## Sample Paper 8 Solutions

#### Class XII 2023-24

## Chemistry

#### Time: 3 Hours General Instructions:

Max. Marks: 70

- 1. There are 33 questions in this question paper with internal choice.
- SECTION A consists of 16 multiple-choice questions carrying 1 mark each.
- SECTION B consists of 5 very short answer questions carrying 2 marks each.
- SECTION C consists of 7 short answer questions carrying 3 marks each.
- SECTION D consists of 2 case-based questions carrying 4 marks each.
- SECTION E consists of 3 long answer questions carrying 5 marks each.
- All questions are compulsory.
- 8. Use of log tables and calculators is not allowed.

## **SECTION-A**

**Directions (Q. Nos. 1-16):** The following questions are multiplechoice questions with one correct answer. Each question carries 1 mark. There is no internal choice in this section.

- Which of the following is/are not affected by temperature?
  - (a) Molarity
- (b) Mole fraction
- (c) Normality
- (d) All of these

Ans: (b) Mole fraction

That is because molality does not depend on temperature, neither number of moles solute nor mass of solvent will be affected by changes of temperature while molarity and normality changes as temperature changes (due to change in volume). Mole fraction also not affected by temperature because if the ratio of number of moles.

- The enzyme which can catalyse the conversion of glucose to ethanol is
  - (a) zymase
- (b) invertase
- (c) maltase
- (d) diastase

Ans: (a) zymase

Zymase catalyses the conversion of glucose to ethanol.

- When one Faraday of electric current is passed, the mass deposited, equal to
  - (a) One gram equivalent
  - (b) One gram mole
  - (c) Electrochemical equivalent
  - (d) Half gram equivalent

Ans: (a) One gram equivalent

The mass deposited is equal to one gram equivalent. Because "Faraday" is not a measure of current. The ampere is the measure of current. The mass of metal transferred in plating depends on the metal and the process.

- 4. Which of the following is not a pyrimidine base?
  - (a) Uracil
- (b) Cytosine
- (c) Thymine
- (d) Guanine

Ans: (d) Guanine

Guamine is not a physimidine base. It is a purine base

- If the rate of the reaction is equal to the rate constant, the order of the reaction is
  - (a) 3

(b) 0

(c) 1

(d) 2

Ans: (b) 0

Since,

 $r = k[A]^n$ 

if

n = 0

 $r = k[A]^0$ 

or r = k

thus for zero order reactions rate is equal to the rate constant.

- Lucas reagent is
  - (a) Conc. HCl and anhydrous ZnCl<sub>2</sub>
  - (b) Conc. HNO<sub>3</sub> and hydrous ZnCl<sub>2</sub>
  - (c) Conc. HCl and hydrous ZnCl<sub>2</sub>
  - (d) Conc. HNO<sub>3</sub> and anhydrous ZnCl<sub>2</sub>

Ans: (a) Conc. HCl and anhydrous ZnCl<sub>2</sub>

Lucas reagent is conc. HCl + anhyd. ZnCl<sub>2</sub>.

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- 7. The transition metal which shows the highest oxidation state is:
  - (a) Mn

(b) Pt

(c) Fe

(d) Ni

Ans: (a) Mn

pt 
$$\rightarrow$$
 + 2 and + 4

 $Mn \rightarrow +2 to +7$  (Highest oxidation state)

Fe 
$$\rightarrow$$
 + 2 to + 6

$$N_1 \rightarrow +1 \text{ to } +4$$

The ionic enthalpy is increase Sc to Mn after that it will be decrease Fe to Cu.

- 8. Which of the following undergo aldol condensation?
  - (a) HCHO
- (b) CH<sub>3</sub>CHO
- (c) C<sub>6</sub>H<sub>5</sub>CHO
- (d) CH<sub>3</sub>COCH<sub>3</sub>

Ans: (b) CH<sub>3</sub>CHO and (d) CH<sub>3</sub>COCH<sub>3</sub>

The criteria for an aldehyde or a ketone to undergo aldol reaction is the presence of alpha hydrogen. The mentioned compound as (b) and (d) have alpha hydrogen, they will undergo for aldol condensation reaction.

- 9. IUPAC name of H<sub>2</sub>[PtCl<sub>6</sub>] is -
  - (a) Hydrogen hexachloro platinate (IV)
  - (b) Hydrogen hexachloro platinate (II)
  - (c) Hydrogen hexa chlorido Pt (IV)
  - (d) Hydrogen hexa chlorido Pt (II)

Ans: (a) Hydrogen hexachloro platinate (IV)

IUPAC name of H<sub>2</sub>[PtCl<sub>6</sub>] is hydrogen hexachloro platinate (IV).

- 10. An isocyanide is prepared:
  - (a) Friedel-Crafts reaction
  - (b) Perkin reaction
  - (c) Carbylamine reaction
  - (d) Wurtz reaction

Ans: (c) Carbylamine reaction

Carbylamine reaction:

$$R - Nh_2 + 3KOH + CHCl_3 \longrightarrow$$

$$R - N \equiv C + 3KCl + 3H_2O$$

- 11. Chlorobenzene give DDT when it reacts with:
  - (a) charcoal
- (b) chloral
- (c) naphthalene
- (d) benzenoid

Ans: (b) chloral

DDT is synthesised by heating a mixture. of chloral (1 mol) with chlorobenzene (2 mol) in the presence of concentrated H<sub>2</sub>SO<sub>4</sub>.

- 12. Volume of one mole of any gas at NTP is:
  - (a) 11.2 litre
- (b) 22.4 litre
- (c) 10.2 litre
- (d) 22.8 litre

Ans: (b) 22.4 litre

One mole of any gas at NTP (normal temperature and pressure) occupies 22.4 litre (by volume) of space. We know that for ideal gas: PV = nRT.

Where,

P = Pressure of gas = (1 atm)

V = Volume of gas

n = moles of gas (n = 1)

R = Gas constant (= 0.0821)

 $T = \text{Temperature} (= 273 \, \text{k} - \text{capital})$ 

Hence,  $V = \frac{nRT}{P} = \frac{1 \times 0.0821 \times 273}{1}$ 

V = 22.4.L (for one mole of gas)

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**Directions (Q. Nos. 13-16):** Each of the following questions consists of two statements, one is Assertion and the other is Reason. Give answer:

13. Assertion: Sucrose undergoes mutarotation.

Reason : Sucrose is a disaccharide.

- (a) Both Assertion and Reason are correct and Reason is a correct explanation of the Assertion.
- (b) Both Assertion and Reason are correct but Reason is not the a correct explanation of the Assertion.
- (c) Assertion is correct but Reason is incorrect.
- (d) Both the Assertion and Reason are incorrect.

Ans: (b) Both Assertion and Reason are correct but Reason is not the a correct explanation of the Assertion.

Sucrose which is a disaccharide undergoes mutarotation because it is converted into glucose and fructose on hydrolysis and the products have different optical activity from that of the reactant.

Assertion: CHCl<sub>3</sub> is stored in dark bottles.

Reason: CHCl, is oxidised in dark.

- (a) Both Assertion and Reason are correct and Reason is a correct explanation of the Assertion.
- (b) Both Assertion and Reason are correct but Reason is not the a correct explanation of the Assertion.
- (c) Assertion is correct but Reason is incorrect.
- (d) Both the Assertion and Reason are incorrect.

Ans: (c) Assertion is correct but Reason is incorrect.

CHCl, is stored in dark bottles to prevent oxidation of

CHCl, in-presence of sunlight.

15. Assertion: Sucrose is a non-reducing sugar.

Reason: It has glycosidic linkage.

- (a) Both Assertion and Reason are correct and Reason is a correct explanation of the Assertion.
- (b) Both Assertion and Reason are correct but Reason is not the a correct explanation of the Assertion.
- (c) Assertion is correct but Reason is incorrect.
- (d) Both the Assertion and Reason are incorrect.

Ans: (a) Both Assertion and Reason are correct and Reason is a correct explanation of the Assertion.

Sucrose is a non-reducing sugar because it has glycosidic linkage which has no free aldehyde or ketonic group.

16. Assertion: In rate law, unlike in the expression for equilibrium constants, the exponents for concentrations do not necessarily match the stoichiometric coefficients.

Reason: It is the mechanism and not the balanced chemical equation for the overall change that governs the reaction rate.

- (a) Both Assertion and Reason are correct and Reason is a correct explanation of the Assertion.
- (b) Both Assertion and Reason are correct but Reason is not the a correct explanation of the Assertion.
- (c) Assertion is correct but Reason is incorrect.
- (d) Both the Assertion and Reason are incorrect.

Ans: (a) Both Assertion and Reason are correct and Reason is a correct explanation of the Assertion.

Rate law is always written according to the slowest step and thus the exponents for concentrations do not necessarily match the stoichiometric coefficients.

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### SECTION-B

**Directions (Q. Nos. 17-21):** This section contains 5 questions with internal choice in one question. The following questions are very short answer type and carry 2 marks each.

 Explain the Henry's law about dissolution of a gas in a liquid.

#### Ans:

Henry's law states that, the partial pressure of the gas in vapour phase (p) is directly Proportional to the mole fraction of the gas  $(\chi)$  in the solution.

$$p = K_H \cdot \chi$$

 $Here, K_H = Henry's law constant.$ 

Different gases have different  $K_{\rm H}$  values at the same temperature.

 Write general expression for the amount of the substance left after n half lives.

#### Ans:

Amount of the substance left after n half lives

$$=\frac{[R]_0}{2^n}$$

Here  $[R]_0$  =Initial concentration.

- 19. Write the IUPAC names of the following compounds:
  - CH<sub>3</sub> CHOH CH<sub>2</sub> CHOH CH<sub>3</sub>
  - C<sub>6</sub>H<sub>50</sub>OC<sub>6</sub>H<sub>5</sub>

#### Ans:

- Pentane-2, 4-diol
- Phenoxy benzene

#### or

You are given benzene, conc. H<sub>2</sub>SO<sub>4</sub> and NaOH. Write the equations for the preparation of phenol using these reagents.

#### Ans:

20. Complete the following reaction equations:

$${\rm (i)} \ \ \, \bigodot^{{\rm CH}_3} + {\rm HI} \ \ \, \longrightarrow \ \ \,$$

(ii)  $CH_3CH_2CH = CH_2 + HBr \longrightarrow$ 

#### Ans:

$$(i)$$
  $\longrightarrow$   $CH_3$   $+ HI \longrightarrow CH_3$ 

(ii) 
$$H_3C-CH_2-CH=CH_2+HBr\longrightarrow H_3C-CH_2-CH-CH_3$$

21. Complete the following reaction equations:

(ii) 
$$^{\text{H}}_{\text{H}}$$
C=C $\stackrel{\text{H}}{\overset{\text{H}}{\longrightarrow}}$  + Br<sub>2</sub>  $\stackrel{\text{CCl}_4}{\overset{\text{CCl}_4}{\longrightarrow}}$  .....

#### Ans:

(i) C<sub>6</sub>H<sub>5</sub>N<sub>2</sub>Cl<sup>−</sup> + KI → C<sub>6</sub>H<sub>5</sub>I + KCl + N<sub>2</sub>

(ii) 
$$_{\rm H}^{\rm H}$$
C=C $_{\rm H}^{\rm H}$  + Br<sub>2</sub>  $\xrightarrow{\rm CCl_4}$  BrCH<sub>2</sub>-CH<sub>2</sub>Br  $_{vic\text{-dibromide}}$ 

## SECTION-C

**Directions (Q. Nos. 22-28):** This section contains 7 questions with internal choice in one question. The following questions are short answer type and carry 3 marks each.

22. How molarity of a solution different from molality?

#### Ans:

#### Molarity (M)

Molarity is defined as the number of moles of solute dissolved in one litre or one cubic decimetre of the solution.

$$Molarity = \frac{Moles \text{ of solute}}{Volume \text{ of solution } (L)}$$

#### Molality (m)

It is defined as the number of moles of the solute per kilogram of the solvent.

$$Molality = \frac{Moles \text{ of solute}}{Mass \text{ of solvent in kg}}$$

Thus, Molarity is the number of moles of solute per litre of solution while molality is the number of moles of solute per kilogram of the solvent.

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23. What is the effect of temperature on the rate constant of reaction? How can this temperature effect on the rate constant be represented quantitatively?

#### Ans:

The rate constant of a reaction increase with increase of temperature and becomes nearly double for every 10° rise of temperature. The effect can be represented quantitatively by Arrhenius equation.

$$K = Ae^{-Ea/RT}$$

Where  $E_a$  represents the activation energy of the reaction and A represents the frequency factor.

24. Define electrode and electrode potential.

#### Ans:

- Electrode: An electrode is a solid electric conductor that allows the passage of electric current through it self. Electrode are of two types, cathode (negative plate) and anode (positive plate).
- Electrode potential: It is the potential difference developed between the electrodes and its electrolyte or

it is the difference set up between the metal and its ions in the solution, it is called electrode potential.

25. How would you account for the irregular variation of ionization enthalpies (first and second) in the first series of the transition elements?

#### Ans:

Along a transition series the ionisation enthalpy gradually increases with increase in atomic number but in first series of the transition elements first ionization enthalpy of Cr is low because loss of one electron gives Cr a stable configuration i.e.  $3d^5$  whereas Zn has very high first ionisation enthalpy because it is difficult to remove electron from 4s orbital of the stable configuration  $(3d^{10}4s^2)$ .

There is decrease in second ionization enthalpy from Cr to Mn form Cu to Zn because after removal of  $1^{st}$  electron, Cr and Cu gain a stable configuration i.e.  $d^5$  and  $d^{10}$ . Hence irregular variation of I.E. is mainly due to varying degree of stability of different 3d-configurations.

- 26. Account for the following :
  - The boiling point of ether is much lower than that of alcohol.
  - 2. Phenol is more acidic than alcohol.

#### Ans:

 The boiling point of ether is much lower than that of alcohol: Boiling point of any liquid depends on the strength of the inter molecular force of attraction. More be the intermolecular force of attraction, more is the boiling point.

Alcohols have strong hydrogen bonding along with dipole-dipole interaction while ethers due to sterichinderence do not form hydrogen bonding thus boiling point of alcohols are much higher than of ethers.

Phenol is more acidic than alcohol: Acidity of any acid depends on the stability of its conjugate. More stable is the conjugate, more acidic be the given acid.

As conjugate of phenol (i.e. phenoxide ion) is more stable due to resonance, while conjugate of alcohol does not, the phenol is more acidic than alcohols.

27. An organic compound (A) (molecular formula C<sub>8</sub>H<sub>16</sub>O<sub>2</sub>) was hydrolysed with dilute sulphuric acid to give a carboxylic acid (B) and an alcohol (C). Oxidation of (C) with chromic acid produced (B). (C) on dehydration gives but-1-ene. Write equation for the reactions involved.

#### Ans :

- Since the given compound on hydrolysis with dil. H<sub>2</sub>SO<sub>4</sub> gives carboxylic acid (B) and an alcohol (C), it must be an ester.
- Since the oxidation of alcohol (C) gives the acid B, therefore, both the carboxylic acid B and alcohol C must contain same number of C atoms.
- Since ester (A) has eight carbon atoms, therefore, both carboxylic acid (B) and the alcohol (C) must contain four C atoms each.
- Alcohol (C) on dehydration gives but-1-ene and therefore, C must be a straight chain alcohol i.e., butan-1-ol.

 (B) is obtained by the oxidation of (C) and therefore, B 28. must be butanoic acid.

This also suggests that the ester (A) must be butyl butanoate. The relevant reactions are:

$$\begin{array}{c} O \\ \parallel \\ CH_3CH_2CH_2-C-OCH_2CH_2CH_2CH_3 \end{array} \xrightarrow{\begin{array}{c} Dil. \ H_2SO_4 \\ \hline Hydrolysis \end{array}}$$
Butyl butanoate (A)
(M.F.  $C_4H_{sc}O_4$ )

$$\begin{array}{c} & \text{O} \\ \parallel \\ \text{CH}_3\text{CH}_2\text{CH}_2 - \text{C} - \text{OH} \\ + \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \\ \text{Butanoic acid (B)} & \text{Butanoi (C)} \end{array}$$

$$\begin{array}{c} \text{CH}_3\text{CH}_2\text{CH}_2\text{COOH} & \xrightarrow{\text{CrO}_3/\text{CH}_3\text{COOH}} \\ \text{Butanoic acid (B)} & \xrightarrow{\text{Oxidation}} \end{array}$$

$$\begin{array}{ccc} \operatorname{CH_3CH_2CH_2OH} & \xrightarrow{\operatorname{Dehydration}} & \operatorname{CH_3CH_2CH} = \operatorname{CH_2} \\ \operatorname{Butanol} (\operatorname{C}) & \operatorname{But-1-ene} \end{array}$$

or

An organic compound with molecular formula  $C_9H_{10}O$ forms, 2, 4-DNP derivatives, reduces Tollen's reagent and undergoes cannizzaro reaction. On vigorous oxidation, it gives 1,2- benzenedicarboxylic acid. Identify the compound.

#### Ans:

The given compound forms a 2, 4-DNP derivative and reduces Tollen's reagent, it must be an aldehyde since it undergoes cannizaro reaction, therefore CHO group is directly attached to the benzene ring.

On vigorous oxidation, it gives 1, 2-benzenedicarboxylic acid, therefore it must be an ortho substituted benzaldehyde and the only o-substituted aromatic aldehyde having molecular formula  $C_9H_{10}O$  is 2- ethyl benzaldehyde.

Reactions are as follows:

28. Write down the electronic configuration of

 $Cr^{3+}$ 

2. Cu<sup>+</sup>

Co<sup>2+</sup>

4.  $Mn^{2+}$ 

Ans:

1.  $Cr^{3+} = [Ar]^{18}3d^3$ 

2.  $Cu^+ = [Ar]^{18} 3d^{10}$ 

3.  $Co^{2+} = [Ar]^{18}3d^7$ 

4.  $Mn^{2+} = [Ar]^{18}3d^5$ 

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### SECTION-D

**Directions (Q. Nos. 29-30):** The following questions are casebased questions. Each question has an internal choice and carries 4 marks each. Read the passage carefully and answer the questions that follow.

29. The substitution reaction of alkyl halide mainly occurs by S<sub>N</sub>1 or S<sub>N</sub>2 mechanism. Whatever mechanism alkyl halides follow for the substitution reaction to occur, the polarity of the carbon halogen bond is responsible for these substitution reactions. The rate of S<sub>N</sub>1 reactions are governed by the stability of carbocation whereas for S<sub>N</sub>2 reactions steric factor is the deciding factor. If the starting material is a chiral compound, we may end up with an inverted product or racemic mixture depending upon the type of mechanism followed by alkyl halide. Cleavage of ethers with HI is also governed by steric factor and stability of carbocation, which indicates that in organic chemistry, these two major factors help us in deciding the kind of product formed.

Answer The following questions:

- (a) Out of chlorobenzene and benzyl chloride, which one gets easily hydrolysed by aqueous NaOH and why?
- (b) Predict the stereochemistry of the product formed if an optically active alkyl halide undergoes substitution reaction by S<sub>N</sub>1 mechanism.
- (c) Following compounds are given to you: 2-Bromopentane, 2-Bromo-2-methylbutane, 1-Bromopentane
  - Write the compound which is most reactive towards S<sub>N</sub>2 reaction.
  - (ii) Write the compound which is optically active.

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(d) What are the points of similarities between S<sub>N</sub>1 and S<sub>N</sub>2 reactions?

#### Ans:

- (a) Benzyl chloride gets easily hydrolysed by aq. NaOH due to formation of stable benzyl carbocation. But due to partial double bond character of C-Cl bond in chlorobenzene, it does not hydrolyse.
- (b) Stereochemical aspects of nucleophilic substitution reaction in S<sub>N</sub>1 proceeds with racemisation.

- (c) (i) 1-Bromopentane
  - (ii) 2-Bromopentane

- (d) Both S<sub>N</sub>1 and S<sub>N</sub>2 reactions undergo substitution of a nucleophile by other nucleophile. In both the reactions configuration of product changes, partially in S<sub>N</sub>1 and completely in S<sub>N</sub>2.
- 30. For the first order decomposition reaction are as follows:  $(CH_3)_3COOC(CH_3)_3 \rightarrow 2CH_3COCH_3 + C_2H_6$

In the gaseous phase, the pressures of the system at t = 0and t = 15 min were found to be 169.3 Torr and 256 Torr, respectively.

Answer the following questions according to the above given paragraph:

- (a) What is the pressure of C<sub>2</sub>H<sub>6</sub> at time t?
- (b) Write integrated rate law expression for this reaction.
- (c) Find out the value of rate constant k.?

(d) What is the total pressure of the system after 9 minutes?

#### Ans:

t = 0	$p_0$	0	0
t	$p_0 - p$	2p	p

Total pressure at time t,

$$p_t = p_0 + 2p$$
  
 $p = \frac{p_1 - p_0}{2}$ 

Thus, from the given data at t = 0 and t = 15 min.

$$256 = 169.3 + 2p$$
  
 $p = \frac{256 - 169.3}{2} = 43.55 \text{ Torr}$ 

(b) The integrated expression

$$kt = 2.303 \log \frac{2p_0}{3p_0 - p_t}$$
  
(c)  $p_0 - p = 169.3 - 43.35 = 125.95 \text{ Torr}$   
 $k = \frac{2.303}{15} \log \frac{169.3}{125.95} = 0.0197 \text{ min}^{-1}$ 

(d) 
$$k \times t = 2.303 \log \frac{p_0}{p_0 - p}$$
  
 $0.0197 \times 9 = 2.303 \log \frac{169.3}{(p_0 - p)}$   
 $p_0 - p = 141.9$   
 $p = 27.38$   
 $p_t = (p_0 - p) + 3p = p_0 + 2p$   
 $= 169.3 + 2 \times 27.38 = 224.06$ 

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## SECTION-E

Directions (Q. Nos. 31-33): The following questions are long answer type and carry 5 marks each. Two questions have an internal choice.

- 31. Predict giving reasons, the order of basicity of the following compounds is
  - gaseous phase and
  - (ii) in aqueous solution (CH<sub>3</sub>)<sub>3</sub>N,(CH<sub>3</sub>)<sub>2</sub>N,CH<sub>3</sub>NH<sub>2</sub>,NH<sub>3</sub>

All amines are more basic than NH<sub>3</sub> due to + I effect of alkyl groups in amines.

 In gaseous phase the basicity of amines depends only on + I effect of the alkyl groups the + I effect increases from 1° to 3° amine therefore the order of basicity of amines is  $3^{\circ} > 2^{\circ} > 1^{\circ}$ .

The overall order of basicity is  $(CH_3)_3N > (CH_3)_2NH > CH_2NH_2 > NH_3$ 

- In aqueous solution basicity of methyl amines depends upon two factors-
  - (a) + I effect- According to this the basicity is  $(CH_3)_3N > (CH_3)_2NH > CH_3NH_2$
  - (b) Solvation effect : On the basis of solavation effect greater the number of H-atoms on N-atom, more stable is the ammonium ion and hence more basic is amine. The ammonium cation derived form a 1° amines is the most stable since it has three H-atoms which can form H-bonds with H<sub>2</sub>O, the ammonium cation derived from 2° amine is less stable since it has two H-atoms which can form H-bands and 3° amine is least stable since it has only one H-atom which can form H-bond with H<sub>2</sub>O. Hence the basicity should decrease in the order: $CH_3Nh_2 > (CH_3)_2NH > (CH_3)_3N.$

$$CH_3$$
 $\dot{N} - H + H^+$ 
 $CH_3$ 
 $\dot{N} - H + H^+$ 
 $\dot{N} - H$ 

$$CH_3$$
 $CH_3$ 
 $N + H^+$ 
 $CH_3$ 
 $CH_3$ 

Trimethylamine

The combined effect of these two opposite factors (a) and (b) is that (CH<sub>3</sub>)<sub>2</sub>NH is the strongest base.

In case of CH<sub>3</sub>NH and (CH<sub>3</sub>)<sub>3</sub>N the stability due to H-bonding prediminates over +I effect of the CH<sub>3</sub> groups. Thereby  $CH_3NH_2$  is more stronger than  $(CH_3)_3$ 

N. Thus te overall relative basicity of methylamines is in the order.

$$(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$$

32. State and explain Kohlrausch law

#### Ans:

Kohlrausch law of independent migration of ions: Limiting molar conductivity of an electrolyte is the sum of the individual contributions of the anion and cation of the electrolyte. If an electrolyte on dissociation gives  $v_+$  cations and  $v_-$  anions then its limiting molar conductivity is given by:

$$\wedge_m^o = v_+ \lambda_+^o + v_- \lambda_-^o$$

Here,  $\lambda_{\perp}^{\circ} = \text{Limiting molar conductivities of cations}$ 

 $\lambda_{-}^{\circ}$  = Limiting molar conductivities of anions

For example : If  $\lambda_{Na+}^{\circ}$  and  $\lambda_{Cl}^{\circ}$  are limiting molar conductivities of the sodium and chloride ions respectively, then the limiting conductivity for sodium chloride is given by the equation :

$$\wedge_{m(NaCl)}^{o} = \wedge_{Na^{+}}^{o} + \wedge_{Cl^{-}}^{o}$$

### Application of Kohlrausch law

 Calculation of Limiting molar conductivity of weak electrolytes: It is not possible to find ∧<sub>in</sub> for a weak electrolyte like CH<sub>3</sub>COOH by extrapolation, we can find it as following using Kohlrausch's law.

$$\wedge_{m(CH,COOH)}^{o} = \lambda_{m}^{o}(CH_{3}COO^{-}) + \lambda_{m}^{o}(H^{+})$$

This equation can be arrived at by knowing the molar conductivities at infinite dilution for the strong electrolytes KCl, CH<sub>3</sub>COOK and HCl

$$\bigwedge_{m(KCI)}^{o} = \lambda_{K^{+}}^{o} + \lambda_{CI}^{o}$$

$$\bigwedge_{m(CH_3COOH)}^{o} = \lambda^{o}CH_3COO^- + \lambda^{o}_{k^+}, \Lambda^{o}_{m(HCI)} = \lambda^{o}_{H^+} + \lambda^{o}_{CI}$$

Hence, we have

$$\lambda_{\text{CH}_3\text{COO}^-}^{\circ} + \lambda_{\text{H}^-}^{\circ} = (\lambda_{\text{CH}_3\text{COO}^-}^{\circ} + \lambda_{\kappa}^{\circ}) + (\lambda_{\text{H}^-}^{\circ} + \lambda_{\text{CI}^-}^{\circ})$$

i.e.,  $\Lambda_{m(CH_3COOH)}^o = \Lambda_{m(CH_3COOK)}^o + \Lambda_{m(HCI)}^o - \Lambda_{m(KCI)}^o$ 

2. Calculation of the Degree of Dissociation:

Degree of dissociation 
$$(\alpha) = \frac{\Lambda_m^c}{\Lambda_o^o}$$

Here,  $\Lambda_m^c =$  Molar conductivity of a solution at any concentration c

 $\Lambda_m^o$  = Limiting molar conductivity or Molar conductivity at infinite dilution

3. Calculation of dissociation constant of a weak electrolyte:

Dissociation constant (K<sub>C</sub>) = 
$$\frac{c\alpha^2}{1-\alpha}$$

c = Concentration

 $\alpha$  = Degree of dissociation

0

Predict the products of electrolysis of the following:

- An aqueous solution of AgNO<sub>3</sub> with silver electrodes
- An aqueous solution of AgNO<sub>3</sub> with platinum electrodes
- An dilute aqueous solution of H<sub>2</sub>SO<sub>4</sub> with platinum

electrodes

An aqueous solution of CuCl<sub>2</sub> with platinum electrodes.

(Given 
$$E_{Ag^+/Ag}^o$$
)=+0.80 V,  $E_{Cu^{2r}/Cu}^o$ =+0.34 V)

#### Ans:

 Electrolysis of aqueous solution of AgNO<sub>3</sub> with silver electrodes:

$$AgNO_3(s) + aq \rightarrow Ag^+_{(aq)} + NO^-_3(aq)$$
  
 $H_2O \rightleftharpoons H^+ + OH^-$ 

At cathode: Ag<sup>+</sup> ions have lower discharge potential that H<sup>+</sup> ions. Hence Ag<sup>+</sup> ions will be deposited.

$$Ag^+ + e^- \rightarrow Ag(s)$$

At Anode: As Ag anode is attacked by NO<sub>3</sub> ions. Ag of the anode will dissolve to form Ag<sup>+</sup> ions in the solution

$$Ag \rightarrow Ag^+ + e^-$$

 Electrolysis of aqueous solution of AgNO<sub>3</sub> with platinum electrodes:

At cathode:  $Ag^+ + e - \rightarrow Ag(s)$ 

At anode: Out of OH<sup>-</sup> and NO<sub>3</sub> ions. OH<sup>-</sup> ions have lower discharge potential.

Hence OH<sup>-</sup> ions will be discharged in preference to NO<sub>3</sub> ions, which then decompose to give out O<sub>2</sub>

$$OH^{-}(aq) \rightarrow OH + e^{-}$$
  
 $4OH \rightarrow 2H_{2}O(1) + O_{2}(g)$ 

 A dilute aqueous solution of H<sub>2</sub>SO<sub>4</sub> with platinum electrodes:

$$H_2SO_4(aq) \rightarrow 2H^+(aq) + SO_4^{2-}(aq)$$
  
 $H_2O \rightleftharpoons H^+ + OH^-$ 

At Cathode :  $H^+ + e^- \rightarrow H$ 

$$H + H \rightarrow H_2(g)$$

At Anode :  $OH^- \rightarrow OH + e^-$ 

$$4OH \rightarrow 2H_2O + O_2(g)$$

Thus,  $H_2$  is liberated at the cathode and  $O_2$  at the anode.

4. Electrolysis of aqueous solution of  $\operatorname{CuCl}_2$  with platinum electrodes :

$$CuCl_2(S) + aq \rightarrow Cu^{2+}(aq) + 2Cl^-(aq)$$
  
 $H_2O \rightleftharpoons H^+ + OH^-$ 

At cathode :  $Cu^{2+}$  ions will be reduced in preference to  $H^+$  ions

$$Cu^{2+} + 2e^{-} \rightarrow Cu$$

At anode: Cl<sup>-</sup> ions will be oxidised in preference to OH<sup>-</sup> ions

$$Cl^- \rightarrow Cl + e^-$$
  
 $Cl + Cl \rightarrow Cl_2(g)$ 

Thus, Cu will be deposited on the cathode and Cl<sub>2</sub> will be liberated at the anode.

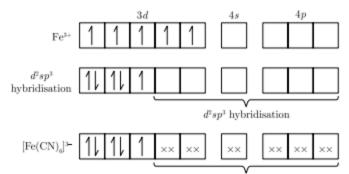
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33. How would you account for the fact that [Fe(CN<sub>6</sub>)]<sup>3-</sup> is weakly paramagnetic while [Fe(CN)<sub>6</sub>]<sup>4-</sup> is diamagnetic?

#### Ans

[Fe(CN)<sub>6</sub>]<sup>3-</sup>

Iron is in +3 oxidation state  $=3d^5$ 

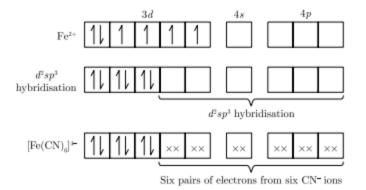


Six pairs of electrons from six CN<sup>-</sup> ions

The presence of one unpaired electron makes the complex weakly paramagnetic.

#### [Fe(CN)<sub>6</sub>]<sup>4-</sup>

Iron is in +2 oxidation state =  $3d^6$ 



There is no unpaired electron therefore it is diamagnetic.

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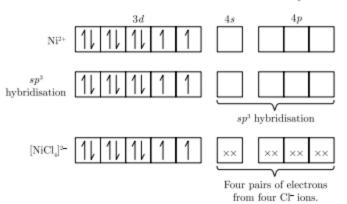
How does valence bond theory explain the bonding in the following complexes of nickel:

- (i) [NiCl<sub>4</sub>]<sup>2-</sup> is tetrahedral
- (ii) [Ni (CN)<sub>4</sub>]<sup>2-</sup> is square planar
- (iii) [Ni (CO)<sub>4</sub>] is tetrahedral?

#### Ans:

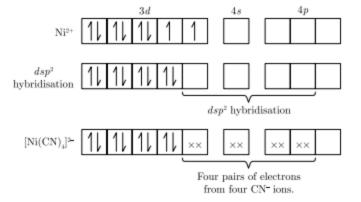
(i) [NiCl<sub>4</sub>]<sup>2-</sup>

Nickel is in +2 oxidation state  $= 3d^8$ .



#### (ii) [Ni(CN)<sub>4</sub>]<sup>2-</sup>

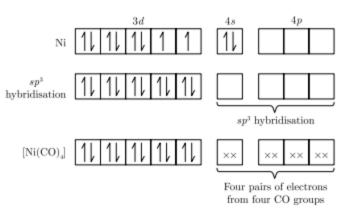
Nickel is in +2 oxidation state  $=3d^8$ .



 $[Ni(CN)_4]^{2-}$  ion is diamagnetic since it contains no unpaired electron.

#### (iii)[Ni(CO)<sub>4</sub>]

Nickel is in 0 oxidation state =  $3d^84s^2$ .



[Ni(CO)<sub>4</sub>] is diamagnetic since it contains no unpaired electron.

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