LIBERTY PAPER SET

STD. 12 : Chemistry

Full Solution

Time : 3 Hours **ASSIGNMENT PAPER 1**

Part A

1. (D) **2.** (A) **3.** (B) **4.** (C) **5.** (D) **6.** (A) **7.** (C) **8.** (D) **9.** (B) **10.** (C) **11.** (A) **12.** (C) **13.** (A) **14.** (B) **15.** (C) **16.** (A) **17.** (C) **18.** (A) **19.** (D) **20.** (B) **21.** (D) **22.** (A) **23.** (C) **24.** (B) **25.** (C) **26.** (D) **27.** (A) **28.** (A) **29.** (C) **30.** (B) **31.** (A) **32.** (D) **33.** (B) **34.** (D) **35.** (C) **36.** (A) **37.** (B) **38.** (A) **39.** (D) **40.** (C) **41.** (A) **42.** (B) **43.** (A) **44.** (D) **45.** (A) **46.** (C) **47.** (D) **48.** (A) **49.** (B) **50.** (C)

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Part B

Section A

➢ **Write the answer of the following questions : (Each carries 2 Mark)**

1.

- $$\text{Anode : } Zn(s) \rightarrow Zn^{+2} + 2e^{-}$$
  $$\text{Cathode : } MnO_2 + NH_4^{+} + e^{-} \rightarrow MnO(OH) + NH_3$$

2.

- For a first order reaction.

$$\log \frac{[R]_1}{[R]_2} = \frac{k(t_2 - t_1)}{2.303}$$

$$k = \frac{2.303}{t_2 - t_1} \log \frac{[R]_1}{[R]_2}$$

$$= \frac{2.303}{60\ \text{min} - 0\ \text{min}} \log \frac{1.24 \times 10^{-2}\ \text{mol L}^{-1}}{0.20 \times 10^{-2}\ \text{mol L}^{-1}}$$

$$= \frac{2.303}{60} \log 6.2\ \text{min}_{-1}$$

$$k = 0.0304\ \text{min}_{-1}$$

3.

- As we move along the lanthanoid series, the atomic number increases gradually by one. This means that the number of electrons and protons present in an atom also increases by one.
- As electrons are being added to the same shell, the effective nuclear charge increases.
- This happens because the increase in nuclear attraction due to the addition of proton is more pronounced than the increase in the interelectronic repulsions due to the addition of electron.
- Also, with the increase in atomic number, the number of electrons in the 4f orbital also increases. The 4f electrons have poor shielding effect.
- Therefore, the effective nuclear charge experienced by the outer electrons increases. Consequently, the attraction of the nucleus for the outermost electrons increases.
- This results in a steady decrease in the size of lanthanoids with the increase in the atomic number. This is termed as lanthanoid contraction.

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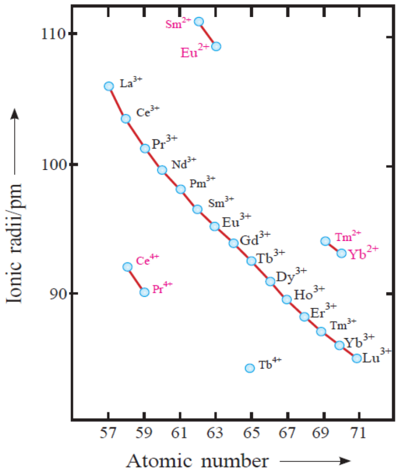

- Consequences of lanthanoid contraction
  - There is similarity in the properties of second and third transition series.
  - Separation of lanthanoids is possible due to lanthanoid contraction.
  - It is due to lanthanoid contraction that there is variation in the basic strength of lanthanoid hydroxides. (Basic strength decreases from $La(OH)_3$ to $Lu(OH)_3$.)

4.

- *"Transition metals are large in size and contain lots of interstitial sites. Transition elements can trap atoms of other elements (that have small atomic size), such as H, C, N, in the interstitial sites of their crystal lattices. The resulting compounds are called interstitial compounds."*
- They are usually non stoichiometric and are neither typically ionic nor covalent,
- For example, TiC, Mn_4N, Fe_3H, $VH_{0.56}$ and $TiH_{1.7}$, etc.
- These compounds are referred to as interstitial compounds.
- The principal physical and chemical characteristics of these compounds are as follows :
  - They have high melting points, higher than those of pure metals.
  - They are very hard, some borides approach diamond in hardness.
  - They retain metallic conductivity.
  - They are chemically inert.

5.

(1) In coordination compounds metal show two types of linkages (valences)- Primary and secondary.

(2) The primary valences are normally ionizable and are satisfied by negative ions.

(3) The secondary valences are non ionizable. These are satisfied by neutral molecules or negative ions. The secondary valence is equal to the coordination number and is fixed for a metal.

(4) The ions / groups bound by the secondary linkages to the metal have characteristic spatial arrangements corresponding to different coordination numbers.

- In modern formulations, such spatial arrangements are called coordination polyhedra.
- The species within the square bracket are called coordination entities or complexes and the ions outside the square bracket are called counter ions.
- Werner further postulated that octahedral, tetrahedral and square planar geometrical shapes are more common in coordination compounds of transition metals.
- Thus, $[Co(NH_3)_6]^{3+}$, $[CoCl(NH_3)_5]^{2+}$, and $[CoCl_2(NH_3)_4]^{+}$ are octahedral entities, while $[Ni(CO)_4]$ and $[PtCl_4]^{2-}$ are tetrahedral and square planar, respectively.

6.

- Solution :
- (i) Potassium trioxalatochromate (III)
- (ii) Dichloridobis (ethane-1, 2 diamine) cobalt(III) chloride

7.

- Finkelstein reaction :
  - Alkyl iodides are often prepared by the reaction of alkyl chlorides/ bromides with NaI in dry acetone.
  - This reaction is known as Finkelstein reaction.

    $R–X + NaI \rightarrow R–I + NaX$

    X = Cl, Br

    Example :

    (i) $CH_3 - Cl + NaI \rightarrow CH_3 - I + NaCl$

    (ii) $CH_3 - CH_2 - Br + NaI \rightarrow CH_3 - CH_2 - I + NaBr$
  - NaCl or NaBr thus formed is precipitated in dry acetone. It facilitates the forward reaction according to Le Chatelier's Principle.

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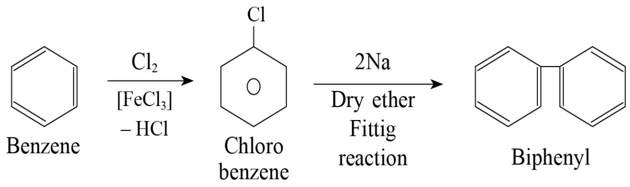
8.

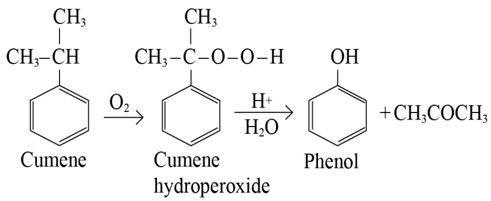
➥ Benzene to biphenyl :



9.

➥ From cumene :

➠ Phenol is manufactured from the hydrocarbon, cumene. Cumene (isopropylbenzene) is oxidised in the presence of air to cumene hydroperoxide. It is converted to phenol and acetone by treating it with dilute acid. Acetone, a by-product of this reaction, is also obtained in large quantities by this method.



10.

➥ Aldehydes are generally more reactive than ketones in nucleophilic addition reactions due to steric and electronic reasons. Sterically, the presence of two relatively large substituents in ketones hinders the approach of nucleophile to carbonyl carbon than in aldehydes having only one such substituent. Electronically, aldehydes are more reactive than ketones because two alkyl groups reduce the electrophilicity of the carbonyl more effectively than in former.

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11.

➥ Open chain structure of glucose has free aldehyde (–CHO) group even though following reactions and facts could not be explained by this structure.

(1) Despite having the aldehyde group, glucose does not give Schiff's test and its does not form the hydrogensulphate addition product with $NaHSO_3$.

(2) The pentaacetate of glucose does not react with hydroxyl amine indicating the absence of free –CHO group.

(3) Glucose is found to exist in two different crystalline forms which are named as α and β. The α form of glucose (m.p 419K) is obtained by crystallization from concentrated solution of glucose at 303 K while the β-form (m.p 423K) is obtained by crystallization from hot and saturated aqueous solution at 371 K.

12.

➥ Proteins can be classified into two types on the basis of their molecular shape.

➥ (a) Fibrous protein compounds :

➠ When the polypeptide chains run parallel and are held together by hydrogen and disulphide bonds, then fibre-like structure is formed. Such proteins are generally insoluble in water. Some common example are keratin (present in hair, wool, silk) and myosin (present in muscles) etc.

➥ (b) Globular protein compounds :

➠ This structures results when the chains of polypeptides coil around to give a spherical shape. These are usually soluble in water. Insulin and albumins are the common examples of globular proteins.

Section B

➢ **Write the answer of the following questions : (Each carries 3 Mark)**

13.

- Let us consider a binary solution of two volatile liquids and denote the two components as 1 and 2.
- When taken in a closed vessel, both the components would evaporate and eventually an equilibrium would be established between vapour phase and the liquid phase.
- Suppose p_1 and p_2 partial vapour pressure of component 1 and 2 and x_1 and x_2 are Mole-Fraction of component 1 and 2 respectively.
- The French chemist, Francois Marte Raoult gave the quantitative relationship between them. The relationship is known as the Raoult's law
- *"For a solution of volatile liquids the partial vapour pressure of each component of the solution is directly proportional to its mole fraction present in solution."*
- For component – 1.

  $p_1 \propto x_1$

  $\therefore p_1 = p_1^o \, . \, x_1$

  where p_1^o is the vapour pressure of pure component 1
- Similarly for component – 2

  $p_2 \propto x_2$

  $\therefore p_2 = p_2^o \, . \, x_2$

  where p_2^o is the vapour pressure of pure component 2
- According to Dalton's law of partial pressures,
- Total pressure over the solution phase in the container will be the sum of the partial pressures of the components of the solution

  $p_{\text{Total}} = p_1 + p_2$

  $= p_1^o \, . \, x_1 + p_2^o \, . \, x_2$

  $= p_1^o \, (1 - x_2) + p_2^o \, . \, x_2$

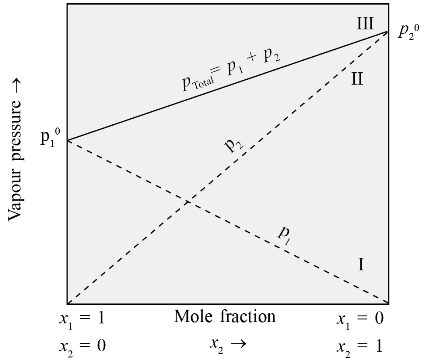
  $= p_1^o - p_1^o \, . \, x_2 + p_2^o \, . \, x_2$

  $p_{\text{Total}} = p_1^o + x_2(p_2^o - p_1^o)$
- Following conclusions can be drawn from above equation

  (i) Total vapour pressure over the solution can be related to the mole fraction of any one component.

  (ii) Total vapour pressure over the solution varies linearly with the mole fraction of component 2.

  (iii) Depending on the vapour pressures of the pure components 1 and 2, total vapour pressure over the solution decreases or increases with the increase of the mole fraction of component 1.
- A plot of p_1 or p_2 versus the mole fractions x_1 and x_2 for a solution gives a linear plot as shown in Fig.



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- These lines (I and II) pass through the points for which x_1 and x_2 are equal to unity.
- Similarly the plot (line III) of p_{total} versus x_2 is also linear Fig.
- The minimum value of p_{Total} is p_1^o and the maximum value is p_2^o, assuming that component –1 is less volatile than component –2 ($p_1^o < p_2^o$)
- The composition of vapour phase in equilibrium with the solution is determined by the partial pressures of the components.
- If y_1 and y_2 are the mole-fraction of the component 1 and 2 respectively in vapour phase then,
- Using Dalton’s Law of partial pressure

$$p_1 = y_1 \cdot p_{Total}$$

$$p_2 = y_2 \cdot p_{Total}$$

- In general

$$p_i = y_i \, p_{Total}$$

14.

- Pt(s) | $Br_2(l)$ | Br^-(0.010M) | | H^+(0.030M) | $H_2(g)$(1bar) | Pt(s)

Cell reaction : $2Br^- + 2H^+ \rightarrow Br_2 + H_2$ (n = 2)

$$E^0_{cell} = E^0_{H^+/\frac{1}{2}H_2} - E^0_{\frac{1}{2}Br_2/Br^-}$$

$$= 0 - 1.09$$

$$= -1.09 \text{ V}$$

$$E_{cell} = E^0_{cell} - \frac{0.059}{n} \log \frac{1}{[Br^-]^2[H^+]^2}$$

$$= -1.09 \times \frac{0.059}{2} \log \frac{1}{(0.01)^2 \times (0.03)^2}$$

$$= -1.09 - \frac{0.059}{2} \log (1.111 \times 10^7)$$

$$= -1.09 \times \frac{0.059}{2} \times 7.0457$$

$$= -1.09 \times 0.208$$

$$E_{cell} = -1.298 \text{ V}$$

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15.

- $$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

$$\log \frac{0.07}{0.02} = \left(\frac{E_a}{2.303 \times 8.314 \text{ JK}^{-1} \text{ mol}^{-1}}\right)\left[\frac{700 - 500}{700 \times 500}\right]$$

$$0.544 = E_a \times 5.714 \times 10^{-4}/19.15$$

$$E_a = 0.544 \times 19.15/5.714 \times 10^{-4} = 18230.8 \text{ J/mol}$$

$$\text{Since } k = A\,e^{-\frac{E_a}{RT}}$$

$$0.02 = A\,e^{-\frac{18230.8}{8.314}} \times 500$$

$$A = 0.2/0.012 = 1.61$$

16.

- Dichromates are generally prepared from chromate. which in turn are obtained by the fusion of chromite ore ($FeCr_2O_4$) with sodium or potassium carbonate in free access of air.
- The reaction with sodium carbonate occurs as follows

$$4\,FeCr_2O_4 + 8\,Na_2CO_3 + 7\,O_2 \rightarrow 8\,Na_2CrO_4 + 2\,Fe_2O_3 + 8\,CO_2$$

- The yellow solution of sodium chromate is filtered and acidified with sulphuric acid to give a solution from which orange sodium dichromate, $Na_2Cr_2O_7.\ 2H_2O$ can be crystallised.

$$2Na_2CrO_4 + 2\,H^+ \rightarrow Na_2Cr_2O_7 + 2\,Na^+ + H_2O$$

- Sodium dichromate is more soluble than potassium dichromate. The latter is therefore, prepared by treating the solution of sodium dichromate with potassium chloride.

$$Na_2Cr_2O_7 + 2\,KCl \rightarrow K_2Cr_2O_7 + 2\,NaCl$$

- Orange crystals of potassium dichromate crystallise out.
- The chromates and dichromates are interconvertible in aqueous solution depending upon pH of the solution.

$$2\,CrO_4^{2-} + 2H^+ \rightarrow Cr_2O_7^{2-} + H_2O$$

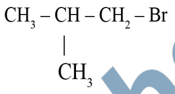
$$Cr_2O_7^{2-} + 2\,OH^- \rightarrow 2\,CrO_4^{2-} + H_2O$$

17.

- There are two primary alkyl halides having the formula, C_4H_9Br. They are *n*- bulyl bromide and isobutyl bromide.

$$CH_3-CH_2-CH_2-CH_2-Br$$

n - Butyl bromide



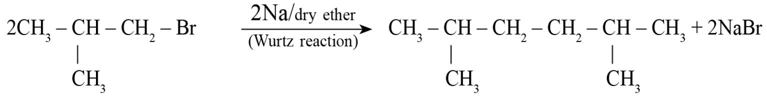
$$\underset{\substack{|\\ CH_3}}{CH_3-CH}-CH_2-Br$$

Isobutyl bromide

- Therefore, compound (a) is either n-butyl bromide or isobutyl bromide.
- Now, compound (a) reacts with Na metal to give compound (b) of molecular formula, C_8H_{18} which is different from the compound formed when n-butyl bromide reacts with Na metal. Hence, compound (a) must be isobutyl bromide.

$$2CH_3CH_2CH_2CH_2Br \xrightarrow[\text{(Wurtz reaction)}]{\text{2Na/dry ether}} CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3 + 2NaBr$$

n-Butly bromide *n*-Octane

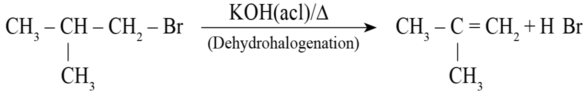


$$2\underset{\substack{|\\ CH_3}}{CH_3-CH}-CH_2-Br \xrightarrow[\text{(Wurtz reaction)}]{\text{2Na/dry ether}} \underset{\substack{|\\ CH_3}}{CH_3-CH}-CH_2-CH_2-\underset{\substack{|\\ CH_3}}{CH}-CH_3 + 2NaBr$$

Isobutyl bromide 2,5-Dimethylhexane

(a) (d)

- Thus, compound (d) is 2, 5-dimethylhexane.
- It is given that compound (a) reacts with alcoholic KOH to give compound (b). Hence, compound (b) is 2-Methylpropane.



$$\underset{\substack{|\\ CH_3}}{CH_3-CH}-CH_2-Br \xrightarrow[\text{(Dehydrohalogenation)}]{\text{KOH(acl)}/\Delta} \underset{\substack{|\\ CH_3}}{CH_3-C}=CH_2 + H\ Br$$

Isobutyl bromide 2-Methylpropene

(a) (b)

- Also, compound (b) reacts with HBr to give compound (c) which is an isomer of (a).
- Hence, compound (c) is 2-bromo-2-methylpropane.

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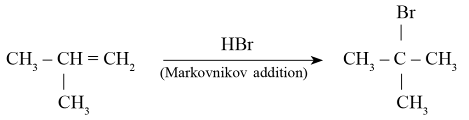


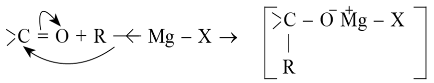
$$CH_3-\underset{\substack{|\\CH_3}}{C}H=CH_2 \xrightarrow[\text{(Markovnikov addition)}]{HBr} CH_3-\overset{\substack{Br\\|}}{\underset{\substack{|\\CH_3}}{C}}-CH_3$$

2-Methylpropene
(b)

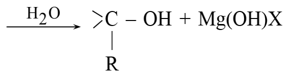
2-Bromo-2-Methylpropane
(c)
(as isomer of (a))

18.

- Alcohols are produced by the reaction of Grignard reagents with aldehydes and ketones.
- The first step of the reaction is the nucleophilic addition of Grignard reagent to the carbonyl group to form an adduct. Hydrolysis of the adduct yields an alcohol.



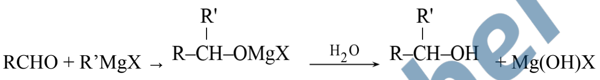
Adduct



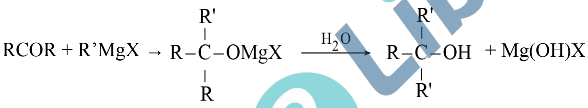
$$\xrightarrow{H_2O} \underset{\substack{|\\R}}{>C}-OH+Mg(OH)X$$

- The overall reactions using different aldehydes and ketones are as follows :

$$HCHO+RMgX \rightarrow RCH_2OMgX \xrightarrow{H_2O} RCH_2OH+Mg(OH)X$$



$$RCHO+R'MgX \rightarrow R-\overset{\substack{R'\\|}}{C}H-OMgX \xrightarrow{H_2O} R-\overset{\substack{R'\\|}}{C}H-OH+Mg(OH)X$$

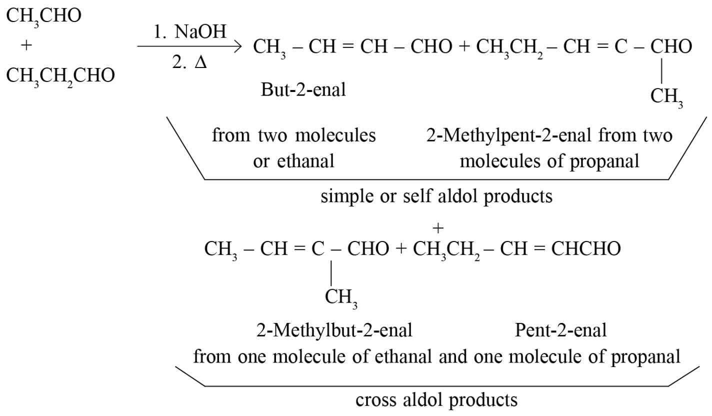


$$RCOR+R'MgX \rightarrow R-\overset{\substack{R'\\|}}{\underset{\substack{|\\R}}{C}}-OMgX \xrightarrow{H_2O} R-\overset{\substack{R'\\|}}{\underset{\substack{|\\R'}}{C}}-OH+Mg(OH)X$$

- You will notice that the reaction produces a primary alcohol with methanal, a secondary alcohol with other aldehydes and tertiary alcohol with ketones.

19.

- Cross aldol condensation : *"When aldol condensation is carried out between two different aldehydes and / or ketones, it is called cross aldol condensation."* If both of them contain α-hydrogen atoms, it gives a mixture of four products. This is illustrated below by aldol reaction of a mixture of ethanal and propanal.



$$\begin{matrix}CH_3CHO\\+\\CH_3CH_2CHO\end{matrix} \xrightarrow[2.\ \Delta]{1.\ NaOH} CH_3-CH=CH-CHO+CH_3CH_2-CH=\underset{\substack{|\\CH_3}}{C}-CHO$$

But-2-enal from two molecules or ethanal

2-Methylpent-2-enal from two molecules of propanal

simple or self aldol products

$$+\ CH_3-CH=\underset{\substack{|\\CH_3}}{C}-CHO+CH_3CH_2-CH=CHCHO$$

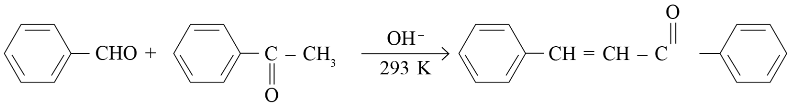
2-Methylbut-2-enal

Pent-2-enal

from one molecule of ethanal and one molecule of propanal

cross aldol products

- Ketones can also be used as one component in the cross aldol reactions.

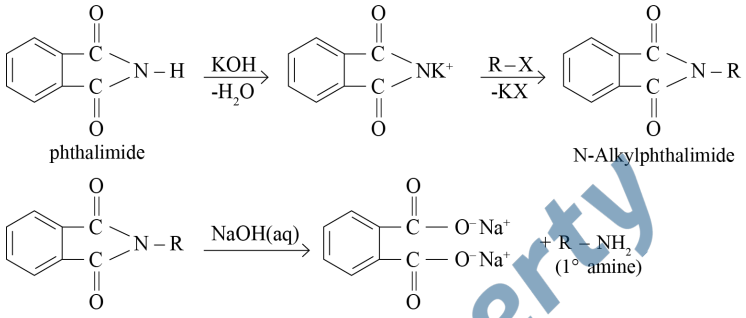


Benzaldehyde Acetophenone

1, 3-Diphenylprop-2-en-1-one
(Benzalacetophenone)
(Major product)

20.

- Gabriel synthesis is used for the preparation of primary amines. Phthalimide on treatment with ethanolic potassium hydroxide forms potassium salt of phthalimide which on heating with alkyl halide followed by alkaline hydrolysis produces the corresponding primary amine. Aromatic primary amines can not be prepared by this method because aryl halides do not undergo nucleophilic substitution with the anion formed by phthalimide.



21.

- (i) Primary aliphatic amines react with nitrous acid to form aliphatic diazonium salts, which are unstable and quantitatively liberate nitrogen gas along with alcohols. Quantitative evolution of nitrogen is used in estimation of amino acids and proteins.

$$R-NH_2 + HNO_2 \xrightarrow{NaNO_2\ +\ HCl} [R-N_2^+Cl^-] \xrightarrow{H_2O} ROH + N_2 + HCl$$

- (ii) Aromatic amines react with nitrous acid at low temperatures to form diazonium salts.
  - A very important class of compounds used for synthesis of a variety of aromatic compounds.

$$\underset{\text{Aniline}}{C_6H_5-NH_2} \xrightarrow[273-278\ K]{NaNO_2\ +\ 2HCl} \underset{\text{Benzenediazonium Chloride}}{C_6H_5-N^+_2Cl^-} + NaCl + 2H_2O$$

Section C

➢ **Write the answer of the following questions : (Each carries 4 Mark)**

22.

- $w_2 = 2\ g,\ K_f = 4.9\ K\ kg\ mol^{-1}$

$w_1 = 50\ g,\ \Delta Tf = 1.62\ K$

$M_2 = 122\ g\ mol^{-1}$

- $$\Delta T_f = i\frac{K_f \times w_2 \times 1000}{M_2 \times w_1}$$

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- $$\therefore\ i = \frac{\Delta T_f \times M_2 \times w_1}{K_f \times w_2 \times 1000}$$

$$= \frac{1.62 \times 122 \times 25}{4.9 \times 2 \times 1000} = 0.504$$

- Depression Constant $\%x = (1-i)\ \frac{n}{n-1} \times 100$

$$n = 2$$

- $$\therefore\ \%x = (1 - 0.504) \times \frac{2}{2-1} \times 100$$

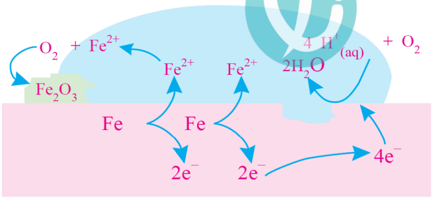
$$\%x = 99.2\ \%$$

- Therefore, –100% association of banzoic acid in bezone.

23.

- Prevention of corrosion is of prime importance.
- One of the simplest methods of preventing corrosion is to prevent the surface of the metallic object to come in contact with atmosphere.
- This can be done by covering the surface with paint or by some chemicals (e.g. bisphenol) Another simple method is to cover the surface by other metals (Sn, Zn, etc.) that are inert or react to save the object.
- An electrochemical method is to provide a sacrificial electrode of another metal (like Mg, Zn, etc.) which corrodes itselt but saves the object.
- In corrosion, a metal is oxidised by loss of electrons to oxygen and informal of oxides.
- Corrosion of iron (commonly known as rusting) occurs in presence of water and air.
- At a particular spot of an object made of iron, oxidation takes place and that spot behaves as anode and we can write the reaction.

Anode : $2Fe(s) \rightarrow 2Fe^{2+} + 4e^-$



Oxidation : $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$

Reduction : $O_2(g) + 4H^-(aq) + 4e^- \rightarrow 2H_2O(l)$

Atmospheric oxidation :

$$2Fe^{2+}(aq) + 2H_2O(l) + \frac{1}{2} O_2(g) \rightarrow Fe_2O_3(s) + 4H^+(aq)$$

- Electrons released at anodic spot move through the metal and go to another spot on the metal, where they reduce oxygen in presence of H^+ (which is believed to be available from H_2CO_3 formed due to dissolution of carbon dioxide from air into water.

Cathode : $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$

$E^6_{H+ \mid O2 \mid H2O} = 1.23$ V

The overall reaction being :

$2Fe(s) + O_2(g) + 4H^+(aq) \rightarrow 2Fe^{2+}(aq) + 2H_2O(l)$

$E^6_{(cell)} = 1.67V$

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- The ferrous ions are further oxidised by atmosphere oxygen to ferric ions which come out as rust in the form of hydrated ferric oxide ($Fe_2O_3 . x H_2O$) and with further production of hydrogen ions.

24.

- *"First order reaction means that the rate of reaction is proportional to the first power of the concentration of the reactant R."*
- For example, consider the following reaction

  $R \rightarrow P$

- Rate of reaction for this reaction can be expressed as

  $$\text{Rate} = -\frac{d[R]}{dt} = k[R]$$

  $$\text{Or } \frac{d[R]}{[R]} = -k\,dt$$

- Integrating this equation, we get

  $\ln [R] = -kt + I$ ... ... Eq. (1)

  where, I is the constant of integration and its value can be determined easily.

- When $t = 0$, $R = [R]_0$, where $[R]_0$ is the initial concentration of the reactant.
- Therefore, equation (1) can be written as

  $\ln [R]_0 = -k \times 0 + I$

  $\ln [R]_0 = I$

- Substituting the value of I in equation (1)

  $\ln [R] = -kt + \ln [R]_0$ ... ... Eq. (2)

- Rearranging this equation

  $$\ln \frac{[R]}{[R]_0} = -kt$$

  $$\text{or } k = \frac{1}{t} \ln \frac{[R]_0}{[R]} \quad \text{... ... Eq. (3)}$$

- At time t_1 from equation (1)

  $\ln [R]_1 = -kt_1 + \ln [R]_0$ ... ... Eq. (4)

  At time t_2

  $\ln [R]_2 = -kt_2 + \ln [R]_0$ ... ... Eq. (5)

  where, $[R]_1$ and $[R]_2$ are the concentration of the reactants at time t_1 and t_2 respectively.

- Subtracting Eq. (5) from (4)

  $\ln [R]_1 - \ln [R]_2 = -kt_1 - (-kt_2)$

  $$\ln \frac{[R]_1}{[R]_2} = k(t_2 - t_1)$$

  $$k = \frac{1}{(t_2 - t_1)} \ln \frac{[R]_1}{[R]_2} \quad \text{... ... Eq. (6)}$$

- So, equation (2) can also be written as

  $$\ln \frac{[R]}{[R]_0} = -kt$$

  Taking antilog of both the side

  $[R] = [R]_0 e^{-kt}$ ... ... Eq. (7)

- Comparing equation (2) with $y = mx + c$, if we plot $\ln [R]$ against t, we get a straight line with slope = – k and intercept equal to $\ln [R]_0$

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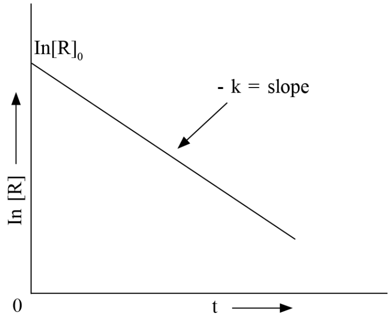


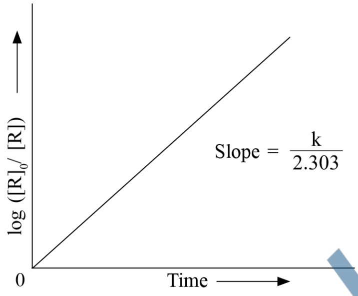
- ➥ The first order rate equation (3) can also be written in the form

$$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]} \quad \text{... ... Eq. (8)}$$

$$\text{or } \log \frac{[R]_0}{[R]} = \frac{kt}{2.303}$$

- ➥ If we plot a graph between $\log \frac{[R]_0}{[R]}$ vs t,

the slope = $\frac{k}{2.303}$



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- ➥ Half-life of a reaction : *"The time in which the concentration of a reactant is reduced to one half of its initial concentration is called half-life* $\left(t_{\frac{1}{2}}\right)$ *of a reaction."*
- ➥ Half-life for zero order reaction :
- ➥ For a zero order reaction, rate constant is given by following equation
- ➥ $k = \frac{[R]_0 - [R]}{t}$

At $t = t_{\frac{1}{2}}$, $[R] = \frac{1}{2}[R]_0$

The rate constant at $t_{\frac{1}{2}}$ becomes

$$k = \frac{[R]_0 - \frac{1}{2}[R]_0}{t_{\frac{1}{2}}}$$

$$t_{\frac{1}{2}} = \frac{[R]_0}{2k}$$

It is clear that $t_{\frac{1}{2}}$ for a zero order reaction is directly proportional to the initial concentration of the reactants and inversely proportional to the rate constant.

- ➥ Half-life for first order reaction :
- ➥ For the first order reaction,

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

at $t = t_{\frac{1}{2}}$ $[R] = \frac{[R]_0}{2}$

➥ So, the above equation becomes

$$k = \frac{2.303}{t_{\frac{1}{2}}} \log \frac{[R]_0}{\frac{[R]_0}{2}}$$

$$\text{or } t_{\frac{1}{2}} = \frac{2.303}{k} \log 2$$

$$t_{\frac{1}{2}} = \frac{2.303}{k} \times 0.301$$

$$t_{\frac{1}{2}} = \frac{0.693}{k}$$

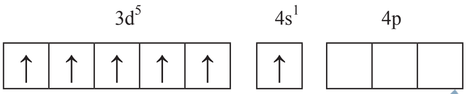
➥ It can be seen that for a first order reaction, half-life period is constant, i.e. it is independent of initial concentration of the reacting species. The half-life of a first order equation is readily calculated from the rate constant and vice versa.

For zero order reaction $t_{\frac{1}{2}} \times [R]_0$ for first order reaction $t_{\frac{1}{2}}$ is independent of $[R]_0$

25.

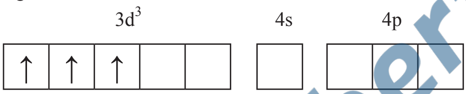
➥ In $[Cr(NH_3)_6]^{3+}$ oxidation state of Cr is +3.

$_{24}Cr$: [Ar]

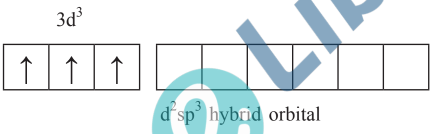


➥ Electronic configuration of Cr^{3+} ion.

$_{24}Cr^{3+}$: [Ar]



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

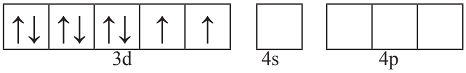


➥ Six pairs of electrons, one from each NH_3 molecule, occupy the six hybrid orbitals.

➥ Therefore, it undergoes d^2sp^3 hybridization and the electrons in the 3d orbitals remain unpaired. Hence, it is paramagnetic in nature.

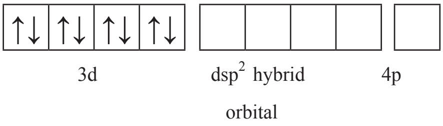
➥ In $[Ni(CN)_4]^{2-}$, Ni exists in the +2 oxidation state. Electronic configuration.

NI^{2+} ion



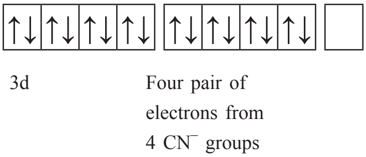
➥ Here CN^- is strong ligand so electrons of 3d orbital gets paired so hybridization involved is dsp^2.

NI^{2+} :



➥ Each of the hybridized orbitals receives a pair of electrons from a cyanide ion.

$[Ni(CN)_4]^{-2}$ (low spin complex)



➥ The compound is diamagnetic as evident from the absence of unpaired electron, and square planar complexes.

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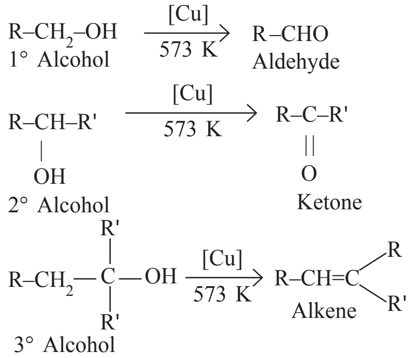
26.

➥ (i) tertiary alcohol heated at 573K in presence of Copper (Cu)

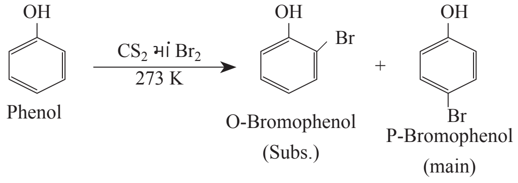


$$\underset{\text{1° Alcohol}}{R{-}CH_2{-}OH} \xrightarrow[573\ K]{[Cu]} \underset{\text{Aldehyde}}{R{-}CHO}$$

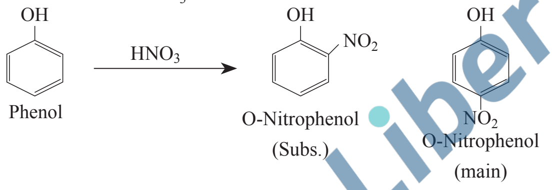
$$\underset{\text{2° Alcohol}}{R{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}R'} \xrightarrow[573\ K]{[Cu]} \underset{\text{Ketone}}{R{-}\underset{\displaystyle O}{\underset{||}{C}}{-}R'}$$

$$\underset{\text{3° Alcohol}}{R{-}CH_2{-}\overset{\displaystyle R'}{\overset{|}{\underset{\displaystyle R'}{\underset{|}{C}}}}{-}OH} \xrightarrow[573\ K]{[Cu]} \underset{\text{Alkene}}{R{-}CH{=}C\begin{matrix}R\\R'\end{matrix}}$$

(ii) Reaction of bromine in CS_2 with Phenol



(iii) Reaction of dil HNO_3 with phenol



(iv) Oxidation of Phenol with chromic acid

$$CH_3CH_2CH_2OH + 2[O] \xrightarrow[\text{Oxidation}]{\text{Alkaline}} CH_3CH_2COOH + H_2O$$

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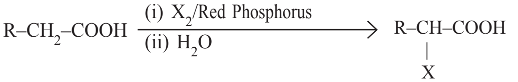
27.

➥ **Fehling's test :** Fehling reagent comprises of two solutions, Fehling solution A and Fehling solution B. Fehling solution A is aqueous copper sulphate and Fehling solution B is alkaline sodium potassium tartrate (Rochelle salt). These two solutions are mixed in equal amounts before test. On heating an aldehyde with Fehling's reagent, a reddish brown precipitate is obtained. Aldehydes are oxidised to corresponding carboxylate anion. Aromatic aldehydes do not respond to this test.

$$R - CHO + 2Cu^{2+} + 5OH^{-} \rightarrow RCOO^{-} + \underset{\text{Red-brown ppt}}{Cu_2O \downarrow} + 3H_2O$$

➥ Carboxylic acids having an α-hydrogen are halogenated at the α-position on treatment with chlorine or bromine in the presence of small amount of red phosphorus to give α-halocarboxylic acids. The reaction is known as Hell-Volhard-Zelinsky reaction.



$$R{-}CH_2{-}COOH \xrightarrow[\text{(ii) } H_2O]{\text{(i) } X_2\text{/Red Phosphorus}} R{-}\underset{\displaystyle X}{\underset{|}{CH}}{-}COOH$$

X = Cl, Br
α-Halocarboxylic
acid