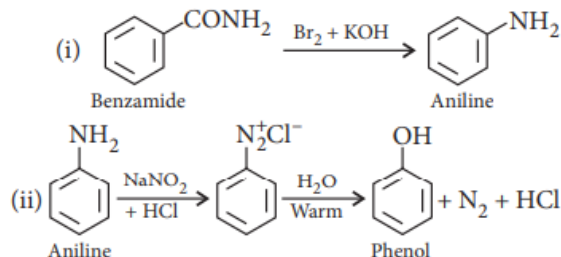(d) Give reasons for the following:

(i) Aniline is a weaker base than cyclohexyl amine.

(ii) It is difficult to prepare pure amines by ammonolysis of alkyl halides.

(iii) Arrange the following compounds in a decreasing order of pKb values:

$C_2H_5NH_2$, $C_6H_5NHCH_3$, $(C_2H_5)_2NH$ and $C_6H_5NH_2$

(c) convert the following:



(i) Benzamide $\xrightarrow{Br_2 + KOH}$ Aniline

(ii) Aniline $\xrightarrow[+ HCl]{NaNO_2}$ $\xrightarrow[Warm]{H_2O}$ Phenol $+ N_2 + HCl$

(d) (i) Aniline is weaker base than cyclohexylamine because of resonance. Due to electrometric effect, the lone pair on nitrogen is attracted by benzene ring. Hence, donor tendency of —NH$_2$ group decreases-ere is no resonance in cyclohexylamine. Electron repelling nature of cyclohexyl group further increases the donor property of NH$_2$ group. So, cyclohexylamine is a stronger base.



Aniline (Resonance structures)    Cyclohexylamine (No resonance)
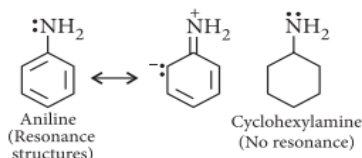
(ii) The ammonolysis of alkyl halides with ammonia is a nucleophilic substitution reaction in which ammonia acts as a nucleophile by donating the electron pair on nitrogen atom to form primary amine as the initial product. Now, the primary amine can act as a nucleophile and combine with alkyl halide (if available) to give secondary amine and the reaction continues in the same way to form tertiary amine and finally quaternary ammonium salt. -us, a mixture of products is formed and it is not possible to separate individual amines from the mixture.

$R-X \xrightarrow[-HX]{NH_2} R-NH_2 \xrightarrow[-HX]{R-X} R_2NH \xrightarrow[-HX]{R-X}$
$R_3N \xrightarrow{R-X} R_4N^+X^-$
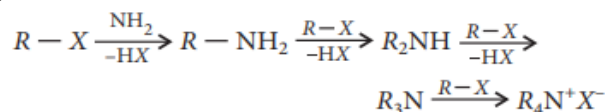
(iii) Stronger the base lower will be its pKb value hence, the decreasing order of pKb values:

$C_6H_5NH_2 > C_6H_5NHCH_3 > C_2H_5NH_2 > (C_2H_5)_2NH$