# CBSE Class–12 Chemistry
# NCERT Solutions
# Chapter – 02
# Solutions

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## In-text question

**1. Calculate the mass percentage of benzene ( $C_6H_6$ ) and carbon tetrachloride ( $CCl_4$ ) if 22 g of benzene is dissolved in 122 g of carbon tetrachloride.**

**Ans.** Mass percentage of $C_6H_6 = \frac{\text{Mass of } C_6H_6}{\text{Total mass of the solution}} \times 100\%$

$$= \frac{\text{Mass of } C_6H_6}{\text{Mass of } C_6H_6 + \text{Mass of } CCl_4} \times 100\%$$

$$= \frac{22}{22 + 122} \times 100\%$$

= 15.28%

Mass percentage of $CCl_4 = \frac{\text{Mass of } CCl_4}{\text{Total mass of the solution}} \times 100\%$

$$= \frac{\text{Mass of } CCl_4}{\text{Mass of } C_6H_6 + \text{Mass of } CCl_4}$$

$$= \frac{122}{22 + 122} \times 100\%$$

=84.72%

Alternatively, Mass percentage of $CCl_4$ = (100 - 15.28) %

= 84.72%

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**2. Calculate the mole fraction of benzene in solution containing 30% by mass in carbon tetrachloride.**

**Ans.** Let the total mass of the solution be 100 g and the mass of benzene be 30 g.

∴Mass of carbon tetrachloride = (100 - 30) g

= 70 g

Molar mass of benzene ($C_6H_6$) = (6× 12 + 6× ) $g\ mol^{-1}$

= 78 $g\ mol^{-1}$

∴Number of moles of $C_6H_6 = \frac{30}{78} mol$

= 0.3846 mol

Molar mass of carbon tetrachloride ($CCl_4$ ) = 1× 12 + 4× 355

= 154 $g\ mol^{-1}$

∴Number of moles of $CCl_4 = \frac{70}{154} mol$

= 0.4545 mol

Thus, the mole fraction of $C_6H_6$ is given as:

$$\frac{\text{Number of moles of } C_6H_6}{\text{Number of moles of } C_6H_6 + \text{Number of moles of } CCl_4}$$

$$= \frac{0.3846}{0.3846 + 0.4545}$$

= 0.458

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**3. Calculate the molarity of each of the following solutions: (a) 30 g of $Co(NO_3)_2 .6H_2O$ in 4.3 L of solution (b) 30 mL of 0.5 M $H_2SO_4$ diluted to 500 mL.**

**Ans.** Molarity is given by:

$$\text{Molarity}=\frac{\text{Moles of solute}}{\text{Volume solution in litre}}$$

**(a)** Molar mass of $Co(NO_3)_2$ = 59 + 2 (14 + 3 $\times$ 16) + 6 $\times$ 18

= 291 $\text{g mol}^{-1}$

Therefore, Moles of $Co(NO_3)_2$ = 30/291 mol

= 0.103 mol

Therefore, molarity $=\frac{0.103\text{mol}}{4.3\text{ L}}$

= 0.023 M

**(b)** Number of moles present in 1000 mL of 0.5 M $H_2SO_4 = 0.5\text{ mol}$

∴Number of moles present in 30 mL of 0.5 M $H_2SO_4 = \frac{0.5\times30}{1000}\text{ mol}$

= 0.015 mol

Therefore, molarity$=\frac{0.015}{0.5\text{L}}\text{mol}$

= 0.03 M

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**4. Calculate the mass of urea ( $NH_2CONH_2$) required in making 2.5 kg of 0.25 molal aqueous solution.**

**Ans.** Molar mass of urea $NH_2CONH_2 = 2(1\times14+2\times1)+1\times12+1\times16$ = 60 $\text{g mol}^{-1}$

0.25 molar aqueous solution of urea means:

1000 g of water contains 0.25 mol = $(0.25\times60)\text{g}$ of urea

= 15 g of urea

That is,

(1000 + 15) g of solution contains 15 g of urea

Therefore, 2.5 kg (2500 g) of solution contains = $\frac{15\times 2500}{1000+15}$ g

= 36.95 g

= 37 g of urea (approximately)

Hence, mass of urea required = 37 g

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**5. Calculate (a)molality (b)molarity and (c)mole fraction of KI if the density of 20% (mass/mass) aqueous KI is $1.202\ \text{g ml}^{-1}$.**

**Ans. (a)** Molar mass of KI = 39 + 127 = 166 $\text{g mol}^{-1}$

20% (mass/mass) aqueous solution of KI means 20 g of KI is present in 100 g of solution.

That is,

20 g of KI is present in (100 - 20) g of water = 80 g of water

Therefore, molality of the solution = $\frac{\text{Moles of KI}}{\text{Mass of water in kg}}$

$$\frac{\frac{20}{166}}{0.08}\ \text{m}$$

= 1.506 m

= 1.51 m (approximately)

**(b)** It is given that the density of the solution = $1.202\ \text{g ml}^{-1}$

Therefore, Volume of 100 g solution = $\frac{\text{Mass}}{\text{Density}}$

= $\frac{100\text{g}}{1.202\text{ g ml}^{-1}}$

= 83.19 mL

= $83.19 \times 10^{-3}\text{L}$

Therefore, molarity of the solution = $\frac{\frac{20}{166}\text{mol}}{83.19 \times 10^{-3}\text{L}}$

= 1.45 M

**(c)** Moles of KI = $\frac{20}{166} = 0.12\text{mol}$

Moles of water = $\frac{80}{18} = 4.44\text{mol}$

Therefore, mole fraction of KI = $\frac{\text{Moles of KI}}{\text{Moles of KI} + \text{Moles of water}}$

= $\frac{0.12}{0.12 + 4.44}$

= 0.0263

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**6. $H_2S$, a toxic gas with rotten egg like smell, is used for the qualitative analysis. If the solubility of $H_2S$ in water at STP is 0.195 m, calculate Henry's law constant.**

**Ans.** It is given that the solubility of $H_2S$ in water at STP is 0.195 m, i.e., 0.195 mol of $H_2S$ is dissolved in 1000 g of water.

Moles of water = $\frac{1000\text{g}}{18\text{g mol}^{-1}}$

= 55.56 mol

∴Mole fraction of $H_2S$, $x$ = $\frac{\text{Moles of } H_2S}{\text{Moles of } H_2S + \text{Moles of wtaer}}$

= $\frac{0.195}{0.195 + 55.56}$

= 0.0035

At STP, pressure (*p*) = 0.987 bar

According to Henry's law:

*p*= KH*x*

$$K_H = \frac{p}{x}$$

$$= \frac{0.987}{0.0035} \text{bar}$$

= 282 bar

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**7. Henry's law constant for $CO_2$ in water is 1.67 x $10^8$ Pa at 298 K. Calculate the quantity of $CO_2$ in 500 mL of soda water when packed under 2.5 atm $CO_2$ pressure at 298 K.**

**Ans.** It is given that:

KH = 1.67 x $10^8$ Pa

$P_{CO_2}$ = 2.5 atm = 2.5 x 1.01325 x $10^5$

= 2.533 x $10^5$ Pa

According to Henry's law:

$P_{CO2} = K_H x$

x= $\frac{2.533125\times10^5}{1.67\times10^8}$

= 0.00152

We can write, $x=\frac{n_{CO_2}}{n_{CO_2}+n_{H_2O}}\approx\frac{n_{CO_2}}{n_{H_2O}}$

[Since, $n_{CO_2}$ is negligible as compared to $n_{H_2O}$ ]

In 500 mL of soda water, the volume of water = 500 mL

[Neglecting the amount of soda present]

We can write:

500 mL of water = 500 g of water

= $\frac{500}{18}$ mol of water

= 27.78 mol of water

Now, $\frac{n_{CO_2}}{n_{H_2O}}=x$

$$\frac{n_{CO_2}}{27.78}=0.00152$$
$$n_{CO_2}=0.042\,\text{mol}$$

Hence, quantity of $CO_2$ in 500 mL of soda water = $(0.042\times44)$ g

= 1.848 g

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**8. The vapour pressure of pure liquids A and B are 450 and 700 mm Hg respectively, at 350 K. Find out the composition of the liquid mixture if total vapour pressure is 600 mm Hg. Also find the composition of the vapour phase.**

**Ans.** It is given that:

$p_A^0$ = 450 mm of Hg

$p_B^0$ = 700 mm of Hg

*P* total= 600 mm of Hg

From Raoult's law, we have:

$$p_A = p_A^0 x_A$$
$$p_B = p_B^0 x_B = p_B^0 (1 - x_A)$$

Therefore, total pressure, $p_{total} = p_A + p_B$

$$p_{total} = p_A^0 x_A + p_B^0 (1 - x_A)$$
$$p_{total} = p_A^0 x_A + p_B^0 - p_B^0 x_A$$
$$p_{total} = \left(p_A^0 - p_B^0\right) x_A + p_B^0$$

600= (450-700)$x_A$ + 700

-100 = -250 $x_A$

$x_A$ = 100/250 = 0.4

Therefore, $x_B = 1 - x_A$

= 1 - 0.4

= 0.6

Now, $p_A = p_A^0 x_A$

= $450 \times 0.4$

= 180 mm of Hg

$$p_B = p_B^0 x_B$$

= $700 \times 0.6$

= 420 mm of Hg

Now, in the vapour phase:

Mole fraction of liquid A = $\frac{p_A}{p_A + p_B}$

$$\frac{180}{180+420}$$

$$= \frac{180}{600}$$

= 0.30

And, mole fraction of liquid B = 1 - 0.30 = 0.70

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**9. Vapour pressure of pure water at 298 K is 23.8 mm Hg. 50 g of urea ($NH_2CONH_2$) is dissolved in 850 g of water. Calculate the vapour pressure of water for this solution and its relative lowering.**

**Ans.** It is given that vapour pressure of water, $p_1^0 = 23.8\text{mm}$ of Hg

Weight of water taken, $w_1 = 850 \text{ g}$

Weight of urea taken, $w_2 = 50 \text{ g}$

Molecular weight of water, $M_1 = 18 \text{ g mol}^{-1}$

Molecular weight of urea, $M_2 = 60\text{g mol}^{-1}$

Now, we have to calculate vapour pressure of water in the solution. We take vapour pressure as *p*1.

Now, from Raoult's law, we have:

$$\frac{p_1^0 - p_1}{p_1^0} = \frac{n_2}{n_1 + n_2}$$

$$\Rightarrow \frac{p_1^0 - p_1}{p_1^0} = \frac{\frac{w_2}{M_2}}{\frac{w_1}{M_1} + \frac{w_2}{M_2}}$$

$$\frac{23.8 - p_1}{23.8} = \frac{\frac{50}{60}}{\frac{850}{18} + \frac{50}{60}}$$

$$\frac{23.8 - p_1}{23.8} = \frac{0.83}{47.22 + 0.83}$$

$$\frac{23.8 - p_1}{23.8} = 0.0173$$

$$p_1 = 23.4 \text{mm of Hg}$$

Hence, the vapour pressure of water in the given solution is 23.4 mm of Hg and its relative lowering is 0.0173.

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**10. Boiling point of water at 750 mm Hg is $99.63°C$ . How much sucrose is to be added to 500 g of water such that it boils at $100°C$ . Molal elevation constant for water is $0.52 \, K \, Kg \, mol^{-1}$.**

**Ans.** Here, elevation of boiling point $\Delta Tb$ = (100 + 273) – (99.63 + 273)

= 0.37 K

Mass of water, $w_1 = 500 \text{ g}$

Molar mass of sucrose ($C_{12}H_{22}O_{11}$ ), $M_2 = 11 \times 12 + 22 \times 1 + 11 \times 16$

= $342 \text{ g mol}^{-1}$

Molal elevation constant, *Kb* = $0.52 \text{ K kg mol}^{-1}$

We know that:

$$\Delta T_b = \frac{K_b \times 1000 \times w_2}{M_2 \times w_1}$$

$$w_2 = \frac{\Delta T_b \times M_2 \times w_1}{K_b \times 1000}$$

$$= \frac{0.37 \times 342 \times 500}{0.52 \times 1000}$$

= 121.67 g (approximately)

Hence, 121.67 g of sucrose is to be added.

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**11. Calculate the mass of ascorbic acid (Vitamin C, $C_6H_8O_6$) to be dissolved in 75 g of acetic acid to lower its melting point by $1.5\,^\circ C \cdot Kf = 3.9\,K\,kg\,mol^{-1}$.**

**Ans.** Mass of acetic acid, $w_1 = 75$ g

Molar mass of ascorbic acid $(C_6H_8O_6)$, $M_2 = 6 \times 12 + 8 \times 1 + 6 \times 16$

= $176\ g\ mol^{-1}$

Lowering of melting point, $\Delta Tf = 1.5\ K$

We know that:

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

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

$$= \frac{1.5 \times 176 \times 75}{3.9 \times 1000}$$

= 5.08 g (approx)

Hence, 5.08 g of ascorbic acid is needed to be dissolved.

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**12. Calculate the osmotic pressure in pascals exerted by a solution prepared by dissolving 1.0 g of polymer of molar mass 185,000 in 450 mL of water at $37°C$.**

**Ans.** It is given that:

Volume of water, $V$= 450 mL = 0.45 L

Temperature, $T$ = (37 + 273) K = 310 K

Number of moles of the polymer, $n = \frac{1}{185000}\,\text{mol}$

We know that:

Osmotic pressure, $\pi = \frac{n}{V}RT$

$$= \frac{1}{185000}\,\text{mol} \times \frac{1}{0.45} \times 8.314 \times 10^{3}\,\text{Pa}\,\text{L}\,\text{K}^{-1}\,\text{mol}^{-1} \times 310\text{K}$$

= 30.98 Pa

= 31 Pa (approximately)

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### Chapter End Questions

**1. Define the term solution. How many types of solutions are formed? Write briefly about each type with an example.**

**Ans.** Homogeneous mixtures of two or more than two components is known as solution. The component present in large amount is known as Solvent and the one present in less amount is known as solute.

There are three types of solutions.

**(i) Gaseous solution:**

The solution in which the solvent is a gas is called a gaseous solution. In these solutions, the solute may be liquid, solid, or gas. For example, a mixture of oxygen and nitrogen gas is a gaseous solution.

**(ii) Liquid solution:**

The solution in which the solvent is a liquid is known as a liquid solution. The solute in these solutions may be gas, liquid, or solid.

For example, a solution of ethanol in water is a liquid solution.

**(iii) Solid solution:**

The solution in which the solvent is a solid is known as a solid solution. The solute may be gas, liquid or solid. For example, a solution of copper in gold is a solid solution.

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**2. Give an example of solid solution in which the solute is a gas.**

**Ans.** In case a solid solution is formed between two substances , an interstitial solid solution (smaller size particle will occupy interstitial position in solid crystal) will be formed. For example, a solution of hydrogen in palladium is a solid solution in which the solute is a gas.

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**3. Define the following terms:**

**(i) Mole fraction**

**(ii) Molality**

**(iii) Molarity**

**(iv) Mass percentage.**

**Ans. (i) Mole fraction:**

The mole fraction of a component in a mixture is defined as the ratio of the number of moles of the component to the total number of moles of all the components in the mixture.

i.e.,

Mole fraction of a component = $\frac{\text{Number of moles of the component}}{\text{Total number of moles of all components}}$

Mole fraction is denoted by ‘x’.

If in a binary solution, the number of moles of the solute and the solvent are *nA* and *nB* respectively, then the mole fraction of the solute in the solution is given by,

$$x_A = \frac{n_A}{n_A + n_B}$$

Similarly, the mole fraction of the solvent in the solution is given as:

$$x_B = \frac{n_B}{n_A + n_B}$$

**(ii) Molality**

Molality (m) is defined as the number of moles of the solute per kilogram of the solvent. It is expressed as:

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

**(iii) Molarity**

Molarity (M) is defined as the number of moles of the solute dissolved in one Litre of the solution.

It is expressed as:

Molarity (M) = $\frac{\text{Moles of solute}}{\text{Volume of solvent in Litre}}$

**(iv) Mass percentage:**

The mass percentage of a component of a solution is defined as the mass of the solute in grams present in 100 g of the solution. It is expressed as:

Mass % of a component = $\dfrac{\text{Mass of component in solution}}{\text{Total mass of solution}} \times 100$

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**4. Concentrated nitric acid used in laboratory work is 68% nitric acid by mass in aqueous solution. What should be the molarity of such a sample of the acid if the density of the solution is $1.504\,\text{g mL}^{-1}$?**

**Ans.** Concentrated nitric acid used in laboratory work is 68% nitric acid by mass in an aqueous solution. This means that 68 g of nitric acid is dissolved in 100 g of the solution.

Molar mass of nitric acid $\left(HNO_3\right) = 1\times1 + 1\times14 + 3\times16 = 63\ \text{g mol}^{-1}$

Then, number of moles of $HNO_3 = \dfrac{68}{63}\,\text{mol}$

= 1.079 mol

Given,

Density of solution = $1.504\ \text{g mL}^{-1}$

Therefore, Volume of 100 g solution = $\dfrac{100}{1.504}\,\text{mL}$

= 66.49 mL

= $66.49\times10^{-3}\,\text{L}$

Molarity of solution = $\dfrac{1.079\,\text{mol}}{66.49\times10^{-3}\,\text{L}}$

= 16.23 M

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**5. A solution of glucose in water is labelled as 10% w/w, what would be the molality and mole fraction of each component in the solution? If the density of solution is $1.2\,\text{g ml}^{-1}$, then what will be the molarity of the solution?**

**Ans.** 10% w/w solution of glucose in water means that 10 g of glucose in present in 100 g of the solution i.e., 10 g of glucose is present in (100 - 10) g = 90 g of water.

Molar mass of glucose $\left(C_6H_{12}O_6\right) = 6\times12+12\times1+6\times16 = 180\ g\ mol^{-1}$

Then, number of moles of glucose = $\frac{10}{180}\text{mol}$

= 0.056 mol

Molality of solution = $\frac{0.056\,\text{mol}}{0.09\,\text{kg}}$ = 0.62 m

Number of moles of water = $\frac{90\,g}{18\,g\,mol^{-1}}$

= 5 mol

Mole fraction of glucose $(x_g) = \frac{0.056}{0.056+5}$

= 0.011

And, mole fraction of water $x_w = 1 - x_g$

= 1 - 0.011

= 0.989

If the density of the solution is $1.2\,g\,ml^{-1}$, then the volume of the 100 g solution can be given as:

$$=\frac{100\,g}{1.2\,g\,ml^{-1}}$$

= 83.33 mL

= $83.33\times10^{-3}\,L$

$\therefore$ Molarity of the solution = $\frac{0.056\,\text{mol}}{83.33\times10^{-3}\,\text{L}}$

= 0.67 M

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**6. How many mL of 0.1 M HCl are required to react completely with 1 g mixture of $Na_2CO_3$ and $NaHCO_3$ containing equimolar amounts of both?**

**Ans.** Let the amount of $Na_2CO_3$ in the mixture be $x$ g.

Then, the amount of $NaHCO_3$ in the mixture is (1 - $x$) g.

Molar mass of $Na_2CO_3 = 2\times23+1\times12+3\times16$

= $106\text{ g mol}^{-1}$

$\therefore$ Number of moles $Na_2CO_3$ = $\frac{x}{106}\text{mol}$

Molar mass of $NaHCO_3 = 1\times23+1\times1\times12+3\times16$

= $84\text{ g mol}^{-1}$

Number of moles of $NaHCO_3$ = $\frac{1-x}{84}\text{mol}$

According to the question,

$$\frac{x}{106}=\frac{1-x}{84}$$

$\Rightarrow 84x = 106 - 106x$

$\Rightarrow 190x = 106$

$\Rightarrow x = 0.5579$

Therefore, number of moles of $Na_2CO_3$ = $\frac{0.5579}{106}$ mol

= 0.0053 mol

And, number of moles of $NaHCO_3$ = $\frac{1-0.5579}{84}$

= 0.0053 mol

HCl reacts with $Na_2CO_3$ and $NaHCO_3$ according to the following equation.

$$\underset{2mol}{2HCl}+\underset{1mol}{Na_2CO_3} \rightarrow 2NaCl + H_2O + CO_2$$

$$\underset{1mol}{HCl}+\underset{1mol}{NaHCO_3} \rightarrow NaCl + H_2O + CO_2$$

1 mol of $Na_2CO_3$ reacts with 2 mol of HCl.

Therefore, 0.0053 mol of $Na_2CO_3$ reacts with $2 \times 0.0053$ mol = 0.0106 mol of HCl.

Similarly, 1 mol of $NaHCO_3$ reacts with 1 mol of HCl.

Therefore, 0.0053 mol of $NaHCO_3$ reacts with 0.0053 mol of HCl.

Total moles of HCl required = (0.0106 + 0.0053) mol

= 0.0159 mol

In 0.1 M of HCl,

0.1 mol of HCl is preset in 1000 mL of the solution.

Therefore, 0.0159 mol of HCl is present in $\frac{1000 \times 0.0159}{0.1}$ mol

= 159 mL of the solution

Hence, 159 mL of 0.1 M of HCl is required to react completely with 1 g mixture of $Na_2CO_3$

and $NaHCO_3$, containing equimolar amounts of both.

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**7. A solution is obtained by mixing 300 g of 25% solution and 400 g of 40% solution by mass. Calculate the mass percentage of the resulting solution.**

**Ans.** Total amount of solute present in the mixture is given by,

$$300\times\frac{25}{100}+400\times\frac{40}{100}$$

= 75 + 160

= 235 g

Total amount of solution = 300 + 400 = 700 g

Therefore, mass percentage (w/w) of the solute in the resulting solution, $=\frac{235}{700}\times100\%$

= 33.57%

And, mass percentage (w/w) of the solvent in the resulting solution,

= (100 - 33.57) %

= 66.43%

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**8. An antifreeze solution is prepared from 222.6 g of ethylene glycol ($C_2H_6O_2$) and 200 g of water. Calculate the molality of the solution. If the density of the solution is $1.072\,g\,mL^{-1}$, then what shall be the molarity of the solution?**

**Ans.** Molar mass of ethylene glycol $\left[C_2H_4(OH)_2\right]=2\times12+6\times1+2\times16$

= $62\ g\,mol^{-1}$

Number of moles of ethylene glycol $\frac{222.6\,g}{62\,g\,mol^{-1}}$

= 3.59 mol

Therefore, molality of the solution = $\frac{3.59\,\text{mol}}{0.200\,\text{kg}}$

= 17.95 m

Total mass of the solution = (222.6 + 200) g

= 422.6 g

Given,

Density of the solution = 1.072 g mL - 1

Therefore, Volume of the solution = $\frac{422.6\,\text{g}}{1.072\,\text{g mL}^{-1}}$

= 394.22 mL

= $0.3942 \times 10^{-3}\,\text{L}$

Molarity of the solution = $\frac{3.59\,\text{mol}}{0.39422 \times 10^{-3}\,\text{L}}$

= 9.11 M

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**9. A sample of drinking water was found to be severely contaminated with chloroform ( $CHCl_3$ ) supposed to be a carcinogen. The level of contamination was 15 ppm (by mass):**

**(i) express this in percent by mass**

**(ii) determine the molality of chloroform in the water sample.**

**Ans. (i)** 15 ppm (by mass) means 15 parts per million ($10^6$) of the solution.

Therefore, percent by mass = $\frac{15}{10^6} \times 100\%$

= $1.5\times10^{-3}\%$

**(ii)** Molar mass of chloroform $\left(CHCl_3\right)=1\times12+1\times1+3\times35.5$

= $119.5\ \text{g mol}^{-1}$

Now, according to the question,

15 g of chloroform is present in 106 g of the solution.

i.e., 15 g of chloroform is present in (106 - 15) per 106 g of water.

Therefore, Molality of the solution = $\dfrac{\dfrac{15}{119.5}\text{mol}}{10^6\times10^{-3}\text{Kg}}$

= $1.26\times10^{-4}\ \text{m}$

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**10. What role does the molecular interaction play in a solution of alcohol and water?**

**Ans.** In pure alcohol and water, the molecules are held tightly by a strong hydrogen bonding. The interaction between the molecules of alcohol and water is weaker than alcohol-alcohol and water-water interactions. As a result, when alcohol and water are mixed, the intermolecular interactions become weaker and the molecules can easily escape. This increases the vapour pressure of the solution, which in turn lowers the boiling point of the resulting solution.

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**11. Why do gases always tend to be less soluble in liquids as the temperature is raised?**

**Ans.** Solubility of gases in liquids decreases with an increase in temperature. This is because dissolution of gases in liquids is an exothermic process.

$$\text{Gas}+\text{Liquid}\rightarrow\text{Solution}+\text{Heat}$$

Therefore, when the temperature is increased, heat is supplied and the equilibrium shifts backwards ( exothermic reactions are favoured at low temp only according to Le-Chaterlie Principle )thereby decreasing the solubility of gases.

**12. State Henry's law and mention some important applications?**

**Ans.** Henry's law states that partial pressure of a gas in the vapour phase is proportional to the mole fraction of the gas in the solution. If *p* is the partial pressure of the gas in the vapour phase and *x* is the mole fraction of the gas, then Henry's law can be expressed as:

$$p = K_H x$$

Where, $K_H$ is Henry's law constant

Some important applications of Henry's law are mentioned below.

**(i)** Bottles are sealed under high pressure to increase the solubility of $CO_2$ in soft drinks and soda water.

**(ii)** Henry's law states that the solubility of gases increases with an increase in pressure. Therefore, when a scuba diver dives deep into the sea, the increased sea pressure causes the nitrogen present in air to dissolve in his blood in great amounts. As a result, when he comes back to the surface, the solubility of nitrogen again decreases and the dissolved gas is released, leading to the formation of nitrogen bubbles in the blood. This results in the blockage of capillaries and leads to a medical condition known as 'bends' or 'decompression sickness'.

Hence, the oxygen tanks used by scuba divers are filled with air and diluted with helium to avoid bends.

**(iii)** The concentration of oxygen is low in the blood and tissues of people living at high altitudes such as climbers. This is because at high altitudes, partial pressure of oxygen is less than that at ground level. Low-blood oxygen causes climbers to become weak and disables them from thinking clearly. These are symptoms of anoxia.

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**13. The partial pressure of ethane over a solution containing $6.56 \times 10^{-3}$ g of ethane is 1 bar. If the solution contains $5.00 \times 10^{-2}$ g of ethane, then what shall be the partial pressure of the gas?**

**Ans.** Molar mass of ethane $(C_2H_6) = 2\times12+6\times1$

= $30\ \text{g mol}^{-1}$

$\therefore$ Number of moles present in $6.56\times10^{-3}$ g of ethane = $\dfrac{6.56\times10^{-3}}{30}$

= $2.187 \times 10^{-4}$

Let the number of moles of the solvent be 55.55 assuming solvent is water.

According to Henry's law,

$p = K_H x$

1 bar = $K_H$ ( $2.187 \times 10^{-4}$ / 55.55) [ assuming dilution condition i.e. moles of solvent >> moles of solute )

KH = 1 bar / ( $0.039 \times 10^{-4}$ )

if mass of ethane =0.05g then moles of ethane = 0.05/30 mol = 0.00166 mol

so $p = K_H x$

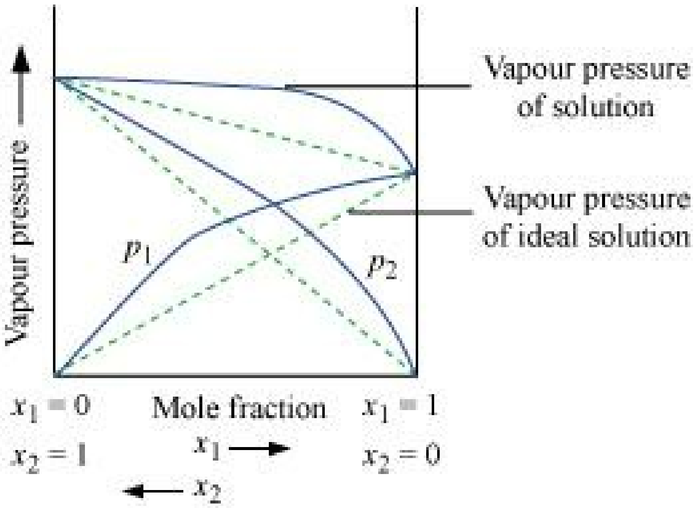
p = 1/ ($0.039 \times 10^{-4}$ ) x ( 0.00166/55.55)

= 7.66 bar

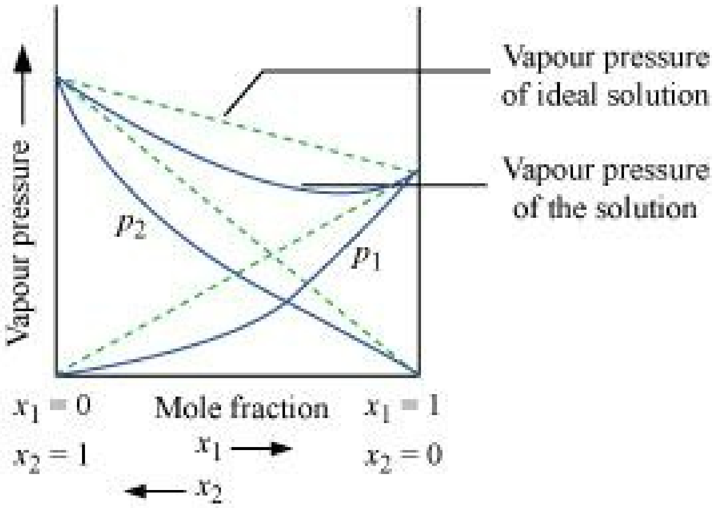
---

**14. What is meant by positive and negative deviations from Raoult's law and how is the sign of $\Delta \text{Sol} H$ related to positive and negative deviations from Raoult's law?**

**Ans.** According to Raoult's law, the partial vapour pressure of each volatile component in any solution is directly proportional to its mole fraction. The solutions which obey Raoult's law over the entire range of concentration are known as ideal solutions. The solutions that do not obey Raoult's law (non-ideal solutions) have vapour pressures either higher or lower than that predicted by Raoult's law. If the vapour pressure is higher, then the solution is said to exhibit positive deviation, and if it is lower, then the solution is said to exhibit negative deviation from Raoult's law.



**Vapour pressure of a two-component solution showing positive deviation from Raoult's law**



**Vapour pressure of a two-component solution showing negative deviation from Raoult's law**

In the case of an ideal solution, the enthalpy of the mixing of the pure components for forming the solution is zero.

$\Delta_{sol} H = 0$ because solute-solute interaction and solvent-solvent interaction = solute - solvent interaction

In the case of solutions showing positive deviations, absorption of heat takes place.

Therefore, $\Delta \text{Sol} H$ = positive beacuse solue - solute interaction and solvent - solvent interaction > solute - solvent interaction.

In the case of solutions showing negative deviations, evolution of heat takes place.

Therefore, $\Delta \text{Sol} H$ = Negative because solute - solute interacation and solvent solvent interaction < solute - solvent interaction.

**15. An aqueous solution of 2% non-volatile solute exerts a pressure of 1.004 bar at the normal boiling point of the solvent. What is the molar mass of the solute?**

**Ans.** Here,

Vapour pressure of the solution at normal boiling point (*p*1) = 1.004 bar

Vapour pressure of pure water at normal boiling point $\left(p_1^0\right) = 1.013 \text{bar}$

Mass of solute, $\left(w_2\right)$ = 2 g

Mass of solvent (water), $\left(w_1\right)$= 98 g

Molar mass of solvent (water), $\left(M_1\right)$ = $18 \text{ g mol}^{-1}$

According to Raoult's law,

$$\frac{p_1^0 - p_1}{p_1^0} = \frac{w_2 \times M_1}{M_2 \times w_1}$$

$$\frac{1.013 - 1.004}{1.013} = \frac{2 \times 18}{M_2 \times 98}$$

$$\frac{0.009}{1.013} = \frac{2 \times 18}{M_2 \times 98}$$

$$M_2 = \frac{1.013 \times 2 \times 18}{0.009 \times 98}$$

= $41.35\ \text{g mol}^{-1}$

Hence, the molar mass of the solute is $41.35\ \text{g mol}^{-1}$.

**16. Heptane and octane form an ideal solution. At 373 K, the vapour pressures of the two liquid components are 105.2 kPa and 46.8 kPa respectively. What will be the vapour pressure of a mixture of 26.0 g of heptane and 35 g of octane?**

**Ans.** Vapour pressure of heptane $\left(p_1^0\right) = 105.2\,\text{kPa}$

Vapour pressure of octane $\left(p_2^0\right)$ = 46.8 kPa

We know that,

Molar mass of heptane $\left(C_7H_{16}\right) = 7 \times 12 + 16 \times 1$

= $100\ \text{g mol}^{-1}$

Therefore, Number of moles of heptane = $\frac{26}{100}\text{mol}$

= 0.26 mol

Molar mass of octane $\left(C_8H_{18}\right) = 8 \times 12 + 18 \times 1$

= $114\ \text{g mol}^{-1}$

Therefore, Number of moles of octane = $\frac{35}{114}\text{mol}$

= 0.31 mol

Mole fraction of heptane, $x_1 = \frac{0.26}{0.26 + 0.31}$

= 0.456

And, mole fraction of octane, $x_2$ = 1 - 0.456

= 0.544

Now, partial pressure of heptane, $p_1 = x_1 p_1^0$

= $0.456 \times 105.2$

= 47.97 kPa

Partial pressure of octane, $p_2 = x_2 p_2^0$

= $0.544 \times 46.8$

= 25.46 kPa

Hence, vapour pressure of solution, $p_{total} = p_1 + p_2$

= 47.97 + 25.46

= 73.43 kPa

---

**17. The vapour pressure of water is 12.3 kPa at 300 K. Calculate vapour pressure of 1 molal solution of a non-volatile solute in it.**

**Ans.** 1 molal solution means 1 mol of the solute is present in 1000 g of the solvent (water).

Molar mass of water = $18 \text{ g mol}^{-1}$

Therefore, Number of moles present in 1000 g of water = $\frac{1000}{18}$

= 55.56 mol

Therefore, mole fraction of the solute in the solution is

$$x_2 = \frac{1}{1+55.56} = 0.0177.$$

It is given that,

Vapour pressure of water, $\left(p_1^0\right)$ = 12.3 kPa

Applying the relation, $\dfrac{p_1^0 - p_1}{p_1^0} = x_2$

$$\frac{12.3 - p_1}{12.3} = 0.0177$$

⇒ 12.3 - $p_1$ = 0.2177

⇒ $p_1$ = 12.0823

= 12.08 kPa (approximately)

Hence, the vapour pressure of the solution is 12.08 kPa.

---

**18. Calculate the mass of a non-volatile solute (molar mass 40 g $mol^{-1}$) which should be dissolved in 114 g octane to reduce its vapour pressure to 80%.**

**Ans.** Let the vapour pressure of pure octane be $p_1^0$

Then, the vapour pressure of the octane after dissolving the non-volatile solute is

$$\frac{80}{100} p_1^0 = 0.8 p_1^0$$

Molar mass of solute, $M_2 = 40\ g\ mol^{-1}$

Mass of octane, $w_1$ = 114 g

Molar mass of octane, $\left(C_8H_{18}\right), M_1 = 8 \times 12 + 18 \times 1$

= $114\ g\ mol^{-1}$

Applying the relation,

$$\frac{p_1^0 - p_1}{p_1^0} = \frac{w_2 \times M_1}{M_2 \times w_1}$$

$$\frac{p_1^0 - 0.8p_1^0}{p_1^0} = \frac{w_2 \times 114}{40 \times 114}$$

$$\frac{0.2p_1^0}{p_1^0} = \frac{w_2}{40}$$

$$0.2 = \frac{w_2}{40}$$

$$w_2 = 8\,g$$

Hence, the required mass of the solute is 8 g.

**19. A solution containing 30 g of non-volatile solute exactly in 90 g of water has a vapour pressure of 2.8 kPa at 298 K. Further, 18 g of water is then added to the solution and the new vapour pressure becomes 2.9 kPa at 298 K. Calculate:**

**i. molar mass of the solute**

**ii. vapour pressure of water at 298 K.**

**Ans. (i)** Let, the molar mass of the solute be $M\ g\ mol^{-1}$

Now, the no. of moles of solvent (water), $n_1 = \frac{90\,g}{18\,g\,mol^{-1}} = 5\,mol$

And, the no. of moles of solute, $n_2 = \frac{30\,g}{M\,mol^{-1}} = \frac{30}{M}\,mol$

$p_1$ = 2.8 kPa

Applying the relation:

$$\frac{p_1^0 - p_1}{p_1^0} = \frac{n_2}{n_1 + n_2}$$

$$\frac{p_1^0 - 2.8}{p_1^0} = \frac{\frac{30}{M}}{5 + \frac{30}{M}}$$

$$1 - \frac{2.8}{p_1^0} = \frac{\frac{30}{M}}{\frac{5M + 30}{M}}$$

$$1 - \frac{2.8}{p_1^0} = \frac{30}{5M + 30}$$

$$\frac{2.8}{p_1^0} = 1 - \frac{30}{5M + 30}$$

$$\frac{2.8}{p_1^0} = \frac{5M + 30 - 30}{5M + 30}$$

$$\frac{2.8}{p_1^0} = \frac{5M}{5M + 30}$$

$$\frac{p_1^0}{2.8} = \frac{5M + 30}{5M} \text{.....................}(i)$$

After the addition of 18 g of water:

$$n_1 = \frac{90 + 18g}{18} = 6\,\text{mol}$$

$$p_1 = 2.9\,\text{kPa}$$

Again, applying the relation:

$$\frac{p_1^0 - p_1}{p_1^0} = \frac{n_2}{n_1 + n_2}$$

$$\frac{p_1^0 - 2.9}{p_1^0} = \frac{\frac{30}{M}}{6 + \frac{30}{M}}$$

$$1 - \frac{2.9}{p_1^0} = \frac{\frac{30}{M}}{\frac{6M + 30}{M}}$$

$$1 - \frac{2.9}{p_1^0} = \frac{30}{6M + 30}$$

$$\frac{2.9}{p_1^0} = 1 - \frac{30}{6M + 30}$$

$$\frac{2.9}{p_1^0} = \frac{6M + 30 - 30}{6M + 30}$$

$$\frac{2.9}{p_1^0} = \frac{6M}{6M + 30}$$

$$\frac{p_1^0}{2.9} = \frac{6M + 30}{6M} \text{.................}(ii)$$

Dividing equation ***(i)*** by ***(ii)***, we have:

$$\frac{2.9}{2.8} = \frac{\frac{5M + 30}{5M}}{\frac{6M + 30}{6M}}$$

$$\frac{2.9}{2.8} \times \frac{6M + 30}{6} = \frac{5M + 30}{5}$$

$$2.9 \times 5 \times (6M + 30) = 2.8 \times 6 \times (5M + 30)$$

87M + 435 = 84 M +504

3M = 69

M = 23u

Therefore, the molar mass of the solute is $23\ \text{g mol}^{-1}$.

**(ii)** Putting the value of M in equation ***(i)***, we have:

$$\frac{p_1^0}{2.8} = \frac{5\times 23+30}{5\times 23}$$
$$\frac{p_1^0}{2.8} = \frac{145}{115}$$
$$p_1^0 = 3.53$$

Hence, the vapour pressure of water at 298 K is 3.53 kPa.

**20. A 5% solution (by mass) of cane sugar in water has freezing point of 271 K. Calculate the freezing point of 5% glucose in water if freezing point of pure water is 273.15 K.**

**Ans.** Here, $\Delta T_f$ = (273.15 - 271) K

= 2.15 K

Molar mass of sugar $\left(C_{12}H_{22}O_{11}\right) = 12\times 12 + 22\times 1 + 11\times 16$

= $342\ \text{g mol}^{-1}$

5% solution (by mass) of cane sugar in water means 5 g of cane sugar is present in (100 - 5) g = 95 g of water.

Now, number of moles of cane sugar = $\frac{5}{342}\text{mol}$

= 0.0146 mol

Therefore, molality of the solution, $m = \frac{0.0146\,\text{mol}}{0.095\text{kg}}$

= $0.1537\ \text{mol kg}^{-1}$

Applying the relation,

$\Delta T_f = K_f \times m$

$K_f = \frac{\Delta T_f}{m}$

$= \frac{2.15\,\text{K}}{0.1537\,\text{mol k}^{-1}}$

= $13.99\ \text{K kg mol}^{-1}$

Molar of glucose $\left(C_6H_{12}O_6\right) = 6\times12+12\times1+6\times16$

= $180\ \text{g mol}^{-1}$

5% glucose in water means 5 g of glucose is present in (100 - 5) g = 95 g of water.

Therefore, Number of moles of glucose = $\frac{5}{180}\text{mol}$

= 0.0278 mol

Therefore, molality of the solution, $m = \frac{0.0278\,\text{mol}}{0.095\text{kg}}$

= $0.2926\ \text{mol kg}^{-1}$

Applying the relation,

$\Delta T_f = K_f \times m$

= $13.99\ \text{K kg mol}^{-1} \times 0.2926\ \text{mol kg}^{-1}$

= 4.09 K (approximately)

Hence, the freezing point of 5% glucose solution is (273.15 - 4.09) K= 269.06 K.

---

**21. Two elements A and B form compounds having formula $AB_2$ and $AB_4$. When dissolved in 20 g of benzene $\left(C_6H_6\right)$, 1 g of $AB_2$ lowers the freezing point by 2.3 K whereas 1.0 g of $AB_4$ lowers it by 1.3 K. The molar depression constant for benzene is $5.1\,K\,kg\,mol^{-1}$. Calculate atomic masses of A and B.**

**Ans.** We know that,

$$M_2 = \frac{1000 \times w_2 \times k_f}{\Delta T_f \times w_1}$$

Then, $M_{AB_2} = \dfrac{1000 \times 1 \times 5.1}{2.3 \times 20}$

= $110.87\ g\ mol^{-1}$

$$M_{AB_4} = \frac{1000 \times 1 \times 5.1}{1.3 \times 20}$$

= $196.15\ g\ mol^{-1}$

Now, we have the molar masses of $AB_2$ and $AB_4$ as $110.87\ g\ mol^{-1}$ and $196.15\ g\ mol^{-1}$ respectively.

Let the atomic masses of A and B be *x* and *y* respectively.

Now, we can write:

$$x + 2y = 110.87 \ldots\ldots\ldots\ldots\ldots\ldots (i)$$
$$x + 4y = 196.15 \ldots\ldots\ldots\ldots\ldots\ldots (ii)$$

Subtracting equation (i) from (ii), we have

2*y* = 85.28

$\Rightarrow y = 42.64$

Putting the value of y in equation (1), we have

$x + 2 \times 42.64 = 110.87$

$\Rightarrow x = 25.59$

Hence, the atomic masses of A and B are 25.59 u and 42.64 u respectively.

---

**22. At 300 K, 36 g of glucose present in a litre of its solution has a osmotic pressure of 4.98 bar. If the osmotic pressure of the solution is 1.52 bar at the same temperature, what would be its concentration?**

**Ans.** Here,

$T = 300$ K

$\pi = 1.52$ bar

R = 0.083 bar L $K^{-1} mol^{-1}$

Applying the relation,

$\pi = CRT$

$$C = \frac{\pi}{RT}$$

$$= \frac{1.52\,\text{bar}}{0.083\,\text{bar L K}^{-1}\,\text{mol}^{-1} \times 300\,\text{k}}$$

= 0.061 mol/L

The concentration of the solution would be 0.061 M.

---

**23. Suggest the most important type of intermolecular attractive interaction in the following pairs.**

**(i) n-hexane and n-octane**

**(ii)** $I_2$ **and** $CCl_4$

**(iii)** $NaClO_4$ **and water**

**(iv) methanol and acetone**

**(v) acetonitrile** $CH_3CN$ **and acetone** $(C_3H_6O)$**.**

**Ans. (i)** Van der Wall forces of attraction as both are non polar.

**(ii)** Van der Wall forces of attraction as they are non polar.

**(iii)** Ion-diople interaction as $NaClO_4$ is ionic in nature.

**(iv)** Dipole-dipole interaction as they are polar.

**(v)** Dipole-dipole interaction as they are polar.

**24. Based on solute-solvent interactions, arrange the following in order of increasing solubility in n-octane and explain. Cyclohexane, KCl,** $CH_3OH$ **,** $CH_3CN$ **.**

**Ans.** *n*-octane is a non-polar solvent. Therefore, the solubility of a non-polar solute is more than that of a polar solute in the *n*-octane as like dissolves in like.

The order of increasing polarity is:

Cyclohexane < $CH_3CN$ < $CH_3OH$ < KCl

Therefore, the order of increasing solubility is:

KCl < $CH_3OH$ < $CH_3CN$ < Cyclohexane

**25. Amongst the following compounds, identify which are insoluble, partially soluble and highly soluble in water?**

**(i) phenol**

**(ii) toluene**

**(iii) formic acid**

**(iv) ethylene glycol**

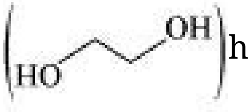
**(v) chloroform**

**(vi) pentanol.**

**Ans. (i)** Phenol $\left(C_6H_5OH\right)$ has the polar group -OH and non-polar group $-C_6H_5$. Thus, phenol is partially soluble in water.

**(ii)** Toluene $\left(C_6H_5-CH_3\right)$ has no polar groups. Thus, toluene is insoluble in water.

**(iii)** Formic acid (HCOOH) has the polar group -OH and can form H-bond with water. Thus, formic acid is highly soluble in water.

**(iv)** Ethylene glycol  has polar -OH group and can form H-bond. Thus, it is highly soluble in water.

**(v)** Chloroform is insoluble in water.

**(vi)** Pentanol $\left(C_5H_{11}OH\right)$ has polar -OH group, but it also contains a very bulky non-polar $-C_5H_{11}$ group. Thus, pentanol is partially soluble in water.

---

**26. If the density of some lake water is $1.25\,g\,ml^{-1}$ and contains 92 g of $Na^+$ ions per kg of water, calculate the molality of $Na^+$ ions in the lake.**

**Ans.** Number of moles present in 92 g of $Na^+$ ions = (92g) /( 23g/mol) = 4 mol

Therefore, molality of $Na^+$ ions in the lake $\frac{4\,mol}{1kg}$ = 4 m

---

**27. If the solubility product of CuS is $6\times10^{-16}$, calculate the maximum molarity of CuS in aqueous solution.**

**Ans.** Solubility product of CuS, $K_sp = 6 \times 10^{-16}$

Let *s* be the solubility of CuS in $\text{mol L}^{-1}$.

$$\underset{}{CuS} \leftrightarrow \underset{s}{Cu^{2+}} + \underset{s}{S^{2+}}$$

Now, $K_sp = \left[Cu^{2+}\right]\left[S^{2-}\right]$

$= s \times s$
$= s^2$

Then, we have, $K_sp = s^2 = 6 \times 10^{-16}$

$s = \sqrt{6 \times 10^{-16}}$

= 2.45 × 10 $^{-8}$ $\text{mol L}^{-1}$

Hence, the maximum molarity of CuS in an aqueous solution is $2.45 \times 10^{-8} \text{mol L}^{-1}$.

---

**28. Calculate the mass percentage of aspirin $(C_9H_8O_4)$ in acetonitrile $(CH_3CN)$ when 6.5 g of $C_9H_8O_4$ is dissolved in 450 g of $CH_3CN$**

**Ans.** 6.5 g of $C_9H_8O_4$ is dissolved in 450 g of $CH_3CN$.

Then, total mass of the solution = (6.5 + 450) g

= 456.5 g

Therefore, mass percentage of $C_9H_8O_4$ = $\frac{6.5}{456.5} \times 100\%$

= 1.424%

---

**29. Nalorphene $C_{19}H_{21}NO_3$, similar to morphine, is used to combat withdrawal symptoms in narcotic users. Dose of nalorphene generally given is 1.5 mg. Calculate the**

**mass of $1.5\times10^{-3}$ m aqueous solution required for the above dose.**

**Ans.** The molar mass of nalorphene $C_{19}H_{21}NO_3$ is given as:

$$19\times12+21\times1+1\times14+3\times16=311\,g\,mol^{-1}$$

In $1.5\times10^{-3}\,m$ aqueous solution of nalorphene,

1 kg (1000 g) of water contains $1.5\times10^{-3}$ mol of nalorphene i.e. $1.5\times10^{-3}\times311\,g$ = 0.4665g of nalorphene

Therefore, total mass of the solution = (1000 + 0.4665) g

= 1000.4665 g

This implies that the mass of the solution containing 0.4665 g of nalorphene is 1000.4665 g.

Therefore, mass of the solution containing 1.5 mg of nalorphene is:

$$\frac{1000.4665\times1.5\times10^{-3}}{0.4665}g$$

= 3.22 g

Hence, the mass of aqueous solution required is 3.22 g.

---

**30. Calculate the amount of benzoic acid $(C_6H_5COOH)$ required for preparing 250 mL of 0.15 M solution in methanol.**

**Ans.** 0.15 M solution of benzoic acid in methanol means,

1000 mL of solution contains 0.15 mol of benzoic acid

Therefore, 250 mL of solution contains = $\frac{0.15\times250}{1000}$ mol of benzoic acid

= 0.0375 mol of benzoic acid

Molar mass of benzoic acid $(C_6H_5COOH)=7\times12+6\times1+2\times16$

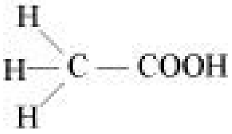
= 122 g $\text{mol}^{-1}$

Hence, required benzoic acid = $0.0375 \text{ mol} \times 122 \text{ g mol}^{-1}$

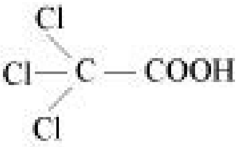
= 4.575 g

**31. The depression in freezing point of water observed for the same amount of acetic acid, trichloroacetic acid and trifluoroacetic acid increases in the order given above. Explain briefly.**

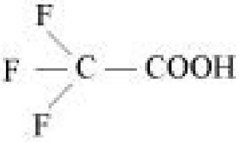
**Ans.**



Acetic acid



Trichloroacetic acid



Trifluoroacetic acid

Among H, Cl, and F, H is least electronegative while F is most electronegative. Then, F can withdraw electrons towards itself more than Cl and H. Thus, trifluoroacetic acid can easily lose $H^+$ ions i.e., trifluoroacetic acid ionizes to the largest extent. Now, the more ions produced, the greater is the depression of the freezing point. Hence, the depression in the freezing point increases in the order:

Acetic acid < trichloroacetic acid < trifluoroacetic acid

**32. Calculate the depression in the freezing point of water when 10 g of $CH_3CH_2CHClCOOH$ is added to 250 g of water.**

$K_a = 1.4 \times 10^{-3}, K_f = 1.86 \, K \, kg \, mol^{-1}$.

**Ans.** Molar mass of $CH_3CH_2CHClCOOH = 15 + 14 + 13 + 35.5 + 12 + 16 + 16 + 1$

= $122.5 \, g \, mol^{-1}$

Therefore, No. of moles present in 10 g of $CH_3CH_2CHClCOOH = \frac{10 \, g}{122.5 \, g \, mol^{-1}}$

= 0.0816 mol

It is given that 10 g of $CH_3CH_2CHClCOOH$ is added to 250 g of water.

Therefore, Molality of the solution, $= \frac{0.0186}{250} \times 1000$

m= 0.3264 $mol \, kg^{-1}$

Let a be the degree of dissociation of $CH_3CH_2CHClCOOH$

$CH_3CH_2CHClCOOH$ undergoes dissociation according to the following equation:

Initial conc. At equilibrium = $CH_3CH_2CHClCOOH$ <--> $CH_3CH_2CHClCOO^- + H^+$

c(1-x) cx cx

Ka = $c^2x^2/c(1-x)$

Since $x$ is very small with respect to 1so x can be ignored , 1 - α =1

now, Ka= $cx^2/1$

x = $(Ka / c)^{0.5}$

$$= \sqrt{\frac{1.4 \times 10^{-3}}{0.3264}} \left(\because K_a = 1.4 \times 10^{-3}\right)$$

= 0.0655

Again, $CH_3CH_2CHClCOOH \leftrightarrow CH_3CH_2CHClCOO^- + H^+$

initial 1 mol 0 0

at eqillibrium 1-x x x

i ( vant hoff factor ) = 1-x+x+x = 1+x

= 1 + 0.0655

= 1.0655

Hence, the depression in the freezing point of water is given as:

$$\Delta T_f = i K_f m$$
$$= 1.0655 \times 1.86\,K\,kg\,mol^{-1} \times 0.3264\,mol\,kg^{-1}$$

= 0.65 K

---

**33. 19.5 g of $CH_2FCOOH$ is dissolved in 500 g of water. The depression in the freezing point of water observed is $1.0°C$ . Calculate the van't Hoff factor and dissociation constant of fluoroacetic acid.**

**Ans.** It is given that:

$$w_1 = 500\,g$$
$$w_2 = 19.5\,g$$
$$K_f = 1.86\,K\,kg\,mol^{-1}$$
$$\Delta T_f = 1K$$

We know that:

$$M_2 = \frac{K_f \times w_2 \times 1000}{\Delta T_f \times w_1}$$
$$= \frac{1.86\,K\,kg\,mol^{-1} \times 19.5\,g \times 1000\,g\,kg^{-1}}{500\,g \times 1K}$$

$72.54\ \text{g mol}^{-1}$

Therefore, observed molar mass of $CH_2FCOOH, (M_2)_{obs} = 72.54\ \text{g mol}$

The calculated molar mass of $CH_2FCOOH$ is:

$$(M_2)_{cal} = 14 + 19 + 12 + 16 + 16 + 1$$
$$= 76\ \text{g mol}^{-1}$$

Therefore, van't Hoff factor, $i = \frac{(M_2)_{cal}}{(M_2)_{obs}}$

$$\frac{78\ \text{g mol}^{-1}}{72.54\ \text{g mol}^{-1}}$$

= 1.0753

Let αbe the degree of dissociation of $CH_2FCOOH$

At equilibrium = $\begin{array}{ccccc} CH_2FCOOH & \leftrightarrow & CH_2FCOO^- & + & H^+ \\ C\,\text{mol}L^{-1} & & 0 & & 0 \\ C(1-\alpha) & & C\alpha & & C\alpha \end{array}$

Total = $C(1+\alpha)$

$$i = \frac{C(1+\alpha)}{C}$$
$$i = 1 + \alpha$$
$$\alpha = i - 1$$

= 1.0753 – 1

= 0.0753

Now, the value of $K_a$ is given as:

$$K_a = \frac{[CH_2FCOO^-][H^+]}{[CH_2FCOOH]}$$

$$= \frac{C\alpha.C\alpha}{C(1-\alpha)}$$

$$\frac{C\alpha^2}{1-\alpha}$$

Taking the volume of the solution as 500 mL, we have the concentration:

$$C = \frac{\frac{19.5}{78}}{500} \times 1000M$$

= 0.5 M

Therefore, $K_a = \frac{C\alpha^2}{1-\alpha}$

$$= \frac{0.5 \times (0.0753)^2}{1-0.0753}$$

$$= \frac{0.5 \times 0.00567}{0.9247}$$

= 0.00307 (approximately)

$$= 3.07 \times 10^{-3}$$

---

**34. Vapour pressure of water at 293 K is 17.535 mm Hg. Calculate the vapour pressure of water at 293 K when 25 g of glucose is dissolved in 450 g of water.**

**Ans.** Vapour pressure of water, $p_1^0$ = 17.535 mm of Hg

Mass of glucose, $w_2 = 25$ g

Mass of water, $w_1 = 450$ g

We know that,

Molar mass of glucose $(C_6H_{12}O_6), M_2 = 6\times12+12\times1+6\times16$

= 180 g $mol^{-1}$

Molar mass of water, $M_1 = 18 \text{ g mol}^{-1}$

Then, number of moles of glucose, $n_2 = \frac{25}{180\,g\,mol^{-1}}$

= 0.139 mol

And, number of moles of water, $n_1 = \frac{450}{18\,g\,mol^{-1}}$

= 25 mol

We know that,

$$\frac{p_1^0 - p_1}{p_1^0} = \frac{n_1}{n_2 + n_1}$$

$$\frac{17.535 - p_1}{17.535} = \frac{0.139}{0.139 + 25}$$

$$17.535 - p_1 = \frac{0.139 \times 17.535}{25.139}$$

$$17.535 - p_1 = 0.097$$

$$p_1 = 17.44 \text{ mm of Hg}$$

Hence, the vapour pressure of water is 17.44 mm of Hg.

---

**35. Henry's law constant for the molality of methane in benzene at 298 K is $4.27 \times 10^{5}$. Calculate the solubility of methane in benzene at 298 K under 760 mm Hg.**

**Ans.** Here,

$p$ = 760 mm Hg

$K_H$ = 4.27 x $10^5$

According to Henry's law,

$$p = k_H x$$

$$x = \frac{p}{k_H}$$

$$= \frac{760\,\text{mm Hg}}{4.27\times10^5\ \text{mm Hg}}$$

= $177.99\times10^{-5}$

= $178\times10^{-5}$ (approximately)

Hence, the mole fraction of methane in benzene is $178\times10^{-5}$.

---

**36. 100 g of liquid A (molar mass 140 g $\text{mol}^{-1}$) was dissolved in 1000 g of liquid B (molar mass 180 g $\text{mol}^{-1}$). The vapour pressure of pure liquid B was found to be 500 torr. Calculate the vapour pressure of pure liquid A and its vapour pressure in the solution if the total vapour pressure of the solution is 475 Torr.**

**Ans.** Number of moles of liquid A, $n_A = \frac{100}{140}\text{mol}$

= 0.714 mol

Number of moles of liquid B, $n_B = \frac{1000}{180}\text{mol}$

= 5.556 mol

Then, mole fraction of A, $x_A = \frac{n_A}{n_A + n_B}$

$$= \frac{0.714}{0.174 + 5.556}$$

= 0.114

And, mole fraction of B, $x_B = 1 - 0.114$

= 0.886

Vapour pressure of pure liquid B, $p_1^0$ = 500 torr

Therefore, vapour pressure of liquid B in the solution,

$$p_B = p_B^0 x_B$$

= $500 \times 0.886$

= 443 torr

Total vapour pressure of the solution, *p*total = 475 torr

Therefore, Vapour pressure of liquid A in the solution,

$$p_A = p_{total} - p_B$$

= 475 - 443

= 32 torr

$$\text{Now}, p_A = p_A^0 x_A$$

$$p_A^0 = \frac{p_A}{x_A}$$

$$= \frac{32}{0.114}$$

= 280.7 torr

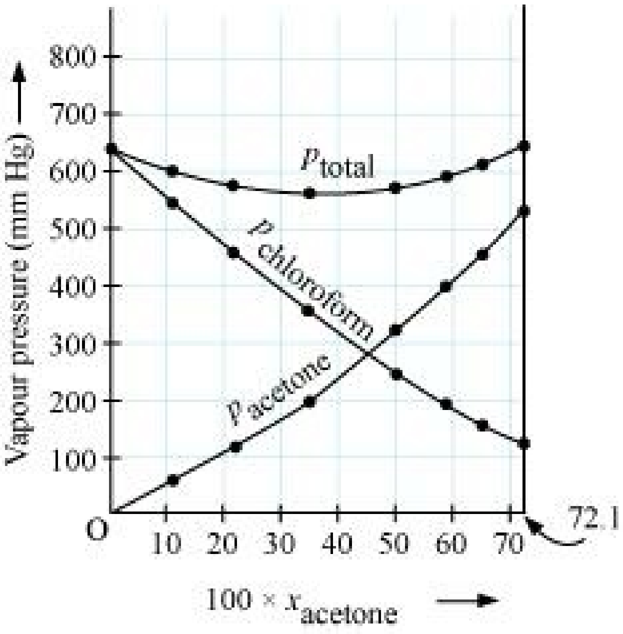
Hence, the vapour pressure of pure liquid A is 280.7 torr.

**37. Vapor pressure of pure acetone and chloroform at 328 K are 741.8 mm Hg and 632.8 mm Hg respectively. Assuming that they form ideal solution over the entire range of composition, plot *p* total' *p* chloroform' and *p* acetone as a function of *x* acetone. The experimental data observed for different compositions of mixture is.**

| 100× x acetones | 0 | 11.8 | 23.4 | 36.0 | 50.8 | 58.2 | 64.5 | 72.1 |
|---|---|---|---|---|---|---|---|---|
| *p* acetone /mm Hg | 0 | 54.9 | 110.1 | 202.4 | 322.7 | 405.9 | 454.1 | 521.1 |
| *p* chloroform/mm Hg | 632.8 | 548.1 | 469.4 | 359.7 | 257.7 | 193.6 | 161.2 | 120.7 |

**Ans.** From the question, we have the following data

| 100× x acetones | 0 | 11.8 | 23.4 | 36.0 | 50.8 | 58.2 | 64.5 | 72.1 |
|---|---|---|---|---|---|---|---|---|
| **p acetone /mm Hg** | 0 | 54.9 | 110.1 | 202.4 | 322.7 | 405.9 | 454.1 | 521.1 |
| **P chloroform/mm Hg** | 632.8 | 548.1 | 469.4 | 359.7 | 257.7 | 193.6 | 161.2 | 120.7 |
| **p tota(mm Hg)** | 632.8 | 603.0 | 579.5 | 562.1 | 580.4 | 599.5 | 615.3 | 641.8 |



It can be observed from the graph that the plot for the *p* total of the solution curves downwards. Therefore, the solution shows negative deviation from the ideal behaviour.

**38. Benzene and toluene form ideal solution over the entire range of composition. The vapour pressure of pure benzene and toluene at 300 K are 50.71 mm Hg and 32.06 mm Hg respectively. Calculate the mole fraction of benzene in vapour phase if 80 g of benzene is mixed with 100 g of toluene.**

**Ans.** Molar mass of benzene $\left(C_6H_6\right) = 6\times12+6\times1$

= $78\,g\,mol^{-1}$

Molar mass of toluene $\left(C_6H_5CH_3\right) = 7\times12+8\times1$

= $92\,g\,mol^{-1}$

Now, no. of moles present in 80 g of benzene = $\frac{80}{78}mol$

= 1.026 mol

And, no. of moles present in 100 g of toluene = $\frac{100}{92}mol$

=1.087 mol

Therefore, Mole fraction of benzene, $x_b = \frac{1.026}{1.025+1.087}$

= 0.486

And, mole fraction of toluene, $x_t = 1-0.486$

= 0.514

It is given that vapour pressure of pure benzene, $p_b^0 = 50.71\,mm\,Hg$

And, vapour pressure of pure toluene, $p_1^0 = 32.06\,mm\,HG$

Therefore, partial vapour pressure of benzene, $p_b = x_b \times p_b$

$= 0.486 \times 50.71$

= 24.645 mm Hg

And, partial vapour pressure of toluene, $p_1 = x_t \times p_t$

$= 0.514 \times 32.06$

= 16.479 mm Hg

Hence, mole fraction of benzene in vapour phase is given by:

$$\frac{p_b}{p_b + p_t}$$

$$= \frac{24.645}{24.645 + 16.479}$$

$$= \frac{24.645}{41.124}$$

= 0.599

= 0.6

---

**39. The air is a mixture of a number of gases. The major components are oxygen and nitrogen with approximate proportion of 20% is to 79% by volume at 298 K. The water is in equilibrium with air at a pressure of 10 atm. At 298 K if the Henry's law constants for oxygen and nitrogen are 3.30 x $10^7$and 6.51 x $10^7$ respectively, calculate the composition of these gases in water.**

**Ans.** Percentage of oxygen $(O_2)$ in air = 20 %

Percentage of nitrogen $(N_2)$in air = 79%

Also, it is given that water is in equilibrium with air at a total pressure of 10 atm, that is,

$(10\times 760)$ mm Hg = 7600 mm Hg

Therefore,

Partial pressure of oxygen, $p_{O_2} = \frac{20}{100}\times 7600\,\text{mm Hg}$

= 1520 mm Hg

Partial pressure of nitrogen, $p_{N_2} = \frac{79}{100}\times 7600\,\text{mm Hg}$

= 6004 mmHg

Now, according to Henry's law:

$p = K_H x$ For oxygen:

$$p_{O_2} = K_H . x_{O_2}$$

$$x_{O_2} = \frac{p_{O_2}}{K_H}$$

$= \frac{1520\,\text{mm Hg}}{3.30\times 10^7\,\text{mm Hg}}$ (Given $K_H = 3.30\times 10^7$ mm Hg )

$$= 4.61\times 10^{-5}$$

For nitrogen:

$$p_{N_2} = K_H . x_{N_2}$$

$$x_{N_2} = \frac{p_{N_2}}{K_H}$$

$$= \frac{6004\,\text{mm Hg}}{6.51\times 10^7\,\text{mm Hg}}$$

$$= 9.22\times 10^{-5}$$

Hence, the mole fractions of oxygen and nitrogen in water are $4.61\times 10^{-5}$ and $9.22\times 10^{-5}$

respectively.

**40. Determine the amount of $CaCl_2$ (*i* = 2.47) dissolved in 2.5 litre of water such that its osmotic pressure is 0.75 atm at $27°C$.**

**Ans.** We know that,

$$\pi = i\frac{n}{V}RT$$

$$\pi = i\frac{w}{MV}RT$$

$$w = \frac{\pi MV}{iRT}$$

$$\pi = 0.75 \text{ atm}$$

V = 2.5 L

i = 2.47

T = (27 + 273)K = 300 K

Here,

R = 0.0821 L atm $K^{-1}mol^{-1}$

$$M = 1 \times 40 + 2 \times 35.5$$

= 111 g $mol^{-1}$

Therefore, $w = \frac{0.75 \times 111 \times 2.5}{2.47 \times 0.0821 \times 300}$

= 3.42 g

Hence, the required amount of $CaCl_2$ is 3.42 g.

**41. Determine the osmotic pressure of a solution prepared by dissolving 25 mg of**

**$K_2SO_4$ in 2 liter of water at $25°C$, assuming that it is completely dissociated.**

**Ans.** When $K_2SO_4$ is dissolved in water, $K^+$ and $SO_4^{2-}$ ions are produced.

$$K_2SO_4 \rightarrow 2K^+ + SO_4^{2-}$$

Total number of ions produced = 3

Therefore, *i* =3

Given,

*w* = 25 mg = 0.025 g

*V* = 2 L

*T* = 250 C = (25 + 273) K = 298 K

Also, we know that:

R = 0.0821 L atm $K^{-1}mol^{-1}$

$$M = (2\times39)+(1\times32)+(4\times16) = 174 \text{ g mol}^{-1}$$

Appling the following relation,

$$\pi = i\frac{n}{v}RT$$
$$= i\frac{w}{M}\frac{1}{v}RT$$

$$= 3\times\frac{0.025}{174}\times\frac{1}{2}\times0.0821\times298$$
$$= 5.27\times10^{-3} \text{ atm}$$

# CBSE Class 12 Chemistry
# NCERT Solutions
# Chapter - 03
# Electro Chemistry

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## In-text Questions

### 1. How would you determine the standard electrode potential of the system $Mg^{2+}$| Mg?

**Ans.** The standard electrode potential of $Mg^{2+}$ | Mg can be measured with respect to the standard hydrogen electrode, represented by Pt(*s*), $H_{2\ (g)}$(1 atm) | $H^+$(aq) (1M).

A cell, consisting of Mg | $MgSO_4$(aq 1 M) as the anode and the standard hydrogen electrode as the cathode, is set up.

Mg | $Mg^{2+}$(aq, 1M)| | $H^+$(aq, 1M)|H2(g, 1 bar), Pt(s)
Then, the emf of the cell is measured and this measured emf is the standard electrode potential of the magnesium electrode.

$$E^{\ominus} = E_R^{\ominus} - E_L^{\ominus}$$

Here,$E_R^{\ominus}$ for the standard hydrogen electrode is zero.

Therefore, $E^{\ominus} = 0 - E_L^{\ominus}$

$= -E_L^{\ominus}$

---

### 2. Can you store copper sulphate solution in a zinc pot?

**Ans.** Zinc is more reactive than copper. Therefore, zinc can displace copper from its salt solution. If copper sulphate solution is stored in a zinc pot, then zinc will displace copper from the copper sulphate solution.

$Zn + CuSO_4 \rightarrow ZnSO_4 + Cu$

Hence, copper sulphate solution cannot be stored in a zinc pot.

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### 3. Consult the table of standard electrode potentials and suggest three substances that can oxidise ferrous ions under suitable conditions.

**Ans.** Substances that are stronger oxidising agents than ferrous ions can oxidise ferrous ions.

$Fe^{2+} \rightarrow Fe^{3+} + e^{-1}$; $E^{\ominus} = 0.77$ V

This implies that the substances having higher reduction potentials than +0.77 V can oxidise ferrous ions to ferric ions. Three substances that can do so are $F_2$, $Cl_2$, and $O_2$.

**4. Calculate the potential of hydrogen electrode in contact with a solution whose pH is 10.**

**Ans.** For hydrogen electrode, $H^+ + e^- \rightarrow \frac{1}{2}H_2$, it is given that pH = 10

Therefore, $[H^+] = 10^{-10}$ M

Now, using Nernst equation:

$E = E^{\ominus} - (0.0591/n) \log (1/[H^+])$

$E = 0 - \frac{0.0591}{1}\log\frac{1}{[10^{-10}]}$

$= -0.0591 \log 10^{10} = -0.0591(10 \log 10) = -0.591$ V

**5. Calculate the emf of the cell in which the following reaction takes place:**

**$Ni(s) + 2Ag^+(0.002\ M) \rightarrow Ni^{2+}(0.160\ M) + 2Ag(s)$**

**Given that** $E^{\ominus}_{(cell)} = 1.05V$

**Ans.** Applying Nernst equation we have:

$E_{(cell)} = E^{\ominus}_{(cell\ )} - \frac{0.0591}{n}\log\frac{[Ni^{2+}]}{[Ag^+]^2}$

$= 1.05 - \frac{0.0591}{2}\log\frac{(0.160)}{(0.002)^2}$

$= 1.05 - 0.02955\log\frac{0.16}{0.000004}$

$= 1.05 - 0.02955 \log 4 \times 10^4$

$= 1.05 - 0.02955 (\log 10000 + \log 4)$

$= 1.05 - 0.02955 (4 + 0.6021)$

$= 1.05 - 0.02955 (4.6021)$

$= 1.05 - 0.14$

$= 0.91$ V

**6. The cell in which the following reactions occurs:**

**$2Fe^{3+}(aq) + 2I^{-}(aq) \longrightarrow 2Fe^{2+}(aq) + I_2(s)$ has $E^{\ominus}_{cell}$ = 0.236 V at 298 K.**

**Calculate the standard Gibbs energy and the equilibrium constant of the cell reaction.**

**Ans.** Here, n = 2, $E^{\ominus}_{cell}$ = 0.236 V, T = 298 K

We know that:

$$\Delta_r G = -\mathrm{n\ F\ E}^{\ominus}$$

$$= -2 \times 96487 \times 0.236$$

= - 45541.864 J mol $^{-1}$

= - 45.54 kJ mol $^{-1}$

Again, $\Delta_r G \ = -2.303\mathrm{RT1ogKc}$

$$\log \mathrm{K_c} = -\frac{\Delta_r G^{\ominus}}{2.303\mathrm{RT}}$$

$$= -\frac{-45.54 \times 10^3}{2.303 \times 8.314 \times 298}$$

= 7.981

$\therefore$ $K_c$= Antilog (7.981) = 9.57 × $10^7$

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**7. Why does the conductivity of a solution decrease with dilution?**

**Ans.** The conductivity of a solution is the conductance of ions present in a unit volume of the solution. The number of ions (responsible for carrying current) per unit volume decreases when the solution is diluted. As a result, the conductivity of a solution decreases with dilution.

---

**8. Suggest a way to determine the $\mathrm{A}^0_m$ value of water.**

**Ans.** Applying Kohlrausch's law of independent migration of ions, the $\mathrm{A}^0_m$ value of water can be determined as follows:

$$\mathrm{A}^0_{m(H_2O)} = \lambda^0_H + \lambda^0_{OH^-}$$

$$= \left(\lambda^0_{\mathrm{H}^-} + \lambda^0_{\mathrm{Cl}^-}\right) + \left(\lambda^0_{\mathrm{Na}^+} + \lambda^0_{\mathrm{OH}^-}\right) - \left(\lambda^0_{\mathrm{Na}^+} + \lambda^0_{\mathrm{Cl}^-}\right)$$

$$= \mathrm{A}^0_{m(HCl)} + \mathrm{A}^0_{m(NaOH)} + \mathrm{A}^0_{m(NaCl)}$$

Hence, by knowing the $\mathrm{A}^0_m$ values of HCl, NaOH, and NaCl, the $\mathrm{A}^0_m$ value of water can be determined.

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**9. The molar conductivity of 0.025 mol $L^{-1}$ methanoic acid is 46.1 S $cm^2$ $mol^{-1}$. Calculate its degree of dissociation and dissociation constant. Given $\lambda^0(H^+)$ = 349.6 S $cm^2$ $mol^{-1}$ and $\lambda^0(HCOO^-)$ = 54.6 S $cm^2$ mol**

**Ans.** C = 0.025 mol $L^{-1}$

$\lambda^0(H^+)$ = 349.6 S $cm^2$ $mol^{-1}$

$\lambda^0(HCOO^-)$ = 54.6 S $cm^2$ mol

$$\Lambda_m^0(\mathrm{HCOOH}) = \lambda^0\left(\mathrm{H}^+\right) + \lambda^0\left(\mathrm{HCOO}^-\right)$$

= 349.6 + 54.6

= 404.2 S $cm^2mol^{-1}$

Now, **degree of dissociation:**

$$\alpha = \frac{\Lambda_m(\mathrm{HCOOH})}{\Lambda_m^0(\mathrm{HCOOH})}$$
$$= \frac{46.1}{404.2}$$

= 0.114(approximately)

**Thus, dissociation constant:**

$$K = \frac{c\alpha^2}{(1-\alpha)}$$
$$= \frac{\left(0.025\mathrm{molL}^{-1}\right)(0.114)^2}{(1-0.114)}$$

**=**3.67 $\times 10^{-4}$ mol $L^{-1}$

---

**10. If a current of 0.5 ampere flows through a metallic wire for 2 hours, then how many electrons would flow through the wire?**

**Ans.** I = 0.5 A

t = 2 hours = $2 \times 60 \times 60$s = 7200 s

Thus, Q = It

= 0.5 A $\times$ 7200= 3600 C

We know that 96487 C = 6.023 $\times$ $10^{23}$ number of electrons.

Then,

$$3600\mathrm{C} = \frac{6.023\times10^{23}\times3600}{96487} \text{ number of electrons}$$

= 2.25 $\times 10^{22}$ number of electrons

Hence, 2.25 $\times 10^{22}$ number of electrons will flow through the wire.

**11. Suggest a list of metals that are extracted electrolytically.**

**Ans.** Fuel cells are voltaic cells in which the reactants are continuously supplied to the electrodes.They convert the energy from the combustion of fuels like hydrogen, CO, Methane directly into electrical energy. Methane & methanol can be used as fuels in fuel cells.

**12. What is the quantity of electricity in coulombs needed to reduce 1 mol of $Cr_2O_7^{2-}$? Consider the reaction**

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 8H_2O$

**Ans.** The given reaction is as follows:

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 8H_2O$

Therefore, to reduce 1 mole of $Cr_2O_7^{2-}$, the required quantity of electricity will be:

= 6 F = $6 \times 96487C$= 578922 C

**13. Write the chemistry of recharging the lead storage battery, highlighting all the materials that are involved during recharging.**

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

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

At anode: $Pb_{(s)} + SO_4^{2-}(aq) \rightarrow PbSO_{4)}(s) + 2e^-$

At cathode: $PbSO_4(s) + SO_4^{2-}(aq) + 4H^-(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$

The overall cell reaction is given by,

$Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$

When a battery is charged, the reverse of all these reactions takes place.

Hence, on charging, $PbSO_4$ (s) present at the anode and cathode is converted into Pb(s) and $PbO_2$(s) respectively.

**14. Suggest two materials other than hydrogen that can be used as fuels in fuel cells.**

**Ans.** Methane and methanol can be used as fuels in fuel cells.

**15. Explain how rusting of iron is envisaged as setting up of an electrochemical cell.**

**Ans.** In the process of corrosion, due to the presence of air and moisture, oxidation takes place at a particular spot of an object made of iron. That spot behaves as the anode. The reaction at the anode is given by, $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$

Electrons released at the anodic spot move through the metallic object and go to another spot of the object.

There, in the presence of $H^+$ ions, the electrons reduce oxygen. This spot behaves as the cathode. These $H^+$ ions come either from $H_2CO_3$, which are formed due to the dissolution of carbon dioxide from air into water or from the dissolution of other acidic oxides from the atmosphere in water.

The reaction corresponding at the cathode is given by, $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l\ )$

The overall reaction is: $2Fe(s) + O_2(g) + 4H^+(aq) \rightarrow 2Fe^{2+}(aq) + 2H_2O(l)$

Also, ferrous ions are further oxidized by atmospheric oxygen to ferric ions. These ferric ions combine with moisture, present in the surroundings, to form hydrated ferric oxide ($Fe_2O_3.xH_2O$) i.e., rust.

Hence, the rusting of iron is envisaged as the setting up of an electrochemical cell.

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**Chapter End Question**

**1. Arrange the following metals in the order in which they displace each other from the solution of their salts. Al, Cu, Fe, Mg and Zn**

**Ans.** The following is the order in which the given metals displace each other from the solution of their salts. Mg, Al, Zn, Fe, Cu. Mg is highly electropositive with

$E^o{}_{Mg^{2+}/Mg} = -2.37V.$

$E^o{}_{Al^{3+}/Al} = -1.66\ V$

$E^o{}_{Fe^{2+}/Fe} = -0.44\ V$

$E^o{}_{Zn^{2+}/zn} = -0.763V$

$E^o{}_{Cu^{2+}/Cu} = +0.153$

**2. Given the standard electrode potentials,**

**$K^+/K = -2.93$, $Ag^+/Ag = 0.80$ V**

**$Hg^{2+}/Hg = 0.79$ V**

**$Mg^{2+}/Mg = -2.73$ V, $Cr^{3+}/Cr = -0.74$ V**

**Ans.** Lower the value of reduction potential, the higher is the reducing power. The given standard electrode potentials increase in the order of $K^+/K < Mg^{2+}/Mg < Cr^{3+}/Cr < Hg^{2+}/Hg < Ag^+/Ag$

Hence, the reducing power of the given metals increases in the following order:

Ag < Hg < Cr < Mg < K

---

**3. Depict the galvanic cell in which the reaction takes place. Further show:**

**(i) Which of the electrode is negatively charged?**

**(ii) The carriers of the current in the cell.**

**(iii) Individual reaction at each electrode.**

**Ans.** The galvanic cell in which the given reaction takes place is depicted as:

$Zn(s) \mid Zn^{2+}(aq) \mid\mid Ag^+(aq) \mid Ag(s)$

**(i)** Zn electrode (anode) is negatively charged.

**(ii)** Ions are carriers of current in the cell and in the external circuit, current will flow from silver to zinc.

**(iii)** The reaction taking place at the anode is given by,

$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$

The reaction taking place at the cathode is given by,

$2Ag^+_{(aq)} + 2e^- \rightarrow 2\ Ag_{(s)}$

---

**4. Calculate the standard cell potentials of galvanic cells in which the following reactions take place:**

**(i) $2Cr(s) + 3Cd^{2+}(aq) \longrightarrow 2Cr^{3+}(aq) + 3Cd$**

**(ii) $Fe^{2+}(aq) + Ag^+(aq) \longrightarrow Fe^{3+}(aq) + Ag(s)$**

**Calculate the $\Delta_r G^{\ominus}$ , and equilibrium constant of the reactions.**

**Ans. (i)**$E^\ominus$ $Cr^{3+}/Cr$ = -0.74V

$E^\ominus$ $Cd^{2+}/Cd$ = 0.40V

The galvanic cell of the given reaction is depicted as:

$Cr(s) \mid Cr^{3+}(aq) \mid\mid Cd^{2+}(aq) \mid Cd(s)$

Now, the standard cell potential is $\mathrm{E}_{\text{cell}}^\ominus = \mathrm{E}_\mathrm{R}^\ominus - \mathrm{E}_\mathrm{L}^\ominus$

= 0.40 – (–0.74)

= +0.34 V

$\Delta_r G^\ominus = -nFE_{\text{cell}}^\ominus$

In the given equation,

n = 6

F = 96487 C mol$^{-1}$

$E_{\text{cell}}^\ominus$ = +0.34 V

Then, $\Delta_r G^\ominus = -6 \times 96487\mathrm{Cmol}^{-1} \times 0.34\mathrm{V}$

= –196833.48 CV mol$^{-1}$

= –196833.48 J mol$^{-1}$

= –196.83 kJ mol$^{-1}$

Again, $\Delta_r G^\ominus = -\mathrm{RT}\ \ln \mathrm{K}$

$\Delta_\mathrm{t} G^\circ = -2.303\mathrm{RT\,In\,K}$

$\log \mathrm{K} = -\frac{\Delta_t \mathrm{G}}{2.303\mathrm{RT}}$

$= \frac{196.83 \times 10^3}{2.303 \times 8.314 \times 298}$ = 34.496

Therefore, K = antilog (34.496)

K= 3.13 $\times$ $10^{34}$

**(ii)** $\mathrm{E}_{\mathrm{Fe}^{3+}/\mathrm{Fe}^{2+}}^\ominus = 0.77\mathrm{V}$

$E_{Ag^+/Ag}^\ominus = 0.80\mathrm{V}$

The galvanic cell of the given reaction is depicted as: $Fe^{2+}$ (aq) | $Fe^{3+}$(aq) || $Ag^+$(aq) | Ag(s)

Now, the standard cell potential is $\mathrm{E}_{\text{cell}}^\ominus = \mathrm{E}_\mathrm{R}^\ominus - \mathrm{E}_\mathrm{L}^\ominus$

= 0.80 – 0.77

= 0.03 V

Here, n = 1.

Then,

$\Delta_r G^\ominus = -nFE_{\text{cell}}^\ominus$

$$= -1 \times 96487\text{Cmol}^{-1} \times 0.03\text{V}$$

= –2894.61 J $\text{mol}^{-1}$

= –2.89 kJ $\text{mol}^{-1}$

Again, $\Delta_r G^{\ominus} = -\text{RT ln K}$

$\Delta_\text{r} G^\circ = -2.303\text{RT In K}$

$\log K = -\frac{\Delta_r G}{2.303\text{RT}}$

$= \frac{-2894.61}{2.303 \times 8.314 \times 298}$ = 0.5073

Therefore, K = antilog (0.5073)

= 3.22 (approximately)

---

**5. Write the Nernst equation and emf of the following cells at 298 K:**

**(i)** Mg(s) I $\text{Mg}^{2+}$ (0.001M ) II $\text{Cu}^{2+}$ (0.0001M) I Cu(s)

**(ii)** Fe(s) I $\text{Fe}^{2+}$ (0.001M ) II $\text{H}^+$(1M) I $\text{H}_2$(g)(1 bar) | Pt(s)

**(iii)** Sn(s) I $\text{Sn}^{2+}$ (0.050M ) II $\text{H}^+$ (0.020M) I $\text{H}_2$(g)(1 bar) | Pt(s)

**(iv)** Pt(s)| $\text{Br}_2$(l)| $\text{Br}^-$(0.010 M) ||$\text{H}^+$ (0.030M) I $\text{H}_2$(g)(1 bar) | Pt(s)

**Ans.** (i) For the given reaction, the Nernst equation can be given as:

$$E_\text{cell} = E^{\ominus}_\text{cell} - \frac{0.0591}{n}\log\frac{[\text{Mg}^{2+}]}{[\text{Cu}^{2+}]}$$

$$= \{0.34 - (-2.36)\} - \frac{0.0591}{2}\log\frac{.001}{.0001}$$

$$= 2.7 - \frac{0.0591}{2}\log 10$$

= 2.7 - 0.02955 = 2.67 V (approximately)

(ii) For the given reaction, the Nernst equation can be given as:

$$E_\text{cell} = E^{\ominus}_\text{elll} - \frac{0.0591}{n}\log\frac{[\text{Fe}^{2+}]}{[\text{H}^+]^2}$$

$$= \{0 - (-0.44)\} - \frac{0.0591}{2}\log\frac{0.001}{1^2}$$

= 0.44 - 0.02955(-3)

= 0.52865 V = 0.53 V (approximately)

(iii) For the given reaction, the Nernst equation can be given as:

$$E_\text{cell} = E^{\ominus}_\text{cell} - \frac{0.0591}{n}\log\frac{[\text{Sn}^{2+}]}{[\text{H}^+]^2}$$

$$= \{0 - (-0.14)\} - \frac{0.0591}{2}\log\frac{0.050}{(0.020)^2}$$

= 0.14 - 0.0295 × log125

= 0.14 - 0.062

= 0.078 V

= 0.08 V (approximately)

(iv) For the given reaction, the Nernst equation can be given as:

$$E_{\text{cell}} = E^{\ominus}_{\text{cell}} - \frac{0.0591}{n}\log\frac{1}{[\text{Br}^-]^2[\text{H}^+]^2}$$

$$= (0-1.09) - \frac{0.0591}{2}\log\frac{1}{(0.010)^2(0.030)^2}$$

$$= -1.09 - 0.02955\times\log\frac{1}{0.00000009}$$

$$= -1.09 - 0.02955\times\log\frac{1}{9\times10^{-8}}$$

$$= -1.09 - 0.02955\times\log\left(1.11\times10^7\right)$$

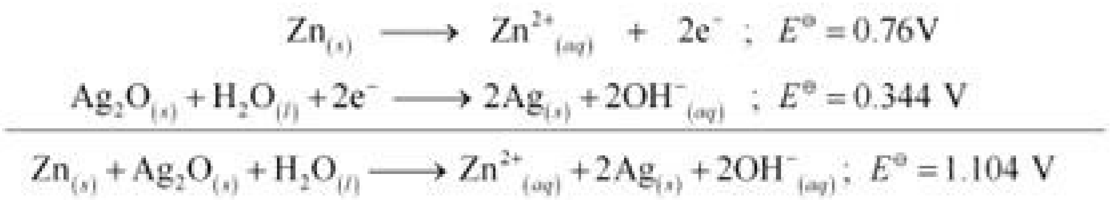
= - 1.09 - 0.02955(0.0453 + 7)

= - 1.09 - 0.208

= -1.298 V

**6. In the button cells widely used in watches and other devices the following reaction takes place: Zn(s) + $Ag_2$O(s) + $H_2$O(l) $\longrightarrow$Zn$^{2+}$(aq) + 2Ag(s) + 2OH$^-$ (aq). Determine $\Delta_r G^{\ominus}$and $\text{E}^{\ominus}$ for the reaction.**

**Ans.**



$$\text{Zn}_{(s)} \longrightarrow \text{Zn}^{2+}_{(aq)} + 2e^- \;;\; E^{\circ} = 0.76\text{V}$$

$$\text{Ag}_2\text{O}_{(s)} + \text{H}_2\text{O}_{(l)} + 2e^- \longrightarrow 2\text{Ag}_{(s)} + 2\text{OH}^-_{(aq)} \;;\; E^{\circ} = 0.344\text{ V}$$

$$\text{Zn}_{(s)} + \text{Ag}_2\text{O}_{(s)} + \text{H}_2\text{O}_{(l)} \longrightarrow \text{Zn}^{2+}_{(aq)} + 2\text{Ag}_{(s)} + 2\text{OH}^-_{(aq)} \;;\; E^{\circ} = 1.104\text{ V}$$

Therefore, $\text{E}^{\ominus}$ = 1.104 V

We know that,

$$\Delta_{\text{r}} G^{\ominus} = -\text{nFE}^{\ominus}$$

$$= -2\times96487\times1.04$$

= –213043.296 J

= –213.04 kJ

**7. Define conductivity and molar conductivity for the solution of an electrolyte. Discuss their variation with concentration.**

**Ans.** Conductivity of a solution is defined as the conductance of a solution of 1 cm in length and area of cross-section 1 sq. cm. The inverse of resistivity is called conductivity or specific conductance. It is represented by the symbol $K$. If $\rho$ is resistivity, then we can write: $\mathrm{K} = \frac{1}{\rho}$ and since length is taken as 1 cm and area of cross section is 1 sq. cm so volume will be 1 $cm^3$ so conductivity of a solution at any given concentration can also be defined as the conductance (G) of 1 $cm^3$ volume of solution kept between two platinum electrodes.

i.e.,$G = K\frac{a}{l}$ = k.1 = k

(Since a = 1sq. cm , l = 1 cm)

Conductivity always decreases with a decrease in concentration, both for weak and strong electrolytes. This is because the number of ions per unit volume that carry the current in a solution decreases with a decrease in concentration.

**Molar conductivity:**

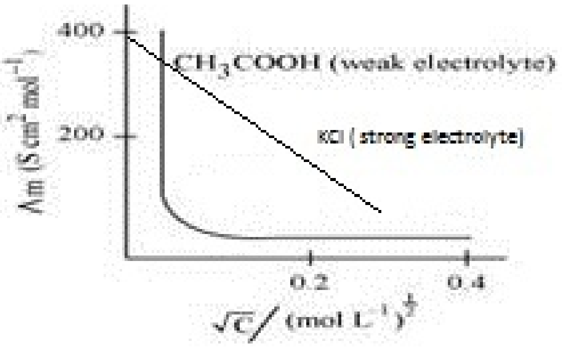
Molar conductivity of a solution at a given concentration is the conductance of volume V of a solution containing 1 mole of the electrolyte kept between two electrodes with the area of cross-section $A$ and distance of unit length.

$A_m$ = KV

Molar conductivity increases with a decrease in concentration. This is because the total volume V of the solution containing one mole of the electrolyte increases on dilution.

For weak electrolyte at any concentration $A_m$ is very less compare to strong electrolyte as weak electrolyte does not dissociate completely.

The variation of $A_m$ with $\sqrt{c}$ for strong and weak electrolytes is shown in the following plot:



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**8. The conductivity of 0.20 M solution of KCl at 298 K is 0.0248 S $cm^{-1}$. Calculate its molar conductivity.**

**Ans.** Given,

$K$= 0.0248 S $cm^{-1}$

c = 0.20 M

Therefore, Molar conductivity, $\Lambda_m = \frac{K \times 1000}{c}$

$= \frac{0.0248 \times 1000}{0.2}$

= 124 S $cm^2mol^{-1}$

---

**9. The resistance of a conductivity cell containing 0.001M KCl solution at 298 K is 1500 $\Omega$ . What is the cell constant if conductivity of 0.001M KCl solution at 298 K is 0.146 $\times$ $10^{-3}$ S $cm^{-1}$ .**

**Ans.** Given,

Conductivity, K = 0.146 $\times 10^{-3}$ S $cm^{-1}$

Resistance, *R* = 1500 $\Omega$

Therefore, Cell constant$= K \times R$

$= 0.146 \times 10^{-3} \times 1500$

= 0.219 $cm^{-1}$

---

**Chapter End Question**

**10. The conductivity of sodium chloride at 298 K has been determined at different concentrations and the results are given below:**

| **Concentration/M** | **0.001** | **0.010** | **0.020** | **0.050** | **0.100** |
|---|---|---|---|---|---|
| **$10^2$ K/S $m^{-1}$** | **1.237** | **11.85** | **23.15** | **55.53** | **106.74** |

**Calculate $A_m$ for all concentrations and draw a plot between $A_m$ and $C^{0.5}$. Find the value of $A_m^0$.**

**Ans.** Given, K = 1.237 $\times 10^{-2}$ S $m^{-1}$, c = 0.001 M

Then, k = 1.237 $\times$ $10^{-2}$ $Sm^{-1}$; $c^{0.5}$ = 0.0316 $M^{0.5}$

Therefore, $A_m = \frac{K}{c}$

$= \frac{1.237 \times 10^{-4} Scm^{-1}}{0.001 molL^{-1}} \times \frac{1000 cm^3}{L}$

= 123.7 S $cm^2mol^{-1}$

Given,

K = 11.85 $\times 10^{-2}$ S $m^{-1}$, c = 0.010 M

Then, K =11.85 $\times$ $10^{-2}$ ; $c^{0.5}$ = 0.1 $M^{0.5}$

Therefore, $A_m = \frac{K}{c}$

$= \frac{11.85 \times 10^{-4} \text{Scm}^{-1}}{0.010 \text{molL}^{-1}} \times \frac{1000 \text{cm}^3}{\text{L}}$

= 118.5 S $cm^2 mol^{-1}$

Given,

K = 23.15 $\times 10^{-4}$ S $m^{-1}$, c = 0.020 M

Then, K = 23.15 $\times 10^{-4}$ S $m^{-1}$, $c^{1/2}$ = 0.1414 $M^{1/2}$

Therefore, $A_m = \frac{K}{c}$

$= \frac{23.15 \times 10^{-4} \text{Scm}^{-1}}{0.020 \text{molL}^{-1}} \times \frac{1000 \text{cm}^3}{\text{L}}$

= 115.8 S $cm^2 mol^{-1}$

Given,$A_m = \frac{K}{c}$

K = 55.53 $\times 10^{-4}$ S $m^{-1}$, c = 0.050 M

Then, K = 55.53 $\times 10^{-4}$ S $m^{-1}$, $c^{1/2}$ = 0.2236 $M^{1/2}$

Therefore,

$= \frac{55.53 \times 10^{-4} \text{Scm}^{-1}}{0.050 \text{molL}^{-1}} \times \frac{1000 \text{cm}^3}{\text{L}}$

= 111.11 S $cm^2 mol^{-1}$

Given,

K = 106.74 $\times 10^{-4}$ S $m^{-1}$, c = 0.100 M

Then, K = 106.74 $\times 10^{-4}$ S $m^{-1}$, $c^{1/2}$ = 0.3162 M $^{1/2}$

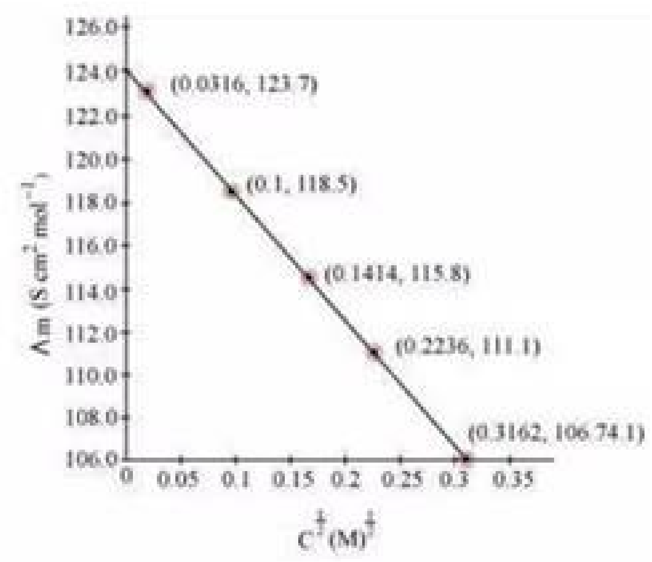
Therefore, $A_m$ = $\frac{K}{c}$

$= \frac{106.74 \times 10^{-4} \text{Scm}^{-1}}{0.100 \text{mol}^{-1}} \times \frac{1000 \text{cm}^3}{\text{L}}$

= 106.74 S $cm^2 mol^{-1}$

Now, we have the following data:

| $\frac{C^{\frac{1}{2}}}{M^{\frac{1}{2}}}$ | 0.0316 | 0.1 | 0.1414 | 0.2236 | 0.3162 |
|---|---|---|---|---|---|
| $A_m$(S $cm^2$ $mol^{-1}$) | 123.7 | 118.5 | 115.8 | 111.1 | 106.74 |



Since the line interrupts $A_m$ at 124.0 S $cm^2mol^{-1}$, $A_m{}^0$ = 124.0 S $cm^2mol^{-1}$

---

**11.Conductivity of 0.00241 M acetic acid is 7.896 $\times$ $10^{-5}$ S $cm^{-1}$. Calculate its molar conductivity and if $A_m{}^o$ for acetic acid is 390.5 S $cm^2$ $mol^{-1}$, what is its dissociation constant?**

**Answer** Given,K = 7.896 $\times$ $10^{-5}$ S $m^{-1}$

c = 0.00241 mol $L^{-1}$

Then, molar conductivity, $A_m$ = K/c

= $\frac{7.896\times10^{-5}\,\mathrm{Scm}^{-1}}{0.00241\mathrm{molL}^{-1}} \times \frac{1000\mathrm{cm}^3}{\mathrm{L}}$

= 32.76 S $cm^2$ $mol^{-1}$

Again, $A_m{}^\circ$ = 390.5 S $cm^2$ $mol^{-1}$

Now, $\alpha = \frac{\Lambda_m}{\Lambda_m^0} = \frac{32.76\mathrm{Scm}^2\mathrm{mol}^{-1}}{390.5\mathrm{Scm}^2\mathrm{mol}^{-1}}$

= 0.084

Dissociation constant, $K_a = \frac{c\alpha^2}{(1-\alpha)}$

= (0.00241 mol $L^{-1}$)$(0.084)^2$ / (1-0.084)

= 1.86 $\times$ $10^{-5}$ mol $L^{-1}$

---

**12. How much charge is required for the following reductions:**

**(i) 1 mol of $Al^{3+}$ to Al.**

**(ii) 1 mol of $Cu^{2+}$ to Cu.**

**(iii) 1 mol of $MnO_4^-$ to $Mn^{2+}$.**

**Ans. (i)** $Al^{3+} + 3e^- \longrightarrow Al$

Therefore, Required charge = 3 F

= 3 $\times$ 96487 C

= 289461 C

**(ii)** $Cu^{2+} + 2e^- \longrightarrow Cu$

Therefore, Required charge = 2 F

= 2 $\times$ 96487 C

= 192974 C

**(iii)** $MnO_4^- \rightarrow Mn^{2+}$

i.e., $Mn^{7+} + 5e^- \longrightarrow Mn^{2+}$

Therefore, Required charge = 5 F

= 5 $\times$ 96487 C

= 482435 C

---

**13. How much electricity in terms of Faraday is required to produce**

**(i) 20.0 g of Ca from molten $CaCl_2$.**

**(ii) 40.0 g of Al from molten $Al_2O_3$.**

**Ans. (i)** According to the question,

$Ca^{2+} + 2e^- \longrightarrow Ca$

Electricity required to produce 40 g of calcium = 2 F

Therefore, electricity required to produce 20 g of calcium = $\frac{2\times20}{40}\mathrm{F}$

= 1 F

**(ii)** According to the question,

$Al^{3+} + 3e^- \longrightarrow Al$

Electricity required to produce 27 g of Al = 3 F

Therefore, electricity required to produce 40 g of Al = $\frac{3\times40}{27}\mathrm{F}$

= 4.44 F

**14. How much electricity is required in coulomb for the oxidation of**

**(i) 1 mol of $H_2O$ to $O_2$**

**(ii) 1 mol of FeO to $Fe_2O_3$.**

**Ans. (i)** According to the question,

$2H_2O \rightarrow 4H^+ + O_2 + 4e^-$

Electricity required for the oxidation of 1 mol of $H_2O$ to $O_2$= 2 F

= $2 \times$ 96487 C

= 192974 C

**(ii)** According to the question,

$Fe^{2+} \rightarrow Fe^{3+} + e^-$

Electricity required for the oxidation of 1 mol of FeO to $Fe_2O_3$= 1 F

= 96487 C

---

**15. A solution of $Ni(NO_3)_2$ is electrolysed between platinum electrodes using a current of 5 amperes for 20 minutes. What mass of Ni is deposited at the cathode?**

**Ans.** Given,

Current = 5A

Time = $20 \times$ 60= 1200 s

Therefore, Charge = $= \text{ current } \times \text{ time } = 5 \times 1200$= 6000 C

According to the reaction,

$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$

Nickel deposited by $2 \times$ 96487 Cof charge =58.71 g

Therefore, nickel deposited by 6000 C $= \frac{58.71 \times 6000}{2 \times 96487}$ g= 1.825 g

Hence, 1.825 g of nickel will be deposited at the cathode.

---

**16. Three electrolytic cells A,B,C containing solutions of $ZnSO_4$, $AgNO_3$ and $CuSO_4$ respectively are connected in series. A steady current of 1.5 amperes was passed through them until 1.45 g of silver deposited at the cathode of cell B. How long did the current flow? What mass of copper and zinc were**

**deposited?**

**Ans.** According to the reaction:

$Ag^+(aq) + e^- \longrightarrow Ag(s)$

i.e., 108 g of Ag is deposited by 96487 C.

Therefore, 1.45 g of Ag is deposited by = $\frac{96487 \times 1.45}{108}$C= 1295.43 C

Given,

Current = 1.5 A

Therefore, Time $= \frac{1295.43}{1.5}$s

= 863.6 s

= 864 s

= 14.40 min

Again,

$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

i.e., ,2 × 96487 C of charge deposit = 63.5 g of Cu

Therefore, 1295.43 C of charge will deposit = $\frac{63.5 \times 1295.43}{2 \times 96487}$g= 0.426 g of C

$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$

i.e.,2 × 96487 C of charge deposit = 65.4 g of Zn

Therefore, 1295.43 C of charge will deposit = $\frac{65.4 \times 1295.43}{2 \times 96487}$g= 0.439 g of Zn

**17. Using the standard electrode potentials given in Table 3.1, predict if the reaction between the following is feasible:**

**(i)** $Fe^{3+}(aq)$ and $I^-(aq)$

**(ii)** $Ag^+(aq)$ and $Cu(s)$

**(iii)** $Fe^{3+}(aq)$ and $Br^-(aq)$

**(iv)** $Ag(s)$ and $Fe^{3+}(aq)$

**(v)** $Br_2(aq)$ and $Fe^{2+}(aq)$

**Ans.**

$$\begin{array}{lll} \text{(i)} & \mathrm{Fe^{3+}_{(aq)}} + e^- \longrightarrow \mathrm{Fe^{2+}_{(aq)}}\ \big]\times 2; & E^\circ = +0.77\ \mathrm{V} \\ & 2\mathrm{I^-_{(aq)}} \longrightarrow \mathrm{I_{2(s)}} + 2e^-; & E^\circ = -0.54\ \mathrm{V} \\ \hline & 2\mathrm{Fe^{3+}_{(aq)}} + 2\mathrm{I^-_{(aq)}} \longrightarrow 2\mathrm{Fe^{2+}_{(aq)}} + \mathrm{I_{2(s)}}\ ; & E^\circ = +0.23\ \mathrm{V} \end{array}$$

Since $E^\ominus$ for the overall reaction is positive, the reaction between $Fe^{3+}$(aq) and $I^-$(aq) is feasible.

$$\begin{array}{lll} \text{(ii)} & \mathrm{Ag^{+}_{(aq)}} + e^- \longrightarrow \mathrm{Ag_{(s)}}\ \big]\times 2\ ; & E^\circ = +0.80\ \mathrm{V} \\ & \mathrm{Cu_{(s)}} \longrightarrow \mathrm{Cu^{2+}_{(aq)}} + 2e^-\ ; & E^\circ = -0.34\ \mathrm{V} \\ \hline & 2\mathrm{Ag^{+}_{(aq)}} + \mathrm{Cu_{(s)}} \longrightarrow 2\mathrm{Ag_{(s)}} + \mathrm{Cu^{2+}_{(aq)}}\ ; & E^\circ = +0.46\ \mathrm{V} \end{array}$$

Since $E^\ominus$ for the overall reaction is positive, the reaction between $Ag^+$(aq) and Cu(s) is feasible.

$$\begin{array}{lll} \text{(iii)} & \mathrm{Fe^{3+}_{(aq)}} + e^- \longrightarrow \mathrm{Fe^{2+}_{(aq)}}\ \big]\times 2\ ; & E^\circ = +0.77\ \mathrm{V} \\ & 2\mathrm{Br^-_{(aq)}} \longrightarrow \mathrm{Br_{2(l)}} + 2e^-\ ; & E^\circ = -1.09\ \mathrm{V} \\ \hline & 2\mathrm{Fe^{3+}_{(aq)}} + 2\mathrm{Br^-_{(aq)}} \longrightarrow 2\mathrm{Fe^{2+}_{(aq)}}\ \text{and}\ \mathrm{Br_{2(l)}}\ ; & E^\circ = -0.32\ \mathrm{V} \end{array}$$

Since $E^\ominus$ for the overall reaction is negative, the reaction between $Fe^{3+}$(aq) and $Br^-$(aq) is not feasible.

$$\begin{array}{lll} \text{(iv)} & \mathrm{Ag_{(s)}} \longrightarrow \mathrm{Ag^{+}_{(aq)}} + e^-\ ; & E^\circ = -0.80\ \mathrm{V} \\ & \mathrm{Fe^{3+}_{(aq)}} + e^- \longrightarrow \mathrm{Fe^{2+}_{(aq)}}\ ; & E^\circ = +0.77\ \mathrm{V} \\ \hline & \mathrm{Ag_{(s)}} + \mathrm{Fe^{3+}_{(aq)}} \longrightarrow \mathrm{Ag^{+}_{(aq)}} + \mathrm{Fe^{2+}_{(aq)}}\ ; & E^\circ = -0.03\ \mathrm{V} \end{array}$$

Since $E^\ominus$ for the overall reaction is negative, the reaction between Ag(s) and $Fe^{3+}$(aq) is not feasible.

$$\begin{array}{lll} \text{(iv)} & \mathrm{Br_{2(aq)}} + 2e^- \longrightarrow 2\mathrm{Br^-_{(aq)}}\ ; & E^\circ = +1.09\ \mathrm{V} \\ & \mathrm{Fe^{2+}_{(aq)}} \longrightarrow \mathrm{Fe^{3+}_{(aq)}} + e^-\ \big]\times 2\ ; & E^\circ = -0.77\ \mathrm{V} \\ \hline & \mathrm{Br_{2(aq)}} + 2\mathrm{Fe^{2+}_{(aq)}} \longrightarrow 2\mathrm{Br^-_{(aq)}} + 2\mathrm{Fe^{3+}_{(aq)}}\ ; & E^\circ = +0.32\ \mathrm{V} \end{array}$$

Since $E^\ominus$ for the overall reaction is positive, the reaction between $Br_2$(aq) and $Fe^{2+}$(aq) is feasible.

---

**18. Predict the products of electrolysis in each of the following:**

**(i) An aqueous solution of $AgNO_3$ with silver electrodes.**

**(ii) An aqueous solution of $AgNO_3$ with platinum electrodes.**

**(iii) A dilute solution of $H_2SO_4$ with platinum electrodes.**

**(iv) An aqueous solution of $CuCl_2$ with platinum electrodes.**

**Ans. (i)** At cathode:

The following reduction reactions compete to take place at the cathode.

$Ag^+(aq) + e^- \rightarrow Ag(s); E^\ominus = 0.80\ V$

$H^+(aq) + e^- \rightarrow \frac{1}{2}H_2; E^\ominus = 0.00\ V$

The reaction with a higher value of $E^\ominus$ takes place at the cathode. Therefore, deposition of silver will take place at the cathode.

At anode:

The Ag anode is attacked by $NO_3^-$ ions. Therefore, the silver electrode at the anode dissolves in the solution to form $Ag^+$.

**(ii)** At cathode:

The following reduction reactions compete to take place at the cathode.

$$Ag^+(aq) + e^- \rightarrow Ag_{(s)}; E^\ominus = 0.80V$$
$$H^+_{(aq)} + e^- \rightarrow \frac{1}{2}H_{2(g)}; E^\ominus = 0.00V$$

The reaction with a higher value of $E^\ominus$ takes place at the cathode. Therefore, deposition of silver will take place at the cathode.

At anode

Since Pt electrodes are inert, the anode is not attacked by $NO_3^-$ ions. Therefore, $OH^-$ or $NO_3^-$ ions can be oxidized at the anode. But $OH^-$ ions having a lower discharge potential and get preference and decompose to liberate $O_2$.

$OH^- \rightarrow OH + e^-$

$4OH- \rightarrow 2H_2O + O_2$

**(iii)** At the cathode, the following reduction reaction occurs to produce $H_2$ gas.

$$H^+_{(aq)} + e^- \rightarrow \frac{1}{2}H_{2(g)}$$

At the anode, the following processes are possible.

2H2O (l) →$O_2$(g) + 4$H^+$ (aq) + 4$e^-$; $E^{\ominus} = +1.23V$ .....................(1)

$2SO_4^{2-}(aq) \rightarrow S_2O_6^{2-}(aq) + 2e^-;E^{\ominus} = +1.96V$ ...................(2)

For dilute sulphuric acid, reaction (i) is preferred to produce $O_2$ gas. But for concentrated sulphuric acid, reaction (ii) occurs.

**(iv)** At cathode: The following reduction reactions compete to take place at the cathode.

$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}; E^{\ominus} = 0.34V$

$H^+_{(aq)} + e^- \rightarrow 1/2H_{2(g)};E^{\ominus} = 0.00V$

The reaction with a higher value of $E^{\ominus}$ takes place at the cathode. Therefore, deposition of copper will take place at the cathode.

At anode: The following oxidation reactions are possible at the anode.

$Cl^-_{(aq)} \rightarrow \frac{1}{2}Cl_{2(g)} + e^{-1}; E^{\ominus} = 1.36V$

$2H_2O_{(l)} \rightarrow O_{2(g)} + 4H^+_{(zq)} + 4e^-; E^{\ominus} = +1.23V$

At the anode, the reaction with a lower value of $E^{\ominus}$ is preferred. But due to the over-potential of oxygen, $Cl^-$ gets oxidized at the anode to produce $Cl_2$ gas.