# Sample Paper 13 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.
- 3. 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 one of the following is the strongest base in aqueous solution?
  - (a) Methylamine
- (b) Trimethylamine
- (c) Aniline
- (d) Dimethylamine

Ans: (d) Dimethylamine

Note: Aromatic amines are less basic than aliphatic amines. Among aliphatic amines the order of basicity is  $2^{\circ} > 1^{\circ} > 3^{\circ}$ . The electron density is decreased in  $3^{\circ}$  amine due to to crowding of alkyl group over N atom which makes the approach and bonding by a proton relatively difficult. Therefore the basicity decreases. Further Phenyl group show-I effect, thus decreases the electron density on nitrogen atom and hence the basicity.

Hence, Dimethylamine (2° aliphatic amine) is strongest base among given choices.

Hence, The correct order of basic strength is Dimethylamine>Methylamine>Trimethylamine>Aniline.

- 2. Which is not colligative property?
  - (a) Freezing Point
  - (b) Lowering of vapour pressure
  - (c) Depression of freezing point
  - (d) Elevation of boiling point

Ans: (a) Freezing Point

Colligative property is strictly true only for dilute solutions which behaves as nearly ideal solution. These properties are: lowering of vapour pressure of the solvent, elevation in boiling point of the solvent, depression in freezing point of the solvent.

Hence, option (a) is not true.

- 3. Which of the following compounds is used as a refrigerant?
  - (a) Acetone
- (b) CCl<sub>4</sub>

(c) CF<sub>4</sub>

(d) CCl<sub>4</sub>F<sub>2</sub>

Ans: (d) CCl<sub>4</sub>F<sub>2</sub>

Under ordinary conditions freon is a gas. Its boiling point is -29.8°C. It can easily be liquified. It is chemically intert. It is used in air-conditioning and in domestic refrigeratiors for cooling purposes (as refrigerant)

- 4. Osmotic pressure of a solution at a given temperature:
  - (a) increases with concentration
  - (b) decreases with concentration
  - (c) remains same
  - (d) initially increases and then decreases

Ans: (a) increases with concentration

According to Boyle-van't Hoff Law,  $\pi \propto c$  (at constant temp)

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- The coordination number of a central metal atom in a complex is determined by
  - (a) the number of ligands around a metal ionbonded by sigma and pi-bonds both
  - (b) the number of ligands around a metal ion bonded by pi-bonds
  - (c) the number of ligands around a metal ion bonded by sigma bonds
  - (d) the number of only anionic ligands bonded to the metal ion

Ans: (c) the number of ligands around a metal ion bonded 10.
by sigma bonds

The coordination number of central metal atom in a complex is equal to number of monovalent ligands, twice the number of bidentate ligands and so on, around the metal ion bonded by coordinate bonds. Hence coordination number = no. of  $\sigma$  bonds formed by metals with ligands.

- A catalyst is used
  - (a) only for increasing the velocity of the reaction
  - (b) for altering the velocity of the reaction
  - (c) Only for decreasing the velocity of the reaction
  - (d) All a, b and c are correct

Ans: (b) All a, b and c are correct

A catalyst is used for increasing or decreasing the velocity of a reaction.

- 7. Which of the following is non-electrolyte?
  - (a) NaCl
- (b) CaCl<sub>2</sub>
- (c) C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>
- (d) CH<sub>3</sub>COOH

Ans : (c)  $C_{12}H_{22}O_{11}$ 

The compounds which when dissolved in water, do not 12. produce ions, are called as non-electrolytes. Therefore,  $C_{12}H_{22}O_{11}$  is non-electrolyte because it does not give ions with water.

- The number of essential amino acids in man is
  - (a) 8

(b) 10

(c) 18

(d) 20

Ans: (b) 10

There are 20 amino acids in man out of which 10 amino acids are essential amino acids. These essential amino acids are supplied to our bodies by food which we take because they cannot be synthesised in the body. These are (1) valine (2) leucine (3) Isoleucine (4) Phenyl alanine (5) Threonine (6) Methionine (7) Lysine (8) Tryptho phone (9) Arginine (10) Histidine.

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- The oxidation state of Cr in K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> is:
  - (a) +5

(b) +3

(c) +6

(d) + 7

Ans: (c) + 6

$$K_2^{+1}Cr_2^x = +2 + 2x - 14 = 0$$

or

$$x = +6$$

- Fuel cells are preferred to other energy producing devices in space because of
  - (a) high efficiency
- (b) pollution free
- (c) less weight
- (d) all of these

Ans: (d) all of these

Fuel cell is preferred over others cell due to:

- They are pollution free.
- 2. They have high efficiency.
- They are of less mass.

Hence, (d) is the correct option.

11. The reaction given below is known as

 $C_2H_5ONa + IC_2H_5 \rightarrow C_2H_5OC_2H_5 + Nal$ 

- (a) Kolbe's synthesis
- (b) Wurtz' synthesis
- (c) Williamson's synthesis
- (d) Grignard's synthesis

Ans: (c) Williamson's synthesis

Preparation of ethers by reacting sodium ethoxide with alkyl halide is called Williamson synthesis.

- 12. Which of the following is incorrect?
  - (a) NaHSO<sub>3</sub> is used in detection of carbonyl compound.
  - (b) FeCl<sub>3</sub> is used in detection of phenolic group.
  - (c) Tollen reagent is used in detection of unsaturation.
  - (d) Fehling solution is used in detection of glucose.

Ans: (c) Tollen reagent is used in detection of unsaturation Tollen's reagent is used to detect of aldehydes. Tollen's reagent is an ammonical solutionnitrate. When aldehyde is added to Tollen's reagent, silver oxide is reduced to metallic silver which deposits as mirror.

 $RCHO + Ag_2O \longrightarrow RCOOH + 2Ag$ 

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

 Assertion: Nitrobenzene is used as a solvent in Friedel-Craft's reaction.

Reason: Fusion of nitrobenzene with solid KOH gives a low yield of a mixture of o-and p-nitrophenols.

- (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. Nitrobenzene is used as solvent in Friedel-Craft's reaction because its- $NO_2$  group deactivates benzene ring for electrophilic substitution.

Although the given statement of the reason is correct, it is not correct explanation of the given statement.

 Assertion: Alcohols are easily protonated as compared to phenols.

Reason: Alcohols undergo intermolecular hydrogen bonding due to the presence of highly electronegative oxygen.

- (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.

In phenols, the lone pairs of electrons on the oxygen atom are delocalised over the benzene ring due to resonance and hence are not easily available for protonation. On the other hand, in alcohols, the lone pairs of electrons on oxygen atom are localised due to the absence of resonance and hence are easily available for protonation.

 Assertion: The [Ni (en)<sub>3</sub>] Cl<sub>2</sub> (en = ethylene-diamine) has lower stability than [Ni (NH<sub>3</sub>)<sub>c</sub>]Cl<sub>2</sub>.

Reason: In [Ni (en)<sub>3</sub>]Cl<sub>2</sub>, the geometry of Ni is trigonal bipyramidal.

- (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: (d) Both the Assertion and Reason are incorrect.

[Ni (en)<sub>3</sub>] Cl<sub>2</sub> is more stable than [Ni(NH<sub>3</sub>)<sub>6</sub>]Cl<sub>2</sub> because ethylene-diamine is a bidentate ligand, hence it forms chelating ring with Ni<sup>2+</sup> ion.

 Assertion: p − O<sub>2</sub>N · C<sub>6</sub>H<sub>4</sub> · COCH<sub>3</sub> is prepared by Freidel Craft's acylation of nitrobenzene.

Reason: Nitrobenzene easily undergoes electrophilic substitution reaction.

- (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.

 ${\bf Ans}$  : (d) Both the Assertion and Reason are incorrect.

Nitrobenzene undergoes electrophilic substitution reaction

with difficulty because NO<sub>2</sub> group is electron withdrawing and therefore, it deactivates the benzene ring.

### SECTION-B

**Directions (Q. No. 17-21):** This section contains 5 questions with internal choice in two questions. The following questions are very short answer type and carry 2 marks each.

17. What do you mean by electrode potential?

#### Ans

The tendency of an electrode to lose or gain electrons is called electrode potential OR The electrical potential difference set up between the metal and its ions in the solution is called electrode potential.

 In first transition series density increases from titanium (Z=22) to copper (Z=29). Give reason.

#### Ans:

From titanium to copper atomic radius decreases but atomic mass increases, hence the density increases.

 Dipole moments of aldehydes and ketones are higher than those of alcohols Explain.

#### Ans:

In  $\pi$  electrons of  $\subset$ C=O are loosely held and hence can be shifted towards O atom more readily  $\left(\begin{array}{c} +\\ -\end{array} C - O \right)$  than more tightly held  $\sigma$ -electrons of C-O bond in alcohols. Thus, dipole moment of aldehydes and ketones are higher than alcohols.

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20. Write the equation relating [R], [R]<sub>0</sub> and reaction time t for a zero order reaction. [R] = concentration of reactant at time t and [R]<sub>0</sub> = initial concentration of reactant.

#### Ans:

Zero order reaction Rate constant  $k\!=\!\frac{[R]_0-[R]}{t}$  Example – Decomposition of  ${\rm NH}_3$ 

$$2NH_{3(g)} \xrightarrow[1130 \, K]{Pt} N_{2(g)} + 3H_{2(g)}$$

$$\mathrm{Rate} = k \left[ \mathrm{NH_3} \right]^0 = k$$

Hence, 
$$\frac{\Delta x}{\Delta t} = k$$
  
 $\Delta x = \Delta t \times k$ 

or

Draw the graph that relates the concentration R, of the reactant and t the reaction time for a zero order reaction.

Ans:

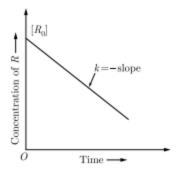


Figure : Variation in the Concentration vs Time Plot for a Zero Order Reaction

21. How will you convert benzene to chlorobenzene?

#### Ans

Benzene and its homologues react with halogens (Cl<sub>2</sub>, Br<sub>2</sub>, etc) in the presence of a Lewis acid (e.g., FeCl<sub>3</sub>/FeBr<sub>3</sub>) as catalyst to yield haloarenes (or aryl halides).

$$+ Cl_2 \xrightarrow{FeCl_5} + HCl$$

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### SECTION-C

**Directions (Q. No. 22-28):** This section contains 5 questions with internal choice in two questions. The following questions are short answer type and carry 3 marks each.

 Write a reaction which shows that aldehyde group is present in glucose.

#### Ans:

Glucose gets oxidised to six carbon carboxylic acid (gluconic acid) on reaction with a mild oxidising agent like bromine water. This indicates that the carboxyl group in present as an aldehydic group. Glucose is an aldose (having aldehyde group).

$$\begin{array}{c|c} \text{CHO} & \text{COOH} \\ \text{I} & \text{Br}_{\text{2}} \, \text{Water} \\ \text{I} & \text{CH}_{\text{2}} \text{OH} \\ \text{D-glucose} & \text{Gluconic acid} \end{array}$$

23. What is salt bridge? Give its functions.

#### Ans:

A salt bridge is a *U*- shaped tube containing concentrated solution of an inert electrolyte like KCl, KNO<sub>3</sub>, K<sub>2</sub>SO<sub>4</sub>, etc.

(An inert electrolyte is one whose ions do not take part in the redox reaction and also do not react with electrolyte used.)

#### Functions:

- 1. It prevents mixing of two electrolytes
- 2. It completes the electrical circuit
- It maintains the electrical neutrality of the solutions in both half cells.
- Explain the variation of molar conductivity with the change in the concentration of the electrolyte. Give reasons.

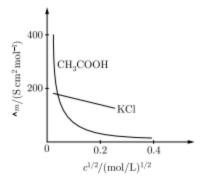
#### Ans

Molar conductivity of a solution at a given concentration is the conductance of the volume of solution containing one mole of electrolyte kept between two electrodes with area of cross section A and distance of unit length.

Molar conductivity,
$$\Lambda_m = \frac{\kappa A}{l}$$
  
 $\Lambda_m = \kappa \times V$  (Since,  $l = 1, A = V$ )  
 $V = \text{Volume containing 1 mole of}$ 

electrolyte

Molar conductivity increase with decrease in concentration of electrolyte (or) increase in dilution. This is due to total volume V of solution containing one mole of electrolyte also increases.



When concentration approaches to zero, the molar conductivity is known as limiting molar conductivity and its is represented by  $\Lambda_m^o$ 

For strong electrolytes molar conductivity is given by

$$\Lambda_m = \Lambda_m^o - A c^{1/2}$$

For weak electrolytes limiting molar conductivity is given by

$$\lambda_{AB^+} = \lambda_{A^+} + \lambda_{B^-}$$
 (Kohlrausch law)

25. Compare the stability of +2 oxidation state for the elements of the first transition series.

#### Ans:

Due to increase int he sum  $IE_1 + IE_2$  negative electrode

potential  $M^2/M$  decrease in the first transition series. Hence the stability of +2 oxidation state decrease form left to right (exception Mn and Zn). Mn has  $d^5$  in  $Mn^{2+}$  and Zn has  $d^{10}$  in  $Zn^{2+}$  due to stable configuration they have grater stability of +2 state.

- How will you distinguish between isopropyl alcohol and ethyl alcohol.
  - How will you distinguish between isopropyl alcohol and t-butyl alcohol.

#### Ans:

1.

- (a) Lucas Test: Isopropyl alcohol (2°) produces turbidity after five minutes ethyl alcohol (1°) do not produce turbidity at room temperature.
- (b) Victor Meyer's Test: Blood red colour indicates ethyl alcohol (1°). Blue colouration indicates Isopropyl alcohol (2°).

2.

- (a) Lucas Test: Isopropyl alcohol (2°) produces turbidity after five minutes t-butyl alcohol (3°) produces turbidity immediately.
- (b) Victor Meyer's Test: Blue colouration indicates isopropyl alcohol (2°). Colourless solution indicates t-butyl alcohol (3°).
- 27. Give reasons for the following :

Aniline is less basic than methylamine.

#### Ans:

If the lone pair of electrons over the nitrogen atom are easily available for donation. The base is stronger than that will not easily give lone pair of electrons. In aniline, nitrogen atom is bonded with the conjugate-system of benzene-ring which decreases the availability of lone pair of electrons over N-atom, while in case of methylamine (CH<sub>3</sub>NH<sub>2</sub>) no such resonance is possible, Hence CH<sub>3</sub>NH<sub>2</sub> donate its electron more easily than of aniline.

Thus methyl amine is a stronger base than aniline.

or

What is the basic structural difference between starch and cellulose?

#### Ans:

Cellulose is a predominant constitutent of cell wall of plant cells.

Cellulose is a straight polymer of  $\beta$ -D-glucose units which are joint by C<sub>1</sub> – C<sub>4</sub> glycosidic linkage starch is a polymer of  $\alpha$ -D-glucose units. Starch has two components Amylose and Amylopectin.

Amylose-Straight chain having C<sub>1</sub> − C<sub>4</sub> glycosidic linkage. Amylopectin-Chain is formed by C<sub>1</sub> − C<sub>4</sub> glycosidic linkage whereas branching occurs by C<sub>1</sub> − C<sub>6</sub> glycosidic linkage.

- 28. How will you convert (Give only chemical equation):
  - Propanamide to ethylamine
  - (ii) Ethyl amine to methane
  - (iii) Aniline to acetanilide.

#### Ans:

(i) 
$$CH_3CH_2CONH_2 \xrightarrow{Br_r+4KO_z} CH_3CH_2NH_2$$
  
 $\xrightarrow{Propanazzide} \xrightarrow{Propanazzide} CH_3CH_2NH_2$   
 $\xrightarrow{-K_LCO_h} \xrightarrow{Ethylamine}$ 

(iii)

$$\begin{array}{c|c} NH_2 & NHCOCH_3 \\ \hline \\ Aniline & CH_3COCl \\ \hline \\ Aniline & Acetanilide \\ \end{array}$$

or

Identify A, B and C in the following equations:

(i) 
$$C_6H_5NO_2 \xrightarrow{Sa/HC1} (A) + H_2O$$

(ii)

$$\begin{array}{c|c} & & & \\ & & & \\ \hline & & \\ & & & \\ \hline & & \\ \hline & & \\ & & \\ \hline & \\ \hline & &$$

#### Ans:

(i) 
$$C_6H_5NO_2 \xrightarrow{G(H)} C_6H_5NH_2 + 2H_2O$$
  
 $C_6H_5NH_2 + 2H_2O$ 

(ii)

NH<sub>2</sub>
N=NCl
$$+ 2H_2O + NaCl$$
Aniline
Benzene diazonium chloride (B)
$$Cl$$

$$+ CuCl_2/HCl$$
Chlorobenzene (C)

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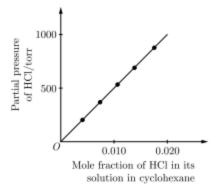
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### SECTION-D

**Directions (Q. No. 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. Many gases dissolve in water, Oxygen dissolves only to small extent which sustains all aquatic life. NH<sub>3</sub> and HCl are highly soluble in water. Solubility of gases increases with increase in pressure and decreases with increase in temperature.



Henry's law states "The partial pressure of the gas in vapour phase (p) is proportional to the mole fraction of the gas in the solution.  $p = K_H x$ ."

Where,  $K_H$  is Henry's law constant. If we draw a graph between partial pressure of the gas versus mole fraction of gas in solution, then we will get straight line as shown in graph.

Different gases have different  $K_H$  values of the same temperature. This suggests,  $K_H$  is a function of nature of gas.

Answer the following questions:

- (a) What is significance of K<sub>H</sub>?
- (b) What is slope of the line given in graph?
- (c) (i) Why does solubility of gas in liquid decreases with increase solution in cyclohexane in temperature?
  - (ii) Why are cold drinks filled with CO<sub>2</sub> at high pressure?

or

- (i) What is cause of anoxia at high altitude?
- (ii) Why do scuba divers take air diluted with helium?

#### Ans:

- (a) Higher the value of K<sub>H</sub>, lower will be solubility of gas
- (b) Slope of line = K<sub>H</sub> (Henry's law constant).
- (c) (i) K<sub>H</sub> increases with increase in temperature, therefore, solubility decreases.
  - (ii) It is because solubility of CO<sub>2</sub> in cold drink increases with increase in pressure.

0

- Low concentration of oxygen in blood and tissues at higher altitude causes people weak and unable to think clearly due to anoxia.
- (ii) To avoid bends (pains) as well as toxic effect of high concentration of N<sub>2</sub> in blood as N<sub>2</sub> is more soluble in blood than Helium.

Phenols are acidic in nature. In substituted phenols, electron withdrawing groups such as —NO<sub>2</sub>, enhances acidic strength of phenol, if —NO<sub>2</sub> group is present at o- and p-position. It is due to effective delocalisation of negative charge on phenoxide ion. Electron releasing groups, such as alkyl groups, do not favour formation of phenoxide ions resulting in decrease in acid strength e.g. cresols are less acidic than phenols.

The following table gives values of some Phenols and Ethanol.

Compound	Formula	$pK_a$
o-Nitrophenol	o-O <sub>2</sub> N—C <sub>6</sub> H <sub>4</sub> —OH	7.2
m-Nitrophenol	m-O <sub>2</sub> N—C <sub>6</sub> H <sub>4</sub> —OH	8.3
p-Nitrophenol	p-O <sub>2</sub> N—C <sub>6</sub> H <sub>4</sub> —OH	7.1
Phenol	C <sub>6</sub> H <sub>5</sub> OH	10.0
o-Cresol	o-CH <sub>3</sub> —C <sub>6</sub> H <sub>4</sub> —OH	10.2
m-Cresol	$m$ - $CH_3$ — $C_6H_4$ — $OH$	10.1
p-Cresol	p-CH <sub>3</sub> —C <sub>6</sub> H <sub>4</sub> —OH	10.2
Ethanol	C <sub>2</sub> H <sub>5</sub> OH	15.9

Answer the following questions:

- (a) From the above data, how many times phenol is more acidic than ethanol?
- (b) Out of phenols given in the table, which phenol is most acidic and why?

(c)

- Arrange the following in increasing order of acidic strength: phenol, o-nitro phenol, m-nitro phenol, p-nitro phenol, p-cresol
- (ii) Why are phenols less acidic than carboxylic acids?

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or

- Arrange 2, 4, 6-trinitro phenol, 3,5-dinitro phenol, 3-nitro phenol, phenol, propan-1-ol, 4-methyl phenol in increasing order of acidic character.
- Convert phenol to 2, 4, 6-trinitro phenol.

#### Ans:

- (a) Million times (10<sup>6</sup>).
- (b) p-nitro phenol is most acidic because p-nitro phenoxide ion is most stable.

(c)

- p-cresol < m-nitro phenol < o-nitro phenol < p-nitro phenol.
- (ii) It is because carboxylate ion is more stable than phenoxide ion as negative charge is delocalised over two oxygen atoms.

or

(i) Propan-1-ol < 4-methyl phenol < phenol < 3-nitro phenol < 3, 5-dinitro phenol < 2, 4, 6- Trinitro phenol.</li>

(ii)

OH

OH

$$+ 3HNO_3(conc.)$$

Conc.  $H_2SO_4$ 
 $NO_2$ 
 $NO_2$ 
 $2.4.6$ -Trinitrophenol

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# SECTION-E

**Directions (Q. No. 31-33):** The following questions are long answer type and carry 5 marks each. Two questions have an internal choice.

 Write a note of effect of substituents on the acidity of phenols.

#### Ans:

Any substituents which stabilizes the phenoxide ion by dispersal of negative change will increase the acidity of phenol while a group which destabilizes the phenoxide ion by intensifying negative charge will decrease the acidity of phenols.

 Electron withdrawing group (EWG) like -NO<sub>2</sub>, -CN, -X, -CHO increase the acidic strength. They stabilize the phenoxide ion by dispersing the negative charge.

 Electron donating group or releasing group (EDG) like -NH<sub>2</sub>, -OR, -R, -OH decrease the acidic strength. They destabilize the phenoxide ion by concentrating the negative charge.

 Both the effects are more significant, when the substituent is present at o-or p-position than m-position to the -OH group.

Comparison of acidic strength of nitrophenols: Nitro group has both -R effects and -I effect. -R effect predominates over the -I effect.

$$\begin{array}{c|ccccc} OH & OH & OH \\ O_2N & NO_2 & NO_2 & NO_2 \\ NO_2 & NO_2 & NO_2 & NO_2 \\ 2, 4, -6 - Trinitro & 2, 4 - Dinitro & 4 - Nitro & Phenol & Phe$$

$$\begin{array}{c|c} \text{OH} & \text{OH} & \text{OH} \\ \hline & \text{NO}_2 & \\ \text{2 - Nitrophenol} & \\ \text{(having intermolecular } \\ \text{H-bonding)} & \\ \end{array} > \begin{array}{c|c} \text{OH} & \\ \text{OH} & \\ \text{OH} & \\ \text{NO}_2 & \\ \end{array}$$

Greater the number of electron withdrawing groups o-and p-position, acidic is the phenol.

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32. What do you mean by vapour pressure? What happens to the vapour pressure, when (i) volatile solute is dissolved in solution. (ii) non-volatile solute is dissolved in solution?

#### Ans:

Vapour Pressure: The pressure exerted by the vapours of a liquid which are in equilibrium with it at a given temperature is called vapour pressure.

1. When volatile solute is dissolved in solution:

Let two volatile liquids 1 and 2 have mole fractions as  $x_1$  and  $x_2$ , respectively. If  $p_1$  and  $p_2$  are vapour pressure of these components in the solution, then according to Raoult's law

For component 1,  $p_1 \propto x_1$  and  $p_1 = p_1^{\circ} x_1$ 

Similarly, for component 2,  $p_2 = p_2^{\circ} x_2$ 

where  $p_1^{\circ}$  is the vapour pressure of pure component 1 and  $p_2^{\circ}$  is the vapour pressure of pure component 2 at same temperature.

According to Dalton's law of partial pressure, the total pressure ( $p_{\text{total}}$ ) over the solution phase in the container will be the sum of the partial pressures of the components of the solution and is given as,

From this equation, following conclusions can be drawn

- (a) The total vapour pressure over the solution can be related to the mole fraction of any one component.
- (b) Total vapour pressure over the solution varies linearly with the mole fraction of component 2.
- (c) The total vapour pressure over the solution increases or decreases with increase in mole fraction of

component 1, depending upon the vapour pressures of the pure components 1 and 2.

2. When Non-volatile solute is dissolved in solution: The vapour pressure of the solution of a non-volatile solute at a given temperature is lower than the vapour pressure of the pure solvent at the same temperature. This decrease in vapour pressure occurs because in solid-liquid solution, the surface has both solute and solvent molecules, so the fraction of the surface covered by solvent molecules gets reduced, so the number of solvent molecules escaping from the surface is reduced resulting in lowering the vapour pressure.

In a binary solution (when solute is non-volatile and non-electrolyte, only the solvent molecules are present in the vapour phase and contribute to vapour pressure), if  $p_1$  is the vapour pressure of the solvent,  $x_1$  is its mole fraction and  $p_1^0$  is its vapour pressure in the pure state, then according to Raoult's law,

$$p_1 \propto x_1$$
 and  $p_1 = x_1 p_1^{\circ}$ 

The proportionally constant is equal to the vapour pressure of pure solvent,  $p_1^{\circ}$ .

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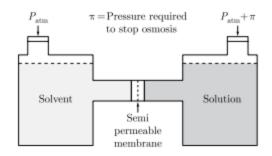
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or

Define osmotic pressure. Prove that osmotic pressure is a molecular property.

#### Ans:

Osmotic Pressure: The excess pressure which must be applied to a solution to prevent the passage of solvent into it through a semipermeable membrane is called osmotic pressure. It is shown in figure. It is a colligative property as it depends on the number of solute molecules (C) of the solution at a given temperature T. Thus,



$$\pi \propto C$$

$$\pi = CRT$$

where,  $\pi = \text{osmotic pressure}$ 

and R = gas constant

But,  $C = \frac{n}{V}$ 

and 
$$n = \frac{W}{M}$$

where, n is the number of moles of solute dissolved in V litre of solution, W is the weight of solute and M is its molar mass.

Therefore,

$$\pi = \frac{WRT}{VM}$$

$$M_2 = \frac{WRT}{V\pi}$$

- 33. Write the following:
  - 1. Allylic halogenation
  - Markovnikov's rule
  - Kharasch effect
  - 4. Swarts reaction
  - 5. Finkelstein reaction
  - 6. Hundsdiecker reaction
  - 7. Sandmeyer reaction
  - 8. Preparation of Iodobenzene
  - 9. Balz-Schiemann reaction
  - 10. Gattermann reaction.

#### Ans:

 Allylic Halogenation: Reactions in which halogenation occurs at the allylic position of an alkene are called allylic halogenation reaction. It occurs in alkene other then ethene.

#### Example:

$$CH_3 - CH = CH_2 + Cl_2 \longrightarrow$$

$$Cl - CH_2 - CH = CH_2 + HCl$$
  
 $_{3-Chloropeop-1-ene}$ 

 Markovnikov's Rule: The addition of unsymmetrical reagents like HX, H<sub>2</sub>O etc to unsymmetrical alkenes occurs in such a way that the negative part of adding molecule goes to that carbon atom of the double bond which carries lesser number of hydrogen atoms.

#### Example:

$$CH_3CH = CH_2 + \stackrel{\delta+\delta-}{HI} \rightarrow CH_3 \stackrel{C}{CH_2} CH_2 I + CH_2 \stackrel{C}{CHI} CH_3$$

 Kharasch Effect: In presence of peroxide like benzoyl peroxide (C<sub>6</sub>H<sub>6</sub>CO - O - O - COC<sub>6</sub>H<sub>5</sub>), the addition of HBr to unsymmetrical alkenes takes place opposite to Markovnikov's rule. This is known as Peroxide effect or Kharasch effect.

#### Example:

$$CH_3CH = CH_2 + HBr \xrightarrow{(C_0H_2COO)_2} CH_3CH_2 - CH_2Br_{1-Brounopropane}$$

 Swarts Reaction: Synthesis of alkyl fluoride (fluoroalkane) by heating an alkyl chloride/bromide in the presence of metallic fluoride like AgF, Hg<sub>2</sub>F<sub>2</sub> or SbF<sub>3</sub> is called Swarts reaction.

$$H_3C - Br + AgF \longrightarrow H_3C - F + AgBr$$

- Finkelstein Reaction: Preparation of alkyl iodide by the reaction of alkyl chlorides/bromides with NaI in dry acetone is known as finkelstein reaction.
- 6. Hundsdiecker Reaction:

$$CH_3CH_2 - Br + CO_2 + AgBr$$
Bromoethane

#### 7. Sandmeyer Reaction:

$$\begin{array}{c} \overset{+}{\operatorname{N}}\equiv\operatorname{NCl^{-}} & \overset{-}{\operatorname{Cl}} & \overset{-}{\operatorname{Chlorobenzene}} \\ & \overset{+}{\operatorname{Chlorobenzene}} & \overset{-}{\operatorname{Br}} & \overset{-}{\operatorname{Br}} \\ & \overset{-}{\operatorname{Chlorobenzene}} & \overset{-}{\operatorname{Br}} & \overset{-}{\operatorname{H}} \\ & \overset{-}{\operatorname{Chlorobenzene}} & \overset{-}{\operatorname{Bromobenzene}} \end{array}$$

#### 8. Preparation of Iodobenzene:

$$N \equiv NCl^ + KI \longrightarrow Iodobenzene$$
 $+ N_2 + K^+Cl^-$ 
Benzenediazonium
chloride

#### 9. Balz-schiemann Reaction:

#### 10. Gattermann Reaction:

$$N \equiv NCl^{-}$$
 $C_{N/HB_{p}}$ 
 $C_{N/$ 

OI

Draw the structures of major mono-halo products in each of the following:

(i) 
$$OH + SOCl_2 \longrightarrow$$

(ii) 
$$O_2N$$
  $CH_2CH_3$   $Br_2$ , heat or uv light

(iii) 
$$CH_2OH + HCl \xrightarrow{heat}$$

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

Ans:

$${\rm (i)} \qquad \qquad {\rm Cl}$$

Chlorocyclohexane

$$\begin{array}{ccc} \text{(ii)} & & \text{CH(Br)CH}_3 \\ & & \text{O}_2\text{N} & & & \\ & & & \text{4-(1-Bromoethyl)} \\ & & & \text{nitrobenzene} \end{array}$$

$$\begin{array}{c} \text{(iv)} & \overbrace{\hspace{1cm}}^{\text{CH}_3} \\ \\ \text{1-Iodo-1-} \\ \\ \text{methylcyclohexane} \end{array}$$

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