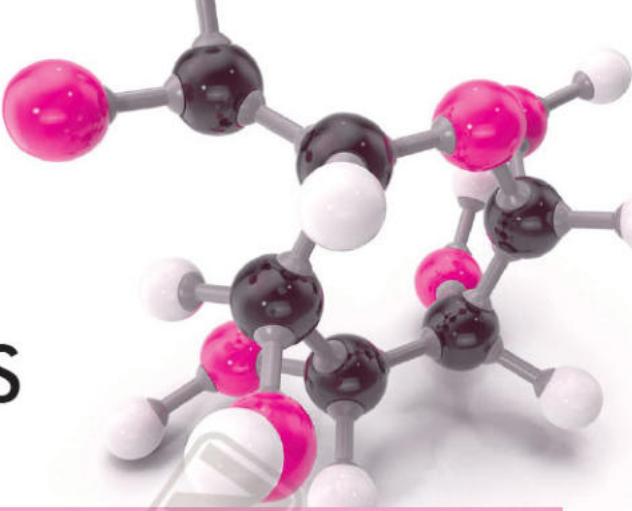


SOLUTIONS



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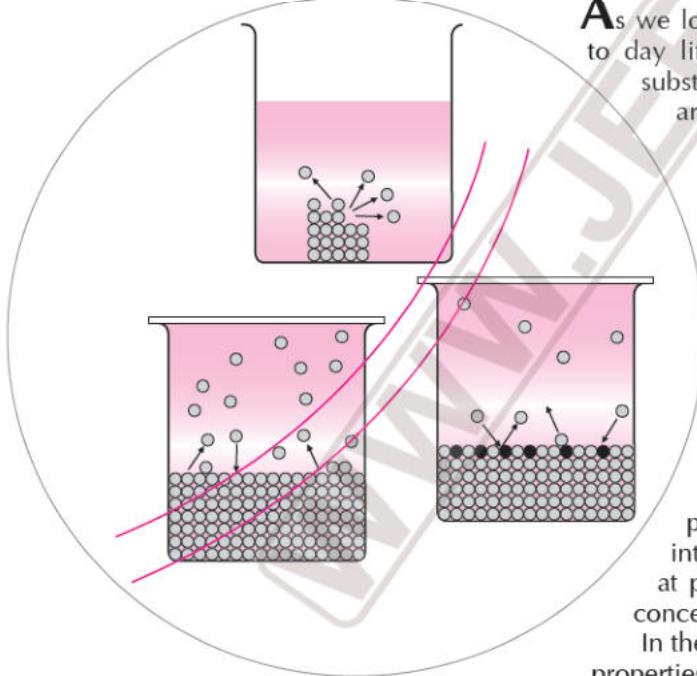
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As we look around, we rarely come across pure substances in our day to day life. Most of these are mixtures containing two or more pure substances. The homogeneous mixtures of two or more substances are called solutions. The air around us is a gaseous mixture of primarily oxygen and nitrogen, our blood is a liquid mixture of different components, the substances like milk, jaggery, sharbat drink etc. which appear to contain only one type of substance are, in fact, mixtures. Alloys such as brass, bronze, stainless steel etc. which we use in our daily life are also mixtures. The homogeneous mixtures of two or more substances are called solutions.

The importance or utility of solutions depends upon their compositions.

Many medicines dissolved in suitable non-aqueous solvents such as alcohol are given to patients. Saline glucose is administered to persons suffering from dehydration, 1 parts per million (ppm) of F^- ions in water prevents tooth decay and intravenous injections are always dissolved in water containing salts at particular ionic concentration which match with blood plasma concentrations and so on.

In the present unit we shall consider mostly liquid solutions and their properties.

SOLUTIONS

A solution is the homogeneous mixture of two or more substances whose composition can be varied within certain limits.

By homogeneous mixture we mean that its composition and properties are uniform throughout the mixture. The substances making up the solution are called **components** of the solution. Depending upon the total components present in the solution, it is called the **binary solution** (two components), **ternary solution** (three components), **quaternary solution** (four components), etc. For simplicity, we shall consider only binary solutions. The components

of a binary solution are generally referred to as **solute** and the **solvent**. In general, **a component which is present in the largest quantity** is called the **solvent** while **the component which is present in lesser quantity** is termed the **solute**.

In other words, a solute is a substance that dissolves and a solvent is a substance in which dissolution takes place. For example, if a crystal of sugar is dropped into a beaker of water, it dissolves to form a solution. In this case, sugar is solute and water is solvent. The solvent determines the physical state in which solution exists. In a solution, the particles are of molecular size (about 1000 pm) and the different components cannot be separated by any of the physical methods such as filtration, settling, centrifugation, etc.

TYPES OF SOLUTIONS

Depending upon the physical states of the solute and the solvent, the solutions can be classified into the following types.

Table 1. Different types of solutions.

Solute	Solvent	Common Examples
Gaseous solutions		
Gas	Gas	Mixture of nitrogen and oxygen gases, air
Liquid	Gas	Chloroform mixed with nitrogen gas, water vapour in air (humidity)
Solid	Gas	Camphor in nitrogen gas, dust or smoke particles in air
Liquid solutions		
Gas	Liquid	Oxygen dissolved in water, CO_2 dissolved in water
Liquid	Liquid	Ethanol or methanol dissolved in water
Solid	Liquid	Sucrose or salt in water
Solid solutions		
Gas	Solid	Solution of hydrogen in palladium (phenomenon of adsorption of gases over metals)
Liquid	Solid	Mercury with sodium (amalgams)
Solid	Solid	Copper dissolved in gold (alloys)

Out of these nine types of solutions, three solutions, namely *solid in liquid*, *liquid in liquid* and *gas in liquid* are very common. In all these three types of solutions, liquid acts as solvent.

The solutions in which water is the solvent are called **aqueous solutions** while those in which the solvent is other than water are called **non-aqueous solutions**. The common non-aqueous solvents are ether, benzene, carbon tetrachloride, etc.

METHODS FOR EXPRESSING THE CONCENTRATION OF SOLUTIONS : UNITS OF CONCENTRATION

The **concentration of a solution** may be defined as **the amount of solute present in the given quantity of the solution**. The concentration of solution may be expressed by several ways as discussed below :

1. Mass percentage or volume percentage

The **mass percentage of a component in a given solution** is **the mass of the component per 100 g of the solution**.

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

For example, if W_A is the mass of component A and W_B is the mass of component B in a solution, then

$$\text{Mass percentage of A} = \frac{W_A}{W_A + W_B} \times 100 \quad \dots(1)$$

This can be expressed as w/w. For example, a 10% (w/w) solution of sodium chloride means that 10 g of sodium chloride is present in 90 g of water so that the total mass of the solution is 100 g or simply 10 g of sodium chloride is present in 100 g of solution.

Volume percentage. In case of a liquid dissolved in another liquid, it is

convenient to express the concentrations in volume percentage. The **volume percentage** is defined as ***the volume of the component per 100 parts by volume of the solution***. For example, if V_A and V_B are the volumes of two components A and B respectively in a solution, then

$$\text{Volume percentage of A} = \frac{\text{Volume of A}}{\text{Volume of A} + \text{Volume of B}} \times 100$$

This may be expressed as *v/v*. For example, 10% by volume of ethanol solution means that 10 mL of ethanol is dissolved in water such that the total volume of the solution is 100 mL.

Mass by volume percentage (*w/v*). Sometimes, we express the concentrations as weight/volume. It is ***the mass of solute dissolved in 100 mL of the solution***. For example, a 10% solution of sodium chloride (*w/v*) means that 10 g of sodium chloride are dissolved in 100 mL of solution.

2. Parts per million

When a solute is present in very minute amounts (trace quantities), the concentration is expressed in *parts per million* abbreviated as **ppm**. It is ***the parts of a component per million parts of the solution***. It is expressed as :

$$\text{ppm A} = \frac{\text{Mass of component A}}{\text{Total mass of solution}} \times 10^6 \quad \dots(2)$$

Like percentage, concentration in parts per million can also be expressed as mass to mass, volume to volume or mass to volume. For example, suppose a litre of sea water (which weighs 1030g) contains about 6×10^{-3} g of dissolved oxygen (O_2). Its mass percentage is :

$$\text{Mass percentage of } O_2 = \frac{6 \times 10^{-3}}{1030} \times 100 = 5.8 \times 10^{-4}\%$$

Parts per million parts of dissolved O_2 is

$$\text{ppm of } O_2 = \frac{6 \times 10^{-3}}{1030} \times 10^6 = 5.8 \text{ ppm}$$

Thus, instead of expressing concentration of dissolved O_2 as $5.8 \times 10^{-4}\%$, it is better to express as 5.8 ppm.

Atmospheric pollution in cities due to harmful gases is generally expressed in *ppm* though in this case the values refer to volumes rather than masses. For example, the concentration of SO_2 in Delhi has been found to be as high as 10 ppm. This means that 10 cm^3 of SO_2 are present in 10^6 cm^3 (or 10^3 L) of air.

The concentration of atmospheric pollutants in cities is generally expressed in terms of $\mu\text{g/mL}$.

SOLVED EXAMPLES

Example 1.

If 11 g of oxalic acid are dissolved in 500 mL of solution (density = 1.1 g mL^{-1}), what is the mass % of oxalic acid in solution ?

Solution : 11 g of oxalic acid are present in 500 mL of solution.

$$\text{Density of solution} = 1.1 \text{ g } \text{mL}^{-1}$$

$$\begin{aligned} \text{Mass of solution} &= (500 \text{ mL}) \times (1.1 \text{ g } \text{mL}^{-1}) \\ &= 550 \text{ g} \end{aligned}$$

$$\text{Mass of oxalic acid} = 11 \text{ g}$$

$$\text{Mass \% of oxalic acid} = \frac{11}{550} \times 100 = 2\%$$

3. Molarity of a solution

Molarity of a solution is defined as ***the number of moles of the solute dissolved per litre of the solution***. It is represented as 'M'. Mathematically,

$$\text{Molarity} = \frac{\text{Moles of solute}}{\text{Volume of solution in litres}} \quad \dots(3)$$

Mass percentage of a component
 $\Rightarrow w/w$

Volume percentage of a component
 $\Rightarrow v/v$

Mass by volume percentage of a component
 $\Rightarrow w/v$

NOTE

Molarity is most common method for expressing concentration of solutions. Solutions of different molarities are commonly expressed as:

1 M = Molar solution

$\frac{M}{2}$ or 0.5 M = Semimolar solution

$\frac{M}{10}$ or 0.1 M = Decimolar solution

$\frac{M}{100}$ or 0.01 M = Centimolar solution

$\frac{M}{1000}$ or 0.001 M = Millimolar solution

It is convenient to express volume in cm^3 or mL so that

$$\text{Molarity} = \frac{\text{Moles of solute}}{\text{Volume of solution (in mL or } \text{cm}^3\text{)}} \times 1000 \quad (\because 1 \text{ litre} = 1000 \text{ mL})$$

Thus, the units of molarity are moles per litre (mol L^{-1}) or moles per cubic decimetre (mol dm^{-3}).* The symbol M is used for mol L^{-1} or mol dm^{-3} .

Moles of solute can be calculated as :

$$\text{Moles of solute} = \frac{\text{Mass of solute}}{\text{Molar mass of solute}}$$

For example, 0.25 M (or 0.25 mol L^{-1}) solution of NaOH means that 0.25 mol (or 10g; molar mass of NaOH = 40) has been dissolved in one litre (or one cubic decimetre) of the solution. If w g of the solute is present in V mL (or cm^3) of the solution, then

$$\text{Molarity, M} = \frac{w}{\text{Molar mass of solute} \times V} \times 1000$$

Molarity is one of the common measures of expressing concentration which is frequently used in the laboratory. However, it has one **disadvantage**. It changes with temperature because of expansion or contraction of the liquid with temperature.

SOLVED EXAMPLES**Example 2.**

2.46 g of sodium hydroxide (molar mass = 40) are dissolved in water and the solution is made to 100 cm^3 in a volumetric flask. Calculate the molarity of the solution.

Solution :

$$\text{Amount of NaOH} = 2.46 \text{ g}$$

$$\text{Volume of solution} = 100 \text{ cm}^3$$

$$\text{Moles of NaOH} = \frac{\text{Mass of NaOH}}{\text{Molar mass}}$$

$$= \frac{2.46 \text{ g}}{40 \text{ g mol}^{-1}} = 0.0615 \text{ mol}$$

$$\text{Molarity} = \frac{\text{Moles of NaOH}}{\text{Volume of solution}} \times 1000$$

$$= \frac{0.0615 \text{ mol}}{100 \text{ mL}} \times 1000 \text{ mL L}^{-1} = 0.615 \text{ mol L}^{-1}$$

or $= 0.615 \text{ M}$

4. Molality of a solution

Molality of a solution is defined as the number of moles of the solute dissolved per 1000 g (or 1 kg) of the solvent. It is denoted by m. Mathematically,

$$\text{Molality (m)} = \frac{\text{Moles of solute}}{\text{Mass of solvent in kg}} \quad \dots(4)$$

$$\text{or } m = \frac{\text{Moles of solute}}{\text{Mass of solvent in gram}} \times 1000$$

Thus, the units of molality are moles per kilogram i.e., mol kg^{-1} . For example, 1.0 m solution of KCl means that 1 mol (74.5 g) of KCl is dissolved in 1 kg or 1000 g of water.

If w g of solute are dissolved in W g of solvent, then

$$\text{Molality, } m = \frac{w}{\text{Molar mass of solute} \times W} \times 1000$$

* In SI units, volume is expressed as dm^3 and 1 litre = 1 dm^3 .

SOLVED EXAMPLES

Example 3.

Calculate the molality of a solution containing 20.7 g of potassium carbonate dissolved in 500 mL of solution (assume density of solution = 1 g mL⁻¹)

(A.I.S.B. 2005)

Solution : Mass of K₂CO₃ = 20.7 g
Molar mass of K₂CO₃ = 138 g mol⁻¹

$$\text{Moles of K}_2\text{CO}_3 = \frac{20.7 \text{ g}}{138 \text{ g mol}^{-1}} = 0.15 \text{ mol}$$

$$\begin{aligned}\text{Mass of solution} &= (500 \text{ mL}) \times (1 \text{ g mL}^{-1}) = 500 \text{ g} \\ \text{Amount of water} &= 500 - 20.7 = 479.3 \text{ g}\end{aligned}$$

$$\begin{aligned}\text{Molality} &= \frac{\text{Moles of solute}}{\text{Mass of solvent in gram}} \times 1000 \\ &= \frac{0.15 \text{ mol}}{479.3 \text{ g}} \times 1000 \text{ g kg}^{-1} \\ &= 0.313 \text{ mol kg}^{-1} \text{ or } = 0.313 \text{ m}\end{aligned}$$

Example 4.

2.5 g of ethanoic acid (CH₃COOH) is dissolved in 75 g of benzene. Calculate the molality of the solution. [N.C.E.R.T.] (Hr.S.B. 2012, Assam S.B. 2012)

Solution : Molar mass of CH₃COOH = 2 × 12 + 4 × 1 + 2 × 16 = 60 g mol⁻¹

$$\text{Moles of CH}_3\text{COOH} = \frac{2.5 \text{ g}}{60 \text{ g mol}^{-1}} = 0.0417 \text{ mol}$$

$$\text{Mass of benzene} = 75 \text{ g}$$

$$\begin{aligned}\text{Molality of CH}_3\text{COOH} &= \frac{\text{Moles of CH}_3\text{COOH}}{\text{Mass of benzene (in g)}} \times 1000 \\ &= \frac{0.0417 \text{ mol}}{75} \times 1000 \\ &= 0.556 \text{ m}\end{aligned}$$

5. Mole fraction

Mole fraction is the ratio of number of moles of one component to the total number of moles (solute and solvent) present in the solution.

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

It is denoted by x and a subscript used on the right hand side of x denotes the component. Let us suppose that a solution contains n_A moles of solute and n_B moles of the solvent. Then,

$$\text{Mole fraction of solute (}x_A\text{)} = \frac{n_A}{n_A + n_B} \quad \dots(5)$$

$$\text{Mole fraction of solvent (}x_B\text{)} = \frac{n_B}{n_A + n_B} \quad \dots(6)$$

The sum of mole fractions of all the components in a solution is always equal to one as shown below :

$$x_A + x_B = \frac{n_A}{n_A + n_B} + \frac{n_B}{n_A + n_B} = 1$$

Thus, if the mole fraction of one component of a binary solution is

KEY NOTE

Like mole fraction, the term **mass fraction** is also used. It is the mass of a given component per unit mass of the solution. If W_A and W_B are the masses of two components of the solution, then mass fraction of A,

$$x_A = \frac{W_A}{W_A + W_B}$$

and mass fraction of B,

$$x_B = \frac{W_B}{W_A + W_B}$$

Evidently, $x_A + x_B = 1$

Mass fraction multiplied by 100 gives **mass percentage** i.e. mass percentage of A = $x_A \times 100$

Like mass fraction, **volume fraction** may also be defined. If v_A and v_B are the volumes of two components A and B,

$$\text{volume fraction of A} = \frac{v_A}{v_A + v_B} \text{ and}$$

$$\text{volume fraction of B} = \frac{v_B}{v_A + v_B}.$$

Volume fraction multiplied by 100 gives **volume percentage**.

known, then that of the other can be calculated. For example, the mole fraction x_A is related to x_B as :

$$x_A = 1 - x_B \quad \text{or} \quad x_B = 1 - x_A$$

Relationship between Normality and Molarity of Solutions

The normality and molarity of a solution are related as :

Normality =

$$\text{Molarity} \times \frac{\text{Molar mass}}{\text{Equivalent mass}}$$

► For acids,

Normality = Molarity × Basicity

where basicity is the number of H^+ ions that a molecule of an acid can give in solution. For example, Normality of H_2SO_4

$$= 2 \times \text{Molarity of } H_2SO_4$$

Normality of H_3PO_4

$$= 3 \times \text{Molarity of } H_3PO_4.$$

► For bases,

Normality = Molarity × Acidity

where acidity is the number of OH^- ions that a molecule of base can give in solution. For example, Normality of KOH

$$= 1 \times \text{Molarity of KOH}$$

Normality of $Ba(OH)_2$

$$= 2 \times \text{Molarity of } Ba(OH)_2$$

► For salts

Normality = Molarity × Total positive valency of metal atoms because

Equivalent mass of salt =

$$\frac{\text{Mol. mass of salt}}{\text{Total positive valency of metal atoms}}$$

► For oxidising and reducing agents

Normality = Molarity × No. of electrons lost or gained by one molecule of the substance because

Equivalent mass of an oxidising or reducing agent

$$= \frac{\text{Mol. mass}}{\text{No. of electrons lost or gained by one molecule of the substance}}$$

► It may be noted that these days the terms normality or equivalent weight are not commonly used.

It may be noted that the **mole fraction is independent of temperature and is unitless.**

If a solution contains ' i ' number of components, we have

$$x_1 = \frac{n_1}{n_1 + n_2 + \dots + n_i} = \frac{n_1}{\sum n_i}$$

$$x_2 = \frac{n_2}{n_1 + n_2 + \dots + n_i} = \frac{n_2}{\sum n_i}, \text{ etc.}$$

In general, for a solution containing ' i ' number of components;

$$x_i = \frac{n_i}{\sum n_i}$$

$$\text{and } x_1 + x_2 + \dots + x_i = 1$$

SOLVED EXAMPLES

□ Example 5.

Calculate the mole fraction of ethylene glycol ($C_2H_6O_2$) in a solution containing 20% of $C_2H_6O_2$ by mass.

(H.P.S.B. 2014, Meghalaya S.B. 2017) N.C.E.R.T.

Solution : 20% ethylene glycol solution means that 20 g of ethylene glycol is present in 100 g of solution or 20 g of ethylene glycol is present in 80 g of water.

$$\text{Molar mass of } C_2H_6O_2 = 2 \times 12 + 6 \times 1 + 2 \times 16 = 62 \text{ g mol}^{-1}$$

$$\text{Moles of } C_2H_6O_2 = \frac{20 \text{ g}}{62 \text{ g mol}^{-1}} = 0.322 \text{ mol}$$

$$\text{Moles of water} = \frac{80 \text{ g}}{18 \text{ g mol}^{-1}} = 4.444 \text{ mol}$$

$$\begin{aligned} x_{\text{glycol}} &= \frac{\text{Moles of } C_2H_6O_2}{\text{Moles of } C_2H_6O_2 + \text{Moles of } H_2O} \\ &= \frac{0.322}{0.322 + 4.444} = 0.068 \end{aligned}$$

$$x_{\text{water}} = \frac{4.444}{0.322 + 4.444} = 0.932$$

or

$$x_{\text{water}} = 1 - 0.068 = 0.932$$

6. Normality

Normality of a solution is **the number of gram equivalents of the solute dissolved per litre of the solution**. It is denoted by N.

$$\text{Normality (N)} = \frac{\text{Number of gram equivalents of solute}}{\text{Volume of solution in litres}} \quad \dots(7)$$

or Normality = $\frac{\text{Number of gram equivalents of solute}}{\text{Volume of solution in mL}} \times 1000$

Thus, the units of normality are gm equivalent per litre i.e., g equiv L⁻¹.

Gram equivalents of solute can be calculated as :

$$\text{Gram equivalents of solute} = \frac{\text{Mass of solute}}{\text{Equivalent mass}}$$

Like molarity, normality of a solution also changes with temperature.

SOLVED EXAMPLES

□ Example 6.

Calculate the normality of solution containing 31.5 g of hydrated oxalic acid ($H_2C_2O_4 \cdot 2H_2O$) in 1250 mL of solution.

Solution : Mass of oxalic acid = 31.5 g

$$\text{Equivalents of oxalic acid} = \frac{31.5}{63} = 0.5 \quad (\text{Eq. wt. } 126/2 = 63)$$

$$\text{Volume of solution} = 1250 \text{ mL}$$

$$\text{Normality} = \frac{0.5}{1250} \times 1000 = 0.4 \text{ N.}$$

Let us sum up different concentration units.

SUM UP	Measure	Unit	Definition
Molarity	mol L ⁻¹ or M		moles of solute per litre of solution
Molality	mol kg ⁻¹ or m		moles of solute per kilogram of solvent
Mole fraction (<i>x</i>)	—		number of moles of a component expressed as a fraction of total number of moles
Mass percentage	%		mass of a component expressed as a percentage of total mass
Volume percentage	%		volume of a component expressed as a percentage of the total volume
Parts per million by mass	ppm (by mass)		mass in grams per million grams of the sample
Parts per million by volume	ppm (by volume)		volume in mL per 10^6 mL or 10^3 L of the sample

Sometimes, the concentrations of ionic substances are expressed as formality.

7. Formality

It is the number of formula mass of the solute dissolved per litre of the solution. It is represented by F.

$$\text{Formality} = \frac{\text{Number of formula masses of solute}}{\text{Volume of the solution in litre}} \quad \dots(8)$$

The term formality is used to express the concentrations of ionic substances. The ionic compounds such as NaCl, KNO₃, CuSO₄, etc. do not exist as discrete molecules. In such cases, we do not use the term mole for expressing the concentration. The sum of the atomic masses of various atoms constituting the formula of the ionic compounds is called **gram formula mass** instead of molar mass.

WATCH OUT !

- Molarity of a solution changes with temperature due to accompanied changes in volume of the solution.
- Molality and mole fraction do not change with temperature.

Competition Plus

► Relation between molarity and molality,

$$\frac{1}{m} = \frac{\rho}{M} - \frac{M_2}{1000}$$

► Relation between molarity and mole fraction,

$$M = \frac{x_2 \times 1000 \times \rho}{x_1 M_1 + x_2 M_2}$$

► Relation between molality and mole fraction,

$$m = \frac{1000 x_2}{x_1 M_1}$$

For details, refer **Competition File** (Page 98).

Solving Numerical Problems

FORMULAE AND UNITS

$$\text{Molarity (M)} = \frac{\text{Moles of solute}}{\text{Vol. of solution (in mL)}} \times 1000$$

$$\text{Molality (m)} = \frac{\text{Moles of solute}}{\text{Mass of solvent (in g)}} \times 1000$$

$$\text{Normality (N)} = \frac{\text{Gram equiv. of solute}}{\text{Vol. of solution (in mL)}} \times 1000$$

$$\text{Normality} = \text{Molarity} \times \frac{\text{Mol. mass}}{\text{Eq. mass}}$$

$$\text{Mole fraction of solute (x}_B\text{)} = \frac{\text{Moles of solute}}{\text{Moles of solute} + \text{Moles of solvent}}$$

$$\text{Mole fraction of solute} + \text{Mole fraction of solvent} = 1$$

$$\text{or Mole fraction of solvent} = 1 - \text{Mole fraction of solute.}$$

SOLVED EXAMPLES

Example 7.

2.82 g of glucose (molar mass = 180) are dissolved in 30 g of water. Calculate (a) the molality (b) mole fraction of glucose and water.

Solution : (a) Calculation of molality of solution.

$$\text{Mass of glucose} = 2.82 \text{ g}$$

$$\text{Moles of glucose} = \frac{2.82}{180} \text{ (Molar mass} = 180)$$

$$\text{Mass of water} = 30 \text{ g}$$

$$\begin{aligned}\text{Molality} &= \frac{\text{Moles of glucose}}{\text{Mass of water}} \times 1000 \\ &= \frac{2.82 \times 1000}{180 \times 30} = 0.522 \text{ m}\end{aligned}$$

(b) Calculation of mole fraction

$$\text{Moles of glucose} = \frac{2.82}{180} = 0.0157$$

$$\text{Moles of water} = \frac{30}{18} = 1.67$$

$$\text{Mole fraction of glucose} = \frac{0.0157}{0.0157 + 1.67} = 0.009$$

$$\text{Mole fraction of water} = \frac{1.67}{0.0157 + 1.67} = 0.991$$

Example 8.

Calculate the molarity of pure water (density of water = 1 g mL⁻¹)

Solution: Density of water = 1 g mL⁻¹

$$\begin{aligned}\text{Mass of 1000 mL of water} &= \text{Volume} \times \text{Density} \\ &= 1000 \times 1 = 1000 \text{ g}\end{aligned}$$

$$\text{Moles of water} = \frac{1000}{18} = 55.55 \text{ mol}$$

Now, 55.55 moles of H₂O are present in 1000 ml or 1L of water

$$\therefore \text{Molarity} = 55.55 \text{ M.}$$

Example 9.

A solution is 25% water, 25% ethanol and 50% acetic acid by mass. Calculate the mole fraction of each component. (H.P.S.B. 2011, 2015, 2018)

Solution : Let the total mass of solution = 100 g

$$\text{Mass of water} = 25 \text{ g}$$

$$\text{Mass of ethanol} = 25 \text{ g}$$

$$\text{Mass of acetic acid} = 50 \text{ g}$$

$$\text{Moles of water} = \frac{25}{18} = 1.388$$

$$(\because \text{Molar mass of H}_2\text{O} = 18)$$

$$\text{Moles of ethanol} = \frac{25}{46} = 0.543$$

$$(\because \text{Molar mass of C}_2\text{H}_5\text{OH} = 46)$$

$$\text{Moles of acetic acid} = \frac{50}{60} = 0.833$$

$$(\because \text{Molar mass of CH}_3\text{COOH} = 60)$$

$$\begin{aligned}\text{Total number of moles} &= 1.388 + 0.543 + 0.833 \\ &= 2.764\end{aligned}$$

$$\text{Mole fraction of water} = \frac{1.388}{2.764} = 0.502$$

$$\text{Mole fraction of ethanol} = \frac{0.543}{2.764} = 0.196$$

$$\text{Mole fraction of acetic acid} = \frac{0.833}{2.764} = 0.302$$

Example 10.

Calculate the moles of methanol in 5 litres of its 2 m solution, if the density of the solution is 0.981 kg L⁻¹ (Molar mass of methanol = 32.0 g mol⁻¹).

Solution : Mass of 5L solution = $5\text{L} \times 0.981 \text{ kg L}^{-1}$
 $= 4.905 \text{ kg} = 4905 \text{ g}$

Mass of 2 m solution = $1000 \text{ g} + 2 \text{ moles of methanol}$
 $= 1000 + 2 \times 32$
 $= 1000 + 64 = 1064 \text{ g}$

Now 1064 g of solution contains methanol = 2 mol
 $4905 \text{ g of solution contains methanol} = \frac{2}{1064} \times 4905$
 $= 9.22 \text{ mol.}$

Example 11.

Calculate the mass percentage of aspirin ($\text{C}_9\text{H}_8\text{O}_4$) in acetonitrile (CH_3CN) when 6.5 g of $\text{C}_9\text{H}_8\text{O}_4$ is dissolved in 450 g of CH_3CN .

N.C.E.R.T.

Solution : Mass of aspirin ($\text{C}_9\text{H}_8\text{O}_4$) = 6.5 g
 Mass of acetonitrile (CH_3CN) = 450 g
 Total mass of solution = $450 + 6.5$
 $= 456.5 \text{ g}$

Mass % aspirin = $\frac{6.5}{456.5} \times 100$
 $= 1.424 \%$

Example 12.

A solution of glucose (molar mass = 180 g mol^{-1}) in water is labelled as 10% by mass. What would be the molality and molarity of the solution? (Density of solution = 1.2 g mL^{-1}) (A.I.S.B. 2014)

Solution : 10% (by mass) solution of glucose means that 10 g of glucose is present in 100 g of solution or in 90 g of water.

(i) Calculation of molality

Mass of glucose = 10 g
 Moles of glucose = $\frac{10}{180} = 0.0556$
 (Molar mass of glucose = 180)
 Mass of water = 90 g
 \therefore Molality = $\frac{\text{Moles of glucose}}{\text{Mass of water}} \times 1000$
 $= \frac{0.0556}{90} \times 1000 = 0.618 \text{ m.}$

(ii) Calculation of molarity

Moles of glucose = 0.0556
 Volume of solution = $\frac{\text{Mass}}{\text{Density}}$
 $= \frac{100}{1.20} = 83.3 \text{ mL}$

Molarity = $\frac{\text{Moles of glucose}}{\text{Vol. of solution}} \times 1000$
 $= \frac{0.0556}{83.3} \times 1000 = 0.667 \text{ M.}$

Example 13.

A commercially available sample of sulphuric acid is 15% H_2SO_4 by weight (density = 1.10 g mL^{-1}). Calculate (i) molarity (ii) normality and (iii) molality of the solution. (Pb.S.B. 2007, 2015)

Solution : 15% H_2SO_4 solution means that 15 g of H_2SO_4 are present in 100 g of solution in water.

(i) Calculation of molarity of solution

Weight of H_2SO_4 per 100 g of solution = 15 g

Gram moles of $\text{H}_2\text{SO}_4 = \frac{15}{98} \text{ mol}$

Volume of solution = $\frac{\text{Mass}}{\text{Density}} = \frac{100 \text{ g}}{1.10} = 90.9 \text{ mL}$

\therefore Molarity of $\text{H}_2\text{SO}_4 = \frac{\text{Moles of H}_2\text{SO}_4}{\text{Volume of solution (mL)}} \times 1000$
 $= \frac{15 \times 1000}{98 \times 90.9} = 1.68 \text{ M.}$

(ii) Calculation of normality

Equivalent mass of $\text{H}_2\text{SO}_4 = \frac{\text{Molar mass}}{2} = \frac{98}{2} = 49$

Gram equivalents of $\text{H}_2\text{SO}_4 = \frac{\text{Mass of H}_2\text{SO}_4}{\text{Equivalent mass}} = \frac{15}{49} = \frac{15}{49}$

Normality = $\frac{\text{Gram equivalent of H}_2\text{SO}_4}{\text{Volume of solution (mL)}} \times 1000$
 $= \frac{15 \times 1000}{49 \times 90.9} = 3.36 \text{ N.}$

(iii) Calculation of molality

Weight of water in solution = $100 - 15 = 85 \text{ g}$

Moles of $\text{H}_2\text{SO}_4 = \frac{15}{98}$

Molality = $\frac{\text{Moles of H}_2\text{SO}_4}{\text{Wt. of solvent in gram}} \times 1000$
 $= \frac{15 \times 1000}{98 \times 85} = 1.8 \text{ m.}$

Example 14.

A sugar syrup of weight 214.2 g contains 34.2 g of sugar ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$). Calculate :

(i) molal concentration, and

(ii) mole fraction of sugar in the syrup.

(H.P.S.B. 2011, Pb. S.B. 2011)

Solution : (i) Weight of sugar syrup = 214.2 g

Weight of sugar in syrup = 34.2 g

Weight of water in syrup = $214.2 - 34.2 = 180.0 \text{ g}$

Moles of sugar = $\frac{34.2}{342} = 0.1$ (Molar mass = 342)

Molality = $\frac{0.1}{180} \times 1000 = 0.56 \text{ m.}$

(ii) Moles of sugar = $\frac{34.2}{342} = 0.1$

Moles of water = $\frac{180}{18} = 10$

Mole fraction of sugar = $\frac{0.1}{10 + 0.1} = 0.0099.$

Example 15.

An antifreeze solution is prepared from 222.6 g of ethylene glycol, $C_2H_4(OH)_2$ and 200 g of water. Calculate the molality of the solution. If the density of this solution be 1.072 g mL^{-1} , what will be the molarity of the solution? **N.C.E.R.T.** (D.S.B. 2007)

Solution : (i) Calculation of molality

$$\begin{aligned}\text{Mass of ethylene glycol} &= 222.6 \text{ g} \\ \text{Molar mass of ethylene glycol} &= 2 \times \text{At. mass of C} + 6 \times \text{At.} \\ &\quad \text{mass of H} + 2 \times \text{At. mass of O} \\ &= 2 \times 12 + 6 \times 1 + 2 \times 16 = 62\end{aligned}$$

$$\text{Moles of ethylene glycol} = \frac{222.6}{62} = 3.59 \text{ mol}$$

$$\text{Mass of water} = 200 \text{ g}$$

$$\begin{aligned}\text{Molality} &= \frac{\text{Moles of ethylene glycol}}{\text{Mass of water}} \times 1000 \\ &= \frac{3.59}{200} \times 1000 = 17.95 \text{ m.}\end{aligned}$$

(ii) Calculation of molarity

$$\text{Moles of ethylene glycol} = 3.59 \text{ mol}$$

$$\text{Mass of solution} = 200 + 222.6 = 422.6 \text{ g}$$

$$\begin{aligned}\text{Volume of solution} &= \frac{\text{Mass}}{\text{Density}} \\ &= \frac{422.6}{1.072} = 394.22 \text{ mL}\end{aligned}$$

$$\begin{aligned}\text{Molarity} &= \frac{\text{Moles of ethylene glycol}}{\text{Vol. of solution}} \times 1000 \\ &= \frac{3.59}{394.22} \times 1000 = 9.11 \text{ M.}\end{aligned}$$

Example 16.

What is the mole fraction of the solute in 2.5 m aqueous solution?

Solution : 2.5 m aqueous solution means that 2.5 moles of solute are present in 1000 g of water. Thus,

$$\text{Moles of solute} = 2.5$$

$$\text{Moles of water} = \frac{1000}{18} = 55.6$$

$$\text{Mole fraction of solute} = \frac{2.5}{2.5 + 55.6} = 0.043.$$

Example 17.

Calculate the volume of 80% H_2SO_4 by weight (density = 1.80 g mL^{-1}) required to prepare 1L of 0.2 M H_2SO_4 .

Solution : 80% H_2SO_4 solution means that 80 g of H_2SO_4 are present in 100 g of solution in water.

$$\text{Moles of } H_2SO_4 \text{ present} = \frac{80}{98} \text{ mol}$$

$$\begin{aligned}\text{Volume of solution} &= \frac{\text{Mass}}{\text{Density}} = \frac{100 \text{ g}}{1.8 \text{ g mL}^{-1}} \\ &= 55.5 \text{ mL} \\ \text{Molarity of solution} &= \frac{80 \times 1000}{98 \times 55.5} = 14.7 \text{ M}\end{aligned}$$

To calculate the volume of 14.7 M H_2SO_4 required to prepare, 1 L of 0.2 M H_2SO_4 , we can apply molarity equation*:

$$\begin{aligned}M_1 V_1 &= M_2 V_2 \\ 14.7 \times V_1 &= 0.2 \times 1000 \\ \therefore V_1 &= \frac{0.2 \times 1000}{14.7} = 13.60 \text{ mL}\end{aligned}$$

Volume of 14.7 M H_2SO_4 required = 13.60 mL.

Example 18.

The mole fraction of benzene in a solution with toluene is 0.50. Calculate the mass percent of benzene in the solution.

Solution : Let mass percentage of benzene in solution is x . This means 100 g of solution contains x g benzene and $(100 - x)$ g of toluene.

$$\text{Mass of benzene} = x \text{ g}$$

$$\text{Moles of benzene} = \frac{x}{78} \text{ (Mol. mass of } C_6H_6 = 78)$$

$$\text{Mass of toluene} = (100 - x) \text{ g}$$

$$\text{Moles of toluene} = \frac{100 - x}{92}$$

$$\text{(Mol. mass of } C_6H_5CH_3 = 92)$$

Now mole fraction of benzene = 0.5

$$\frac{\text{Moles of benzene}}{\text{Moles of benzene} + \text{Moles of toluene}} = 0.5$$

$$\frac{\frac{x}{78}}{\frac{x}{78} + \frac{100 - x}{92}} = 0.5$$

$$\frac{x}{78} \times \left[\frac{78 \times 92}{92x + 78(100 - x)} \right] = 0.5$$

$$92x = 46x + 3900 - 39x$$

$$85x = 3900$$

$$x = 45.9$$

∴ Mass percent of benzene = 45.9 wt%.

Example 19.

A sample of drinking water was found to be severely contaminated with chloroform ($CHCl_3$), supposed to be 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.

Solution : 15 ppm (by mass) means 15 g of CHCl_3 is present in 10^6 g of solution.

$$(i) \text{ Percent by mass} = \frac{\text{Mass of chloroform}}{\text{Total mass}} \times 100 \\ = \frac{15}{10^6} \times 100 = 1.5 \times 10^{-3}\%$$

(ii) Calculation of molality

$$\text{Mass of } \text{CHCl}_3 = 15 \text{ g}$$

$$\text{Moles of } \text{CHCl}_3 = \frac{15}{119.5}$$

$$(\text{Molar mass of } \text{CHCl}_3 = 119.5) \\ = 0.1255 \text{ mol}$$

$$\text{Mass of water} = 10^6 - 15 \approx 10^6$$

$$\text{Molality} = \frac{\text{Moles of } \text{CHCl}_3}{\text{Mass of water}} \times 1000 \\ = \frac{0.1255}{10^6} \times 1000 \\ = 1.255 \times 10^{-4} \text{ m.}$$

Note. If we use mass of water as $10^6 - 15 = 9999085$ g, even then molality comes out to be 1.255×10^{-4} m.

□ Example 20.

The mole fraction of water in a sulphuric acid solution is 0.85. Calculate the molality of the solution.

Solution : Mole fraction of water in solution = 0.85.

Mole fraction of H_2SO_4 in solution = $1 - 0.85 = 0.15$.

If n_1 is the number of moles of water and n_2 is the number of moles H_2SO_4 in the solution, then

$$\text{Mole fraction of } \text{H}_2\text{SO}_4 = \frac{n_2}{n_1 + n_2} = 0.15$$

Molality of H_2SO_4 solution means the number of moles of H_2SO_4 present in 1000 g of H_2O . Thus, we have,

$$w_1 = 1000 \text{ g or } n_1 = \frac{1000}{18} = 55.55, n_2 = ?$$

$$\frac{n_2}{55.55 + n_2} = 0.15$$

$$n_2 = 0.15 n_1 + 8.3325 \text{ or } n_2 = 9.8$$

$$\therefore \text{Molality} = 9.8 \text{ m.}$$

Alternatively,

If n_1 and n_2 are the number of moles of water and H_2SO_4 respectively, then

$$x_{\text{water}} = \frac{n_1}{n_1 + n_2} = 0.85 \quad \dots(i)$$

Learning Plus

To calculate the volume of a given molarity of a solution, required to prepare solution of other molarity, we use **molarity equation**:

$$M_1 V_1 = M_2 V_2$$

where M_1 is the molarity of the given solution, M_2 is the molarity of the required solution, V_1 is the volume of given solution and V_2 is the volume of the required solution.

Molarity equation is commonly used :

- to calculate the molarity of a solution after mixing two or more solutions.

□ If V_1 mL of a solution of molarity M_1 is mixed with V_2 mL of solution of molarity M_2 , then the molarity of the final solution, M_3 is

$$M_1 V_1 + M_2 V_2 = M_3 (V_1 + V_2)$$

or

$$M_3 = \frac{M_1 V_1 + M_2 V_2}{V_1 + V_2}$$

- to calculate the volume of the solution of given molarity required to dilute to get solution of known molarity.

□ To dilute V_1 mL of a solution of molarity M_1 to molarity M_2 so that the final volume is V_2 , volume of water to be added i.e., $V_2 - V_1$ will be

$$V_2 - V_1 = \left(\frac{M_1 - M_2}{M_2} \right) V_1$$

This can be easily calculated as

$$M_1 V_1 \text{ (undiluted solution)} = M_2 V_2 \text{ (diluted solution)}$$

$$V_2 \text{ (of diluted solution)} = \frac{M_1 V_1}{M_2}$$

$$\therefore \text{Vol. of water to be added, } V_2 - V_1 = \frac{M_1 V_1}{M_2} - V_1 = \left(\frac{M_1 - M_2}{M_2} \right) V_1$$

- to calculate the volume of reactants for reactions between two reactants.

$$\left(\frac{M_1 V_1}{n_1} \right) = \left(\frac{M_2 V_2}{n_2} \right)$$

where n_1 and n_2 are their stoichiometric coefficients in the balanced chemical equation.

Like molarity equation, we have normality equation $N_1 V_1 = N_2 V_2$ (where N_1 and N_2 are the normalities of two solutions). This can be used for dilution or reactions between two reactants.

$$x_{\text{H}_2\text{SO}_4} = \frac{n_2}{n_1 + n_2} = 0.85 = 1 - 0.85 = 0.15 \quad \dots(ii)$$

Dividing eq. (ii) by eq. (i)

$$\frac{n_2}{n_1} = \frac{0.15}{0.85}$$

$$\text{Now, } n_1 = \frac{1000}{18} = 55.55$$

$$\therefore n_2 = \frac{0.15}{0.85} \times 55.55 = 9.8 \text{ moles}$$

Hence, molality of solution = 9.8 m.

Example 21.

How many mL of a 0.1M HCl are required to react completely with 1 g mixture of Na_2CO_3 and NaHCO_3 containing equimolar amounts of two? **N.C.E.R.T.**

Solution : Let the amount of Na_2CO_3 be x in the mixture.

$$\text{Amount of NaHCO}_3 = 1 - x$$

$$\text{Moles of Na}_2\text{CO}_3 = \frac{x}{106}$$

(Molar mass of Na_2CO_3 = 106)

$$\text{Moles of NaHCO}_3 = \frac{1-x}{84}$$

(Molar mass of NaHCO_3 = 84)

Since number of moles of both are equal

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

$$84x = 106 - 106x$$

$$190x = 106 \therefore x = 0.558$$

$$\therefore \text{Moles of Na}_2\text{CO}_3 = \frac{0.558}{106} = 0.00526$$

$$\text{Moles of NaHCO}_3 = \frac{1-0.558}{84}$$

= 0.00526 (Moles are equal)

Now, HCl reacts with Na_2CO_3 as :



According to the reactions, 1 mol of NaCO_3 will react with 2 mol of HCl and therefore, 0.00526 mol of Na_2CO_3 will react with 2×0.00526 mol of HCl. Similarly, 1 mol of NaHCO_3 will react with 1 mol of HCl and therefore, 0.00526 mol of NaHCO_3 will react with 0.00526 mol of HCl. Total mols of HCl required to react with mixture of NaHCO_3 and Na_2CO_3

$$= 2 \times 0.00526 + 0.00526 \\ = 0.01578 \text{ mol}$$

To calculate volume of 0.1 M HCl corresponding to 0.01578 mol, we have

0.1 mol of 0.1 M HCl is present in 1000 mL

$$0.01578 \text{ mol of 0.1 M HCl is present in } \frac{1000}{0.1} \times 0.01578 \\ = 157.8 \text{ mL}$$

Example 22.

A 6.90 M solution of KOH in water contains 30% by mass of KOH. Calculate the density of the KOH solution. (Molar mass of KOH = 56 g mol^{-1}). **(A.I.S.B. 2006)**

Solution : 6.90 M solution of KOH contains 6.90 moles of KOH in 1000 mL of solution.

$$\text{Wt. of KOH in solution} = 6.90 \times 56 = 386.4 \text{ g}$$

$$\text{Wt of KOH in 1000 mL solution} = 386.4 \text{ g}$$

Since the solution is 30% by weight, it means that 30 g of KOH are present in 100 g of solution.

$$\therefore 386.4 \text{ g of KOH is present in } \frac{100}{30} \times 386.4 \\ = 1288 \text{ g of solution}$$

$$\text{Density} = \frac{\text{Weight}}{\text{Volume}} \\ = \frac{1288}{1000} = 1.288 \text{ g mL}^{-1}$$

Practice Problems

- Calculate the percentage composition in terms of mass of a solution obtained by mixing 300 g of a 25% and 400 g of a 40% solution by mass.
- 18 g of glucose (molar mass 180 g mol^{-1}) is present in 500 cm³ of its aqueous solution. What is the molarity of the solution? What additional data is required if the molality of the solution is also required to be calculated?
- A solution of glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) in water is labelled as 10% by weight. What would be the molality of the solution? **(A.I.S.B. 2013)**
- What volume of 10% (w/v) solution of Na_2CO_3 will be required to neutralise 100 mL of HCl solution containing 3.65 g of HCl? **(Assam S.B. 2012)**
- What volume of 95 mass % sulphuric acid (density = 1.85 g/cm³) and what mass of water must be taken to prepare 100 cm³ of 15 mass % solution sulphuric acid (density = 1.10 g cm³)?
- Calculate the mole fraction of ethanol and water in a sample of rectified spirit which contains 95% ethanol by mass.

(H.P.S.B. 2009, Pb. S.B. 2011, Meghalaya S.B. 2013)

Answers to Practice Problems

- 33.57%, 66.43%
- 0.2 M, density of the solution is needed to calculate molality of the solution.
- 0.618 m
- 53.19 mL
- 9.4 cm³, 92.6 g.
- Ethanol = 0.88, water = 0.12

7. Calculate the mole fraction of water in a mixture of 12 g water, 108 g acetic acid and 92 g ethanol.
8. One litre solution of N/2 HCl is heated in a beaker. It was observed that when the volume of the solution is reduced to 600 mL, 3.25 g of HCl is lost. Calculate the normality of the new solution.
9. Concentrated sulphuric acid has a density 1.9 g/mL and is 99% H_2SO_4 by weight calculate molarity of sulphuric acid in the acid. (Pb. S.B. 2015)
10. Calculate the molality and mole fraction of the solute in aqueous solution containing 3 g of urea per 250 g of water.
11. The molality of a solution of ethyl alcohol ($\text{C}_2\text{H}_5\text{OH}$) in water is 1.55 m. How many grams of ethyl alcohol are dissolved in 2 kg of water?
12. Commercially available concentrated hydrochloric acid contains 38% HCl by mass and has density 1.19 g cm^{-3} . Calculate the molarity of this solution. (Pb.S.B. 2005, 2007, 2015)
13. Calculate the formality of sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) solution, 1.24 g of which are dissolved in 100 cm^3 of the solution.
14. 4.0 g of NaOH are contained in one decilitre of a solution. Calculate (i) mole fraction of NaOH (ii) molarity of NaOH (iii) molality of solution. (density of solution = 1.038 g mL^{-1}). (Pb. S.B. 2010)
15. Calculate the molarity and molality of a solution prepared by mixing equal volumes of 30% by weight of H_2SO_4 (density = 1.218 g/mL) and 70% by weight of H_2SO_4 of solution (density = 1.610 g/mL). (Pb. S.B. 2010)
16. The concentration of solution of sulphuric acid is 18 M and has density 1.84 g cm^{-3} . What is the mole fraction and weight percentage of H_2SO_4 in the solution?
17. Calculate the number of molecules of oxalic acid ($\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) in 100 mL of 0.2 N oxalic acid solution.
18. In a solution of benzene in chloroform (CHCl_3), the mole fraction of benzene is 0.45. Calculate its percentage by weight in the mixture.
19. 8.0575×10^{-2} kg of Glauber's salt is dissolved in water to obtain 1 dm^3 of solution of density 1077.2 kg m^{-3} . Calculate (i) the molality and (ii) mole fraction of Na_2SO_4 in the solution (Atomic masses : Na = 23.00, S = 32.10, O = 16.00, H = 1.01)
20. Calculate the molarity of a solution of CaCl_2 if on chemical analysis it is found that 500 mL of CaCl_2 solution contain $1.505 \times 10^{23} \text{ Cl}^-$ ions.
21. 100 mL of a solution containing 5 g of NaOH are mixed with 200 mL of $\frac{\text{M}}{5}$ NaOH solution. Calculate the molarity of the resulting solution.
22. The density of a 2.05 M acetic acid in water is 1.02 g cm^{-3} . Calculate the molality of the solution. (Pb. S.B. 2005)
23. Concentrated HNO_3 used in the laboratory is usually 69% by mass of HNO_3 . Calculate the volume of the solution which contains 23 g of HNO_3 . The density of concentrated HNO_3 is 1.41 g cm^{-3} .
24. Battery acid is 4.27 M H_2SO_4 (aq) and has density of 1.25 g mL^{-1} . What is the molality of H_2SO_4 in the solution? (Pb. S.B. 2005)
25. Hundred gram of $\text{Al}(\text{NO}_3)_3$ [molar mass 213 g mol^{-1}] is dissolved in 1L of water at 20°C . The density of water at this temperature is 0.9982 g cm^{-3} and the density of resulting solution is 0.9990 g cm^{-3} . Calculate the molarity and molality of this solution.

Answers to Practice Problems

7. 0.15
8. 0.685 N
9. 19.19 M
10. Molality = 0.2 m
Mole fraction = 0.0036
11. 142.6 g
12. 12.4 M
13. 0.05 F
14. (i) 0.018 (ii) 1M (iii) 1.002 m.
15. 7.6 M, 11.4 m
16. 0.81, 95.87%
17. 6.02×10^{21} molecules.
18. 34.8%
19. (i) 0.25 M (ii) 0.24 m (iii) 0.0043
20. 0.25 M
21. 0.55 M
22. 2.29 m
23. 23.6 cm^3
24. 5.135 m
25. 0.427 M, 0.470 m

Hints & Solutions on page 66**Advanced Level****PROBLEMS****Accelerate Your Potential
(for JEE Advance)**

Problem 1. How many mL of sulphuric acid of density 1.84 g mL^{-1} containing 95.6 mass % of H_2SO_4 should be added to one litre of 40 mass % solution of H_2SO_4 of density 1.31 g mL^{-1} in order to prepare 50 mass % solution of sulphuric acid of density 1.40 g mL^{-1} .

Solution Let v mL of 95.6 mass % sulphuric acid of density 1.84 g mL^{-1} be added to 1000 mL of 40 mass %

H_2SO_4 so that total solution of 50 mass % H_2SO_4 becomes $(1000 + v)$ mL.

$$\text{Volume of solution of 95.6\% } \text{H}_2\text{SO}_4 = \frac{100}{1.84}$$

$$\text{Amount of } \text{H}_2\text{SO}_4 \text{ in } v \text{ mL of solution} = 95.6 \times \frac{1.84}{100} \times v$$

$$\text{Volume of solution of 40\% } \text{H}_2\text{SO}_4 = \frac{100}{1.31}$$

$$\text{Amount of H}_2\text{SO}_4 \text{ in } 1000 \text{ mL of solution} = \frac{40 \times 1.31}{100} \times 1000$$

$$\text{Volume of solution of } 50\% \text{ H}_2\text{SO}_4 = \frac{100}{1.40}$$

$$\begin{aligned}\text{Amount of H}_2\text{SO}_4 \text{ in } (1000 + v) \text{ mL of solution} \\ = 50 \times \frac{1.40}{100} \times (1000 + v)\end{aligned}$$

$$\text{Thus, } \frac{95.6 \times 1.84 \times v}{100} + \frac{40 \times 1.31}{100} \times 1000 = \frac{50 \times 1.40}{100} (1000 + v)$$

$$175.90v + 52400 = 70000 + 70v$$

$$105.90v = 17800$$

$$\text{or } v = 166.2 \text{ mL.}$$

Vol. of H_2SO_4 of density 1.84 containing 95.6 mass % of H_2SO_4 to be added = 166.2 mL.

Problem 2. Calculate the density of H_2SO_4 solution whose molarity and molality are 10.8 M and 92.6 m respectively.

Solution Molarity 10.8 means that 10.8 moles of H_2SO_4 are present in 1L of the solution.

Let the density of the solution is $d \text{ g mL}^{-1}$, then

$$\text{Mass of } 1000 \text{ mL of solution} = (1000 \times d) \text{ g}$$

$$\text{Mass of } \text{H}_2\text{SO}_4 \text{ in solution} = 10.8 \times 98 = 1058.4 \text{ g}$$

$$\therefore \text{Mass of water} = (1000d - 1058.4) \text{ g}$$

$$\text{Molality} = \frac{10.8}{(1000d - 1058.4)} \times 1000 = 92.6$$

$$10800 - 92.6 \times (1000d - 1058.4)$$

$$1000d - 1058.4 = \frac{10800}{92.6} = 116.6$$

$$\text{or } 1000d = 116.6 + 1058.4 = 1175$$

$$\therefore d = \frac{1175}{1000} = 1.175 \text{ g mL}^{-1}$$

Problem 3. How many grams of wet NaOH containing 15% water is required to prepare 6L of 0.5 M NaOH solution?

Solution 1 L of 0.5 M NaOH contains = 0.5 mol NaOH
or $0.5 \times 40 = 20 \text{ g NaOH}$

6 L of 0.5 M NaOH contains = $20 \times 6 = 120 \text{ g NaOH}$

Since wet NaOH contains 15% water, then

100 g of wet NaOH contain 85 g pure NaOH

or 85 g of NaOH is contained in 100 g wet NaOH

120 g of NaOH is contained in $\frac{100}{85} \times 120 = 141.18 \text{ g}$

\therefore Wet NaOH required to prepare 6 L of 0.5 M NaOH = 141.18 g

Problem 4. Calculate the resulting molarity of a solution obtained by adding 6.2 g of KOH to 500 mL of $\frac{M}{5}$ KOH solution (density = 1.06 g mL^{-1}). The density of resulting solution is 1.10 g mL^{-1} .

Solution 1000 mL of $\frac{M}{5}$ KOH solution contains KOH
 $= \frac{1}{5} \text{ mol}$

or $\frac{1}{5} \times 56 = 11.2 \text{ g}$
(Molar mass of KOH = 56)

500 mL of $\frac{M}{5}$ KOH solution contains KOH = $\frac{11.2}{1000} \times 500 = 5.6 \text{ g}$

Mass of 500 mL of KOH solution = $500 \times 1.06 = 530 \text{ g}$

After adding 6.2 g of KOH,

Mass of KOH = $5.6 + 6.2 = 11.8 \text{ g}$

Mass of solution = $530 + 6.2 = 536.2 \text{ g}$

Volume of new solution = $\frac{536.2}{1.10} = 487.45 \text{ mL}$

Molarity = $\frac{11.8 \times 1000}{56 \times 487.45} = 0.43 \text{ M}$

SOLUBILITY OF GASES AND SOLIDS IN LIQUIDS

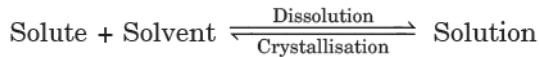
Solubility of a substance expresses the maximum amount of it which can be dissolved in a specific amount of solvent at a specified temperature.

The solubility of a substance depends upon the nature of solute, nature of the solvent, temperature and pressure.

Let us consider the effect of these factors on the solubility of a solid in a liquid and a gas in a liquid.

Solubility of Solids in Liquids

When a solid (solute) is added to the solvent, the solute dissolves because its particles go into the liquid and its concentration in the solution increases. This process is known as **dissolution**. Some solute particles in solution collide with the solid solute particles and get precipitated out. This process is called **crystallisation**. The process of dissolution continues until the solution attains a certain maximum concentration. Such a solution in which no more solute can be dissolved at a given conditions of temperature and pressure is called **saturated solution**. A solution in which more solute can be dissolved at the same temperature is called **unsaturated solution**. At the saturated solution stage, an equilibrium gets established between the process of dissolution and crystallisation. Under such conditions, the number of solute particles going into the solution will be equal to the number of solute particles separating out and a state of dynamic equilibrium is reached.



REMEMBER

- **Saturated solution.** A solution which contains maximum amount of solute which dissolves completely in a given solvent at a particular temperature.
- **Unsaturated solution.** A solution which contains less amount of solute than required for forming saturated solution.
- **Supersaturated solution.** A solution which contains excess of solute than required for formation of saturated solution.
- Added excess solute does not dissolve.

Therefore, in saturated solution, the concentration of solute in the solution will remain constant under the given conditions i.e., temperature and pressure. The maximum amount of solute that dissolves completely in a given amount of solvent at a particular temperature is called its **solubility**.

Thus, the **solubility** of a substance at a given temperature is defined as *the amount of the solid that dissolves in 100 g of the solvent at a given temperature to form a saturated solution.*

The solubility is also expressed as **molar solubility** which gives the molar concentration of a substance in a saturated solution i.e., mol dm⁻³. Thus,

the concentration of the solute has the highest value in a saturated solution.

Factors affecting the solubility of a solid in a liquid.

The solubility of a solid in a liquid, in general, depends upon the following factors:

- (i) Nature of the solute and the solvent.
- (ii) Temperature

The pressure has almost insignificant effect on the solubility of a solid in a liquid.

(i) Nature of the solute and the solvent. Every solid does not dissolve in a given liquid. In general, a solid dissolves in a liquid (solvent) if the intermolecular interactions are similar in solute and the solvent. This is in accordance with basic rule “**like dissolves like.**” This means that ionic (or polar) compounds dissolve more readily in polar solvents like water and are very little soluble or almost insoluble in non-polar solvents like benzene, ether, carbon tetrachloride. Similarly, non-polar (covalent or organic) compounds are soluble in non-polar solvents like benzene, ether, carbon tetrachloride but are very little soluble in water (polar solvent). For example, common salt (sodium chloride) and sugar dissolve readily in water and solubility of common salt in water is much more than that of sugar (covalent compound). Their solubilities in water are 5.3 mol L⁻¹ and 3.8 mol L⁻¹ respectively. However, naphthalene and anthracene (non-polar compounds) are not soluble in water. On the other hand, naphthalene and anthracene dissolve readily in benzene but sodium chloride and sugar do not.

(ii) Effect of temperature. Temperature has a marked effect on the solubility of a solid in a solvent. The solubility may increase or decrease with increase in temperature. The variation of solubilities of some common substances with temperature is shown in Fig. 1.

We observe **three types of trends** in the behaviour of different solutes :

(a) The solubility of solutes increases with increase in temperature. The solubility of most of substances such as sodium nitrate (NaNO₃), potassium nitrate (KNO₃), ammonium chloride (NH₄Cl), potassium chloride (KCl), sodium chloride (NaCl), silver nitrate (AgNO₃), potassium iodide (KI), etc. increase with rise in temperature. This is because the dissolution process for these substances is endothermic ($\Delta_{\text{sol}}H > 0$).



Since these substances absorb heat on forming solution and therefore, their solubility increases with increase in temperature in accordance with Le-Chatelier's principle. As is clear from Fig. 1.(a), the variation of sodium chloride with temperature is very small, though it also increases.

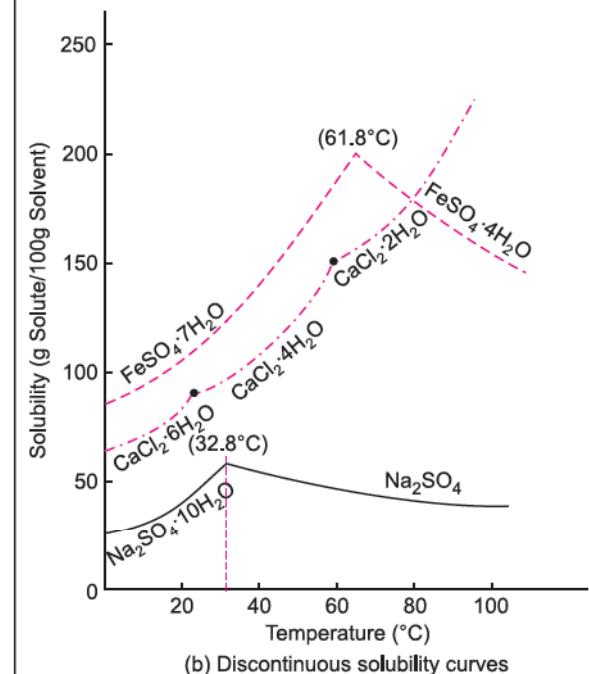
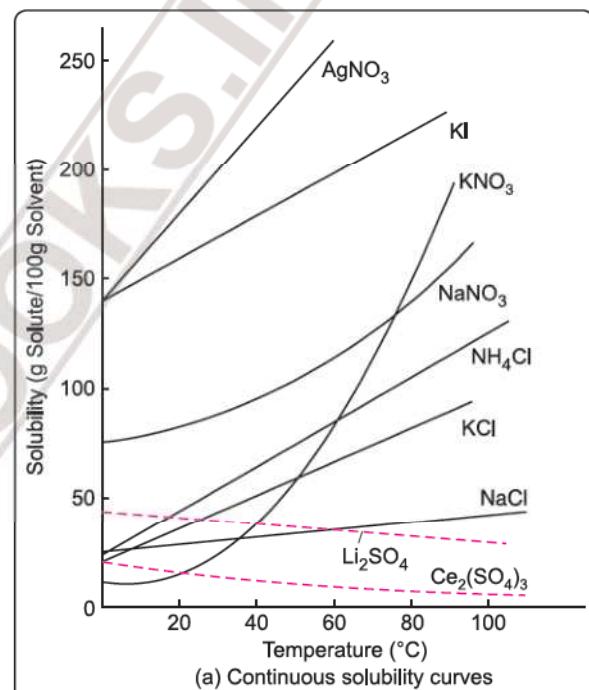


Fig. 1. Variation of solubilities of some substances with temperature.

In general

- if the solute dissolves with absorption of heat (endothermic process), the solubility increases with rise in temperature.
- if the solute dissolves with evolution of heat (exothermic process), the solubility decreases with rise in temperature.

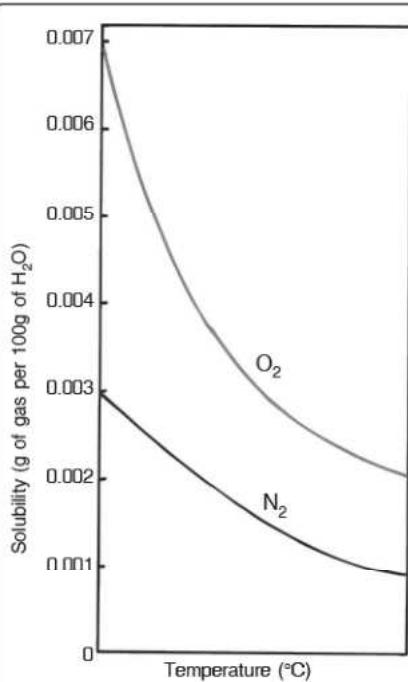


Fig. 2. Solubility of N₂ and O₂ in water at 1 atm pressure.

Learning Plus

Quantitatively, the effect of temperature on the solubility of a gas in a liquid at constant pressure may be expressed as :

$$\frac{d \ln s}{dT} = \frac{\Delta H}{RT^2} \quad \dots(i)$$

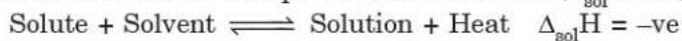
where s is the solubility in moles per litre of the gas in the liquid and ΔH is the enthalpy of solution at temperature T . If ΔH is regarded as independent of temperature, then integration of equation (i) gives

$$\ln \frac{s_1}{s_2} = \frac{\Delta H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad \dots(ii)$$

where s_1 and s_2 are the solubilities at temperature T_1 and T_2 , respectively. This expression is similar to Clausius-Clapeyron equation which gives the effect of pressure on the boiling point of a liquid.

(b) The solubility of solids decreases with increase in temperature.

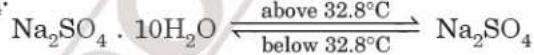
The solubility of some substances like lithium sulphate (Li₂SO₄), cerium sulphate [Ce₂(SO₄)₃], some calcium salts of organic acids, sodium carbonate monohydrate (Na₂CO₃·H₂O), etc. decrease with rise in temperature. This is because their dissolution process is exothermic ($\Delta_{sol}H < 0$):



Since these dissolve with evolution of heat, a decrease of solubility with temperature is expected in accordance with Le-Chatelier's principle.

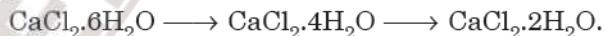
It may be noted that in these two types, there is continuous increase or decrease with increase in temperature as shown in Fig. 1.(a).

(c) The solubility shows irregular behaviour with increase in temperature. For some substances, the solubility behaviour is not regular. For example, the solubility of sodium sulphate (Na₂SO₄) increases upto a certain temperature and then decreases as the temperature is further raised. In this case, the solubility curves are not continuous but discontinuous and show breaks. The temperature corresponding to the break in the solubility curve is known as the **transition temperature**. For example, the solubility curve of sodium sulphate shows a sharp break at 32.8°C. This is due to change in one solid form into another solid form. For example, in case of sodium sulphate at 32.8°C, there is an equilibrium between solid decahydrate Na₂SO₄·10H₂O and anhydrous Na₂SO₄:



Below this temperature, only sodium sulphate decahydrate (Na₂SO₄·10H₂O) exists while above this temperature, anhydrous sodium sulphate (Na₂SO₄) exists.

The solubility curve for FeSO₄·7H₂O is also discontinuous and shows break at 61.8°C. At this temperature heptahydrate changes to tetrahydrate. The curve for CaCl₂·6H₂O shows two breaks corresponding to



(iii) Effect of pressure. The effect of pressure on the solubility of solids in liquids is generally very small or insignificant. This is because solids and liquids are highly incompressible and practically remain unaffected by changes in pressure. For example, a change of 500 atm in pressure increases the solubility of sodium chloride in water only by 2.3%.

Solubility of Gases in Liquids

Gases dissolve in liquids to form homogeneous solutions. Many gases dissolve in water. Oxygen dissolves only to a small extent in water. The natural water contains dissolved oxygen which is vital in **sustaining all aquatic life in lakes, rivers, sea, etc.** The different gases are soluble in water to different extents. Some gases are also soluble in solvents like ethyl alcohol, ether, benzene, etc. The **solubility** of a gas in a particular liquid may be expressed as the

volume of the gas (in cm³ converted to S.T.P.) that can dissolve in a fixed volume of the liquid to form the saturated solution at a given temperature.

The solubility of a gas may also be expressed in terms of **molarity** or **mole fraction of the gas**.

Factors affecting the solubility of a gas in a liquid.

The solubility of a gas in a liquid depends upon:

- The nature of the gas and the solvent
- Temperature of the solution
- Pressure

(i) **Nature of the gas and the solvent.** The solubility of different gases in the same solvent varies considerably. For example, gases like nitrogen, hydrogen, oxygen, helium, etc. dissolve in water only to a small extent whereas the gases like ammonia, sulphur dioxide, hydrogen chloride, etc. are highly soluble in water. The solubility of the latter gases in water is due to the

chemical reactions of these gases with water to form ammonium hydroxide, sulphurous acid and hydrochloric acid respectively. Therefore, *the most soluble gases are those which chemically react with the liquid solvent.*

Oxygen, nitrogen and carbon dioxide are much more soluble in ethyl alcohol than in water at the same temperature and pressure. On the other hand, gases like NH_3 and H_2S are less soluble in ethyl alcohol than water at the same temperature and pressure.

(ii) Effect of temperature. *The solubility of a gas decreases with increase of temperature* (Fig. 2). This is because, in general, gases dissolve in a liquid with the evolution of heat i.e., exothermic process.



Therefore, in accordance with Le-Chatelier's principle, the increase in temperature will result in decrease in the solubility of the gas. It is for this reason that most of gases which dissolve without ionizing are readily expelled from solutions by boiling.

It may be noted that there are certain gases such as hydrogen and inert gases whose solubility increases slightly with increase of temperature especially in the non-aqueous solvents such as alcohols, acetone, hydrocarbons, etc.

(iii) Effect of pressure. *The solubility of gases increases with increase of pressure.* This behaviour is also in accordance with Le-Chatelier's principle.

To understand this, consider a gas in dynamic equilibrium with a solution [Fig. 3(a)]. The lower part represents the solution and the upper part is gaseous system at a pressure p and temperature T . Since there is dynamic equilibrium, the number of gas molecules entering the solution is equal to the number of dissolved molecules leaving the solution phase. Now increase the pressure over the solution phase by compressing the gas to a smaller volume as shown in Fig. 3 (b). This will increase the number of gaseous particles per unit volume over the solution. As a result, the more molecules will be striking the surface of the liquid and hence more molecules will dissolve and the solubility of gas will increase until a new equilibrium is reached. Thus, *increasing the pressure of a gas above the solution, increases the solubility of the gas.*

The concentration of the dissolved gas is proportional to the pressure on the gas above the solution.

William Henry made systematic studies of the solubility of a gas in a liquid. He gave a quantitative relationship between solubility of a gas in a solvent and pressure which is known as **Henry's law**. The law states that

the mass of a gas dissolved per unit volume of the solvent at a constant temperature is directly proportional to the pressure of the gas in equilibrium with the solution.

If m is the mass of the gas dissolved in a unit volume of the solvent and p is the pressure of the gas in equilibrium with the solution, then

$$m \propto p$$

$$\text{or } m = K \cdot p \quad \dots(9)$$

where K is the proportionality constant. The magnitude of K depends on the nature of the gas, nature of the solvent, temperature and the units of pressure. Thus, Henry's law may also be stated as: *the solubility of a gas in a liquid at a particular temperature is directly proportional to the pressure of the gas in equilibrium with the solution.*

Dalton, during the same period, also concluded independently that the solubility of a gas in a liquid solution depends upon the partial pressure of the gas. Now, if we use mole fraction of the gas in the solution as a measure of its solubility, then *mole fraction of the gas in the solution is proportional*

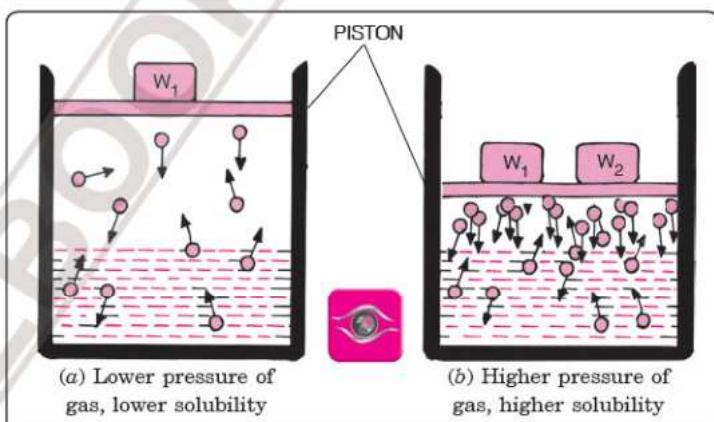


Fig. 3. Effect of pressure on the solubility of a gas.

to the partial pressure of the gas over the solution, i.e.,

$$x \propto p$$

$$\text{or } x = K'p$$

$$\text{or } p = \frac{1}{K'}x$$

$$\text{or } p = K_H x \quad \left(K_H = \frac{1}{K'} \right) \quad \dots(10)$$

where K_H is called **Henry's law constant**. Thus, Henry's law may alternatively be stated as :

the partial pressure of the gas in the vapour phase is directly proportional to the mole fraction of the gas in the solution.

The units of K_H will be atm or bar (or k bar)

Thus, when we draw a graph between partial pressure of the gas against the mole fraction of the gas in solution at a given temperature, then a straight line passing through the origin is obtained. The plot of experimental results for the solubility of HCl gas in cyclohexane at 293 K is given in Fig. 4. The straight line graph shows the validity of Henry's law. The slope of the line gives the Henry's law constant, K_H . Different gases have different K_H values at the same temperature. This suggests that K_H is a function of the nature of the gas.

When a mixture of a number of gases is brought in contact with a solvent, each constituent gas dissolves in proportion to its own partial pressure. Therefore, Henry's law is applied to each gas independent of the presence of other gas.

The Henry's law constant values for some gases in water at 298 K are given in Table 2 below.

Table 2. Henry's law constants (K_H) for some gases in water at different temperatures.

Gas	Temp(K)	K_H (kbar)	Gas	Temp(K)	K_H (kbar)
He	293	144.97	CO_2	298	1.67
H_2	293	69.16	Ar	298	40.3
N_2	293	76.48	Methane	298	0.413
N_2	303	88.84	Vinyl chloride	298	0.611
O_2	293	34.86			
O_2	303	46.82			

R U Curious...



- **Aquatic species like fish feel more comfortable in lakes in winter than in the summer.**
- Aquatic species require dissolved O_2 for breathing. As solubility of gases decreases with increase of temperature, less oxygen is available in summer than in winter. Hence, they feel more comfortable in winter (low temperature) when the solubility of O_2 is higher.
- In summer during hot day, temperature at the surface of water is relatively high and therefore, the solubility of oxygen in the upper layer is less. At the same time, the temperature of water at lower level is much less and therefore, it contains more amount of dissolved oxygen. Hence, **marine life like fish prefers to stay at lower level and stay away from the upper layer of water.**

From these values, it may be concluded that

(i) Henry's law constant, K_H depends upon the nature of the gas.
(ii) Higher the value of K_H at a particular pressure, *the lower is the solubility of the gas in the liquid.* ($\because x = \frac{1}{K_H} \cdot p$; from Eq. 10).

(iii) The value of K_H increases with increase in temperature indicating that the solubility of gases decreases with increase of temperature. (It is clear from Table 2 that K_H values of N_2 and O_2 increase with increase in temperature.) *This is the reason that aquatic species are more comfortable in cold water rather than warm water.*

Limitation of Henry's law. It has been observed that Henry's law is valid if

- pressure is low. At high pressure, the law becomes less accurate and the proportionality constant shows considerable deviations.
- the temperature is not too low.
- the gas is not highly soluble and
- the gas neither reacts chemically with the solvent nor dissociates or associates in the solvent.

The solubility of most of the gases in a liquid decreases with increase in temperature and therefore, Henry's law constants have smaller values at higher temperatures.

Because of the decrease in solubility of gases with increase in temperature, the dissolved gases may be removed from liquids by heating. But this is not always the case. Some gases are more soluble at higher temperature than at lower temperature and hence these are not readily removed by heating.

Applications of Henry's law

Henry's law finds many applications in industry and helps to explain several biological phenomena. Some important applications are :

1. In the production of carbonated beverages. To increase the solubility of CO₂ in soft drinks, soda water, beer or champagne, the bottles are sealed under high pressure. When the bottle is opened under normal atmospheric conditions, the pressure inside the bottle falls to atmospheric pressure and the excess CO₂ bubbles out of the solution **causing effervescence**.

2. In deep sea diving (Scuba diving). Deep sea divers depend upon compressed air for breathing at high pressure under water. The compressed air contains N₂ in addition to O₂, which are not very soluble in blood at normal pressure. However, at great depths when the diver breathes in compressed air from the supply tank, more N₂ dissolves in the blood and other body fluids because the pressure at that depth is far greater than the surface atmospheric pressure. When the diver comes towards the surface, the pressure decreases, N₂ comes out of the body quickly forming bubbles in the blood stream. These bubbles restrict blood flow, affect the transmission of nerve impulses. The bubbles can even burst the capillaries or block them and starve the tissues of O₂. This condition is called "**the bends**," which are painful and dangerous to life. To avoid this condition, most professional divers these days use air diluted with helium gas (about 11.7% He, 56.2% N₂ and 32.1% O₂), because of lower solubility of He in the blood than nitrogen. Moreover, because of small size of He atoms (unlike nitrogen molecules), they can pass through cell walls without damaging them. The excess O₂ dissolved in the blood is used in metabolism and does not cause the condition of bends.

3. At high altitudes. At high altitudes, the partial pressure of O₂ is less than that at the ground level. This results in low concentration of oxygen in the blood and tissues of the people living at high altitudes or climbers. The low blood oxygen causes climbers to become weak and unable to think clearly known as **anoxia**.

4. In the function of lungs. To minimise the painful effects of deep sea divers during the decompression, oxygen diluted with less soluble helium gas is used as breathing gas.

SOLVED EXAMPLES

□ **Example 23.**

If N₂ gas is bubbled through water at 293 K, how many millimoles of N₂ gas would dissolve in 1 litre of water. Assume that N₂ exerts a partial pressure of 0.987 bar. The K_H for N₂ at 293 K is 76.48 k bar.

N.C.E.R.T.

Solution : The solubility of gas is related to its mole fraction in aqueous solution.

The mole fraction of the gas in solution,

$$x_{N_2} = \frac{p_{N_2}}{K_H} = \frac{0.987 \text{ bar}}{76480 \text{ bar}} = 1.29 \times 10^{-5}$$

If n is the number of moles of N₂ in solution and 1 litre of water contains 55.5 mol, then

$$x_{N_2} = \frac{n}{n + 55.5} \approx \frac{n}{55.5} = 1.29 \times 10^{-5}$$

(n in the denominator is neglected because it is << 55.5)

$$\begin{aligned} \therefore n &= 55.5 \times 1.29 \times 10^{-5} \\ &= 7.16 \times 10^{-4} \text{ mol} \\ \text{or} \quad &= 7.16 \times 10^{-1} \text{ m mol} \\ &= \mathbf{0.716 \text{ m mol.}} \end{aligned}$$

□ **Example 24.**

The Henry's law constant for oxygen dissolved in water is $4.34 \times 10^4 \text{ atm}$ at 25°C . If the partial pressure of oxygen in air is 0.2 atm, under atmospheric conditions, calculate the concentration (in moles per litre) of dissolved oxygen in water in equilibrium with air at 25°C .

Solution : According to Henry's law :

$$\begin{aligned} p &= K_H x \\ K_H &= 4.34 \times 10^4 \text{ atm,} \\ p_{O_2} &= 0.2 \text{ atm} \\ p_{O_2} &= K_H x_{O_2} \\ x_{O_2} &= \frac{p_{O_2}}{K_H} \\ &= \frac{0.2}{4.34 \times 10^4} = 4.6 \times 10^{-6} \end{aligned}$$

Changing mole fraction into molarity

$$\text{Moles of water} = \frac{1000}{18} = 55.5 \text{ mol}$$

Since n_{O_2} is very small in comparison to n_{H_2O}

$$n_{O_2} + n_{H_2O} \approx n_{H_2O}$$

$$x_{O_2} = \frac{n_{O_2}}{n_{H_2O}}$$

$$x_{O_2} \times n_{H_2O} = n_{O_2}$$

$$4.6 \times 10^{-6} \times 55.5 = n_{O_2}$$

$$n_{O_2} = 2.55 \times 10^{-4} \text{ mol}$$

Since 2.55×10^{-4} mol are present in 1000 mL of solution,
Molarity = 2.55×10^{-4} M.

Example 25.

Dry air contains 79% N_2 and 21% O_2 . Determine the proportion of N_2 and O_2 (in terms of mole fractions) dissolved in water at 1 atm pressure. Henry's law constant for N_2 and O_2 in H_2O are 8.54×10^4 atm and 4.56×10^4 atm respectively.

Solution : Total pressure of air over water = 1 atm
Partial pressure of N_2 and O_2 are :

$$P_{N_2} = \frac{1 \times 79}{100} = 0.79 \text{ atm}$$

$$P_{O_2} = \frac{1 \times 21}{100} = 0.21 \text{ atm}$$

Applying Henry's law

$$P_{N_2} = K_H \cdot x$$

$$x_{N_2} = \frac{P_{N_2}}{K_{N_2}} = \frac{0.79}{8.54 \times 10^4} = 9.25 \times 10^{-6}$$

$$x_{O_2} = \frac{P_{O_2}}{K_{O_2}} = \frac{0.21}{4.56 \times 10^4} = 4.60 \times 10^{-6}$$

$$\begin{aligned} \text{Proportion of } N_2 \text{ and } O_2 \\ &= 9.25 \times 10^{-6} : 4.60 \times 10^{-6} \\ &= 2 : 1 \end{aligned}$$

Practice Problems

Answers to Practice Problems

26. 4.99×10^{-4} M

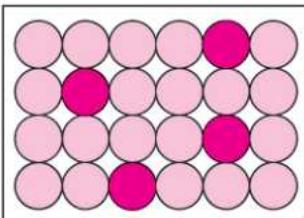
27. 7.75×10^4 atm

28. 5.85 g

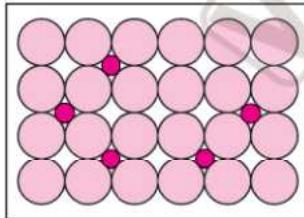
29. 1.58 bar

30. 0.181 bar

Hints & Solutions on page 66



(a) Substitutional solid solution



(b) Interstitial solid solution

Fig. 5 Solid solutions

26. What concentration of nitrogen should be present in a glass of water at room temperature? Assume a temperature of 25°C, a total pressure of 1 atmosphere and mole fraction of nitrogen in air of 0.78.
(K_H for nitrogen = 8.42×10^{-17} M/mm Hg). (A.I.S.B. 2009)
27. One litre of water under a nitrogen pressure 1 atm dissolves 0.02g of nitrogen at 293 K. Calculate Henry's law constant.
28. Calculate the amount of CO_2 dissolved at 4 atm in 1 dm³ of water at 298 K. The Henry's law constant for CO_2 at 298 K is 1.67 k bar.
29. At what partial pressure, oxygen will have a solubility of 0.06 gL⁻¹ in water at 293 K? Henry's law constant (K_H) of O_2 in water at 303 K is 46.82 k bar. (Assume the density of the solution to be the same as that of water).
30. The mole fraction of He gas in a saturated solution at 20°C is 1.25×10^{-6} . Calculate the pressure of He gas above the solution. (K_H of He at 20°C = 144.98 k bar).

SOLID SOLUTIONS

As we have already learnt, solid solutions are those solutions in which both the components (*i.e.*, solute and the solvent) are solids.

Solid solutions are of two types :

- (i) *Substitutional solid solutions and*
- (ii) *Interstitial solid solutions.*

(i) **Substitutional solid solutions** are those in which atoms, molecules or ions of one substance take the place of particles of another substance in a crystal lattice as shown in Fig. 5 (a). Brass is a common example of substitutional solid solution of copper and zinc. Bronze, monel and steel are other familiar examples of this type of solid solution. Zinc sulphide and cadmium sulphide also form such solid solutions in which cadmium ions randomly replace zinc ions in the ZnS lattice.

(ii) **Interstitial solid solutions** are those which are formed by placing atoms of one kind into voids or interstices in the lattice of atoms of other substance. This is shown in Fig. 5(b) in which solute particles are shown in the interstices present in the atoms of solvent lattice. The common example of interstitial solid solution is tungsten carbide (WC). In this case, tungsten atoms are arranged in a face centred cubic pattern with carbon atoms in octahedral holes i.e., spaces within the crystal where carbon atoms are surrounded by six tungsten atoms at the vertices of an octahedron. Tungsten carbide is extremely hard substance and has many uses in making of cutting and grinding tools.

Even, some metals have a tendency to dissolve large quantities of gases and form solid solutions of gases in metals. For example, palladium and platinum are capable of taking up hydrogen at room temperature to form solid solutions of the hydrogen in the metal.

add on

Conceptual Questions

1

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QA

**Q.1. Which aqueous solution has higher concentration : 1 molar or 1 molal solution of the same solute?
Give reason.**

(C.B.S.E. Sample Paper 2007)

Ans. 1 Molar solution has higher concentration than 1 molal solution. A molar solution contains one mole of solute in one litre of solution while a one molal solution contains one mole of solute in 1000 g of solvent. If density of water is one, then one mole of solute is present in 1000 ml of water in 1 molal solution while one mole of solute is present in less than 1000 mL of water in 1 molar solution (1000 mL solution = amount of solute + amount of solvent). Thus, 1 molar solution is more concentrated.

Q.2. Ethanol is an organic compound, yet it is freely miscible with water, Explain.

Ans. The miscibility of ethanol in water is due to hydrogen bonding between the molecules.

Q.3. What is the normality of

(a) 1.5 M H_2SO_4 (b) 1.2 M CH_3COOH (c) 1.0 M NaOH ?

Ans. (a) Normality = $1.5 \times 2 = 3 \text{ N}$ (b) $1.2 \times 1 = 1.2 \text{ N}$ (c) $1.0 \times 1 = 1.0 \text{ N}$

Q.4. Which out of molarity or molality will change with change in temperature and why ?

Ans. Molarity changes with rise in temperature. Volume of a solution increases with rise in temperature and this causes change in molarity because it is related as moles of solute in a given volume of solution.

Q.5. Will the molarity of a solution at 50°C be same, less or more than molarity at 25°C ?

Ans. Molarity at 50°C of a solution will be less than that at 25°C because molarity decreases with temperature. This is because volume of the solution increases with increase in temperature but number of moles of solute remains the same.

Q.6. What is the sum of the mole fractions of all the components in a three component system ?

Ans. 1. $x_1 + x_2 + x_3 = 1$

Q.7. How is the molality of a solution different from its molarity ?

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

Q.8. State the formula relating pressure of a gas with its mole fraction in liquid solution in contact with it.

(D.S.B. 2005)

Ans. The pressure of a gas over a solution in which the gas is dissolved is proportional to the mole fraction of the gas dissolved in the solution i.e., $p \propto x$

or $p = K_H x$ (where K_H is Henry's law constant)

Q.9. At a same temperature, hydrogen is more soluble in water than helium. Which of them will have a higher value of K_H and why ?

(A.I.S.B. 2005)

Ans. Helium will have higher value of K_H because if gas has more solubility, its K_H value is lower.

Q.10. What is the relation between normality and molarity of a given solution of sulphuric acid ?

Ans. Normality = $2 \times \text{Molarity}$.

Q.11. What is the effect of temperature on the solubility of sodium sulphate decahydrate ($\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$) ?

Ans. The solubility first increases upto 32.8°C (called transition temperature) and then decreases.

Q.12. The dissolution of ammonium chloride in water is endothermic process. What is the effect of temperature on its solubility ?

Ans. Since dissolution of NH_4Cl in water is endothermic process, its solubility increases with rise in temperature (Le-Chatelier principle).

Q.13. Give reasons, at higher altitudes, people suffer from a disease called anoxia. In this disease, they become weak and cannot think clearly. (C.B.S.E. Sample Paper 2007)

Ans. At high altitudes, the partial pressure of oxygen is less than that at the ground level. This leads to low concentration of oxygen in the blood and the tissues of the people living at high altitudes. As a result of low oxygen in the blood, the people become weak and unable to think clearly. These are the symptoms of a condition known as anoxia.

VAPOUR PRESSURE OF LIQUID SOLUTIONS

Vapour Pressure of Liquid

When a liquid is allowed to evaporate in a closed vessel, a part of the liquid evaporates and fills the available space with the vapours. Since the vapours do not leave the container, these get collected in the vapour state above the surface of the liquid. Due to vaporisation, liquid changes into vapours and level of liquid decreases. As the evaporation proceeds, the number of gaseous molecules in the vapour phase increases gradually. These molecules move about at random in a limited space and during their random movement, some of these strike the surface of liquid and get condensed. The process of condensation acts in opposite direction to the process of evaporation. Thus, both evaporation and condensation processes go on simultaneously. Ultimately, a stage is reached when the rate of evaporation becomes equal to rate of condensation and an equilibrium gets established between liquid and vapour phases. The pressure exerted by the vapours at the equilibrium is called vapour pressure. Thus,

the pressure exerted by the vapours above the liquid surface in equilibrium with the liquid at a given temperature is called **vapour pressure**.

Factors on which vapour pressure of a liquid depends

The vapour pressure of a liquid depends upon :

(i) **Nature of the liquid.** Each liquid has a characteristic vapour pressure because each liquid has different magnitude of intermolecular forces. The liquids, which have weaker intermolecular forces, tend to escape readily into vapour phase and therefore, have greater vapour pressure. For example, dimethyl ether and alcohol have higher vapour pressure than water at a given temperature because of weaker intermolecular forces in them as compared to water.

(ii) **Temperature.** The vapour pressure of a liquid increases with increase in temperature. This is due to the fact that with increase in temperature, more molecules will have larger kinetic energies. Therefore, larger number of molecules will escape from the surface of the liquid to the vapour phase resulting in higher vapour pressure.

Vapour Pressure of Liquid Solutions

Liquid solutions are formed when solvent is a liquid and the solute may be a gas, a liquid or a solid. We have already learnt about solutions of gases in liquids. Let us learn about the solutions of liquids and solids in a liquid. Such solutions may contain one or more volatile components. Generally, the liquid solvent is volatile. The solute may or may not be volatile.

(a) Vapour Pressure of Liquid-liquid Solutions and Raoult's Law (Raoult's Law for Volatile Solutes)

When a binary solution of two volatile liquids is placed in a closed vessel, both the components would evaporate and eventually an equilibrium would be established between vapour phase and the liquid phase. In the case of binary solution of volatile liquids, the vapour phase consists of vapours of both the components.

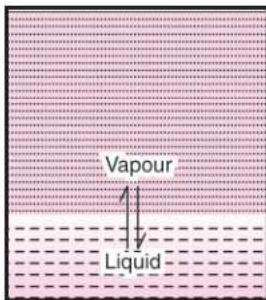


Fig. 6. Vapour pressure of a liquid.

Learning Plus

Quantitatively, the effect of temperature on vapour pressure of a liquid is given by **Clausius-Clapeyron equation** as:

$$\log \frac{p_2}{p_1} = \frac{\Delta_{\text{vap}} H}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

where p_1 and p_2 are the vapour pressure at temperatures T_1 and T_2 respectively and $\Delta_{\text{vap}} H$ is the enthalpy of vaporisation of the liquid.

The French chemist Francois Marie Raoult (1886) gave a quantitative relationship between the partial pressures and the mole fractions of two components. This relationship is known as **Raoult's law** which states that

at a given temperature, for a solution of volatile liquids, the partial vapour pressure of each component in solution is equal to the product of the vapour pressure of the pure component and its mole fraction.

Let us consider a binary solution of two volatile liquids and denote the components as A and B having the mole fraction x_A and x_B respectively. If p_A and p_B are the vapour pressures of the components in the solution, then according to Raoult's law

$$p_A = p_A^\circ x_A$$

and

$$p_B = p_B^\circ x_B$$

where p_A° is the vapour pressure of the pure component A and p_B° is the vapour pressure of pure component B at the same temperature.

According to Dalton's law of partial pressures, the total pressure p will be the sum of the partial pressure of the components of the solution. This is given as :

$$p = p_A + p_B$$

Substituting the values of p_A and p_B , we get

$$p = p_A^\circ x_A + p_B^\circ x_B \quad \dots(11)$$

As we know,

$$x_A + x_B = 1 \text{ or } x_A = 1 - x_B$$

∴

$$p = p_A^\circ (1 - x_B) + p_B^\circ x_B$$

or

$$p = p_A^\circ - p_A^\circ x_B + p_B^\circ x_B$$

$$p = p_A^\circ + (p_B^\circ - p_A^\circ) x_B \quad \dots(12)$$

From equation 12, the following conclusions can be drawn :

- (i) Total vapour pressure over the solution can be related to the mole fraction of any one component [x_B or x_A as $x_A = (1 - x_B)$].
- (ii) Total vapour pressure of the solution varies linearly with the mole fraction of component B because p_A° and p_B° are constant.
- (iii) Depending on the vapour pressure of the pure components A and B, total vapour pressure over the solution decreases or increases with the increase of the mole fraction of the component A.

The equation 12 shows that the total vapour pressure (p) is a linear function of the mole fraction x_B (or x_A as $x_A = 1 - x_B$) because p_A° and p_B° are constant at a particular temperature. This is shown in Fig 7. The dotted lines give the partial pressures of the two components versus composition and the solid line gives the total vapour pressure versus composition. The graph can be easily understood as:

According to Raoult's law, the partial vapour pressures of two components A and B of a solution are given as :

$$p_A = p_A^\circ x_A \quad \text{and} \quad p_B = p_B^\circ x_B$$

Therefore, the vapour pressures of the components are **linear functions** of their mole fractions. Now,

- (i) when $x_A = 1$, i.e., the liquid is pure A

$$p_A = p_A^\circ \times 1 = p_A^\circ$$

- (ii) when $x_A = 0$, i.e., the liquid is pure B

$$p_A = p_A^\circ \times 0 = 0$$

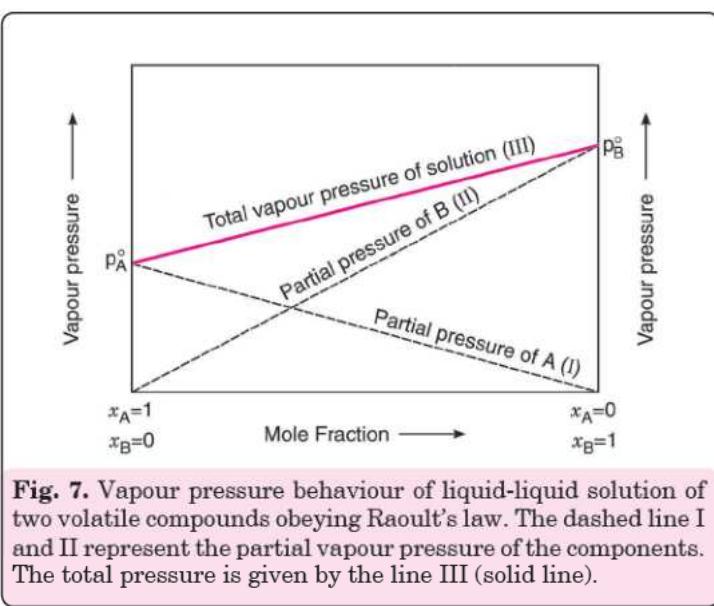


Fig. 7. Vapour pressure behaviour of liquid-liquid solution of two volatile compounds obeying Raoult's law. The dashed line I and II represent the partial vapour pressure of the components. The total pressure is given by the line III (solid line).

Thus, the plot of p_A against x_A should give a straight line passing through p_A° (when $x_A = 1$) and 0 (when $x_A = 0$). This is shown by line I in Fig. 7. It is clear from the curve that when the liquid is pure ($x_A = 1$), its vapour pressure is equal to p_A° . As component B is added to component A (x_A decreases), the vapour pressure decreases along the line I till it becomes zero ($x_A = 0$).

Similarly, the variation of partial pressure of component B (p_B) with its mole fraction (x_B) is represented by the plot from $x_B = 0$ (i.e., $p_B = p_B^\circ \times 0 = 0$) to $x_B = 1$ (i.e., $p_B = p_B^\circ \times 1 = p_B^\circ$). It is shown by line II.

The total vapour pressure p , exerted by the solution as a whole at any composition is given by the sum of partial vapour pressures according to Dalton's law of partial pressures. Thus,

$$\begin{aligned} p &= p_A + p_B \\ &= p_A^\circ x_A + p_B^\circ x_B \end{aligned}$$

This is shown by line III in Fig. 7, obtained by joining the points p_A° and p_B° . It is clear from the figures that *the vapour pressure of solutions of different compositions*, lies between the vapour pressure of the pure components (p_A° and p_B°) and they lie on the straight line joining p_A° and p_B° . The minimum value of p (total vapour pressure) is p_A° and the maximum value is p_B° assuming that the component A is less volatile than component B i.e., $p_A^\circ < p_B^\circ$.

Composition in vapour phase

The composition of vapour phase in equilibrium with the solution is determined by the partial pressure of the components. If y_1 and y_2 are the mole fractions of the two components 1 and 2 respectively in the vapour phase, then according to Dalton's law of partial pressures :

Partial pressure of a component = Mole fraction of the component \times Total pressure in vapour phase

$$\therefore \quad p_1 = y_1 p$$

$$\text{or} \quad p_2 = y_2 p$$

In general, $p_i = y_i p_{\text{total}}$

$$\therefore \quad \text{Mole fraction of component 1 in vapour phase, } y_1 = \frac{p_1}{p}$$

$$\text{Mole fraction of component 2 in vapour phase, } y_2 = \frac{p_2}{p}$$

In general, mole fraction of a component in vapour phase

$$= \frac{\text{Partial vapour pressure of component}}{\text{Total vapour pressure}}$$

(b) Vapour Pressure of Solutions of Solids in Liquids (Raoult's Law for Non-Volatile Solutes)

This is a most common class of solutions formed by the dissolution of solids in liquids such as sodium chloride, glucose, urea, sugar in water and iodine and sulphur in carbon disulphide. Some physical properties such as vapour pressure are quite different from those of pure solvents.

Let us add a small amount of a *non-volatile* solute to the solvent (e.g., sugar in water) to form the solution (Fig. 8). When evaporation of this solution takes place, the vapour phase again consists of vapours of the solvent (i.e., of water) because the solute is non-volatile. *However, the vapour pressure of the solution is found to be less than that of the pure solvent.* This can be explained as follows :

We know that evaporation is a surface phenomenon. The vapour pressure depends on the

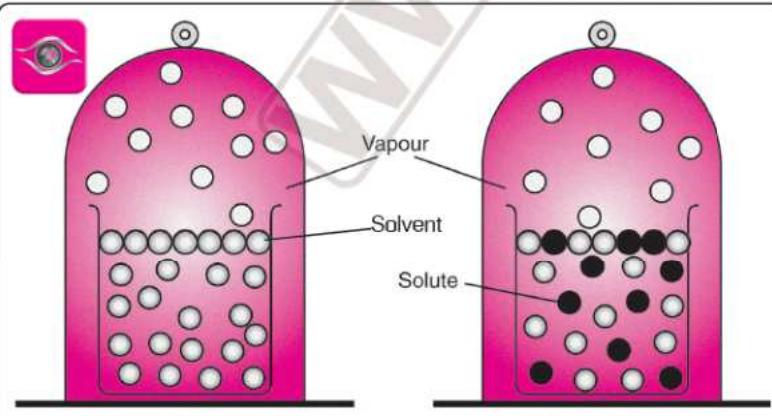


Fig. 8. Vapour pressure of (a) pure liquid and of (b) solution.

escape of solvent molecules from the surface of the liquid. In the case of solution, the non-volatile sugar molecules [as shown by small black spheres in Fig. 8(b)] also occupy a certain surface area. Therefore, the surface has both solute and solvent molecules; and the fraction of surface covered by solvent molecules gets reduced. As a result, lesser number of solvent molecules will escape into vapours. In other words, vapour pressure of the solution will be less than that of the pure solvent or there will be a lowering in vapour pressure. The increase in the concentration of sugar in the solution will further lower the vapour pressure of the solution.

Raoult's law for liquid solutions containing non-volatile solutes.

According to Raoult's law, the partial vapour pressure of volatile component in the solution is directly proportional to the mole fraction in it. When the solute is non-volatile, only the solvent molecules are present in the vapour phase. Therefore, *the vapour pressure of the solution will be the vapour pressure due to solvent only*.

Vapour pressure of the solution = Vapour pressure of the solvent in the solution.

If p_A is the vapour pressure of the solvent over a solution containing non-volatile solute and x_A is its mole fraction, then according to Raoult's law, the vapour pressure of the solvent in the solution,

$$\begin{aligned} p_A &\propto x_A \\ p_A &= p_A^\circ x_A \\ \text{or } p &= p_A^\circ x_A \quad (\because p = p_A) \end{aligned}$$

i.e., p (solution) = p (pure solvent) \times mole fraction of solvent.

This relationship is known as **Raoult's law**.

Thus, for solutions containing non-volatile solutes, the **Raoult's law** may be stated as

at a given temperature, the vapour pressure of a solution containing non-volatile solute is directly proportional to the mole fraction of the solvent.

The above expression also implies that $p \propto x_A$

i.e., vapour pressure of solution is directly proportional to the mole fraction of the solvent in the solution. The proportionality constant is equal to vapour pressure of pure solvent (p_A°). Thus, if vapour pressure of the solution containing a non-volatile solute is plotted against the mole fraction of the solvent, a straight line plot will be obtained as shown in Fig. 9.

The above relationship may also be expressed in different ways as :

Rearranging the above equation,

$$\frac{P}{p_A^\circ} = x_A$$

Subtracting each side of the equation from 1, we have

$$1 - \frac{P}{p_A^\circ} = 1 - x_A$$

$$\text{or } \frac{p_A^\circ - P}{p_A^\circ} = x_B \quad (\because x_A + x_B = 1 \text{ or } 1 - x_A = x_B)$$

$$\text{or } \frac{p_{\text{solvent}}^\circ - p_{\text{solution}}}{p_{\text{solvent}}^\circ} = x_{\text{solute}}$$

Here, $p_A^\circ - p_A$ (difference in vapour pressure of pure solvent and solution) represents the lowering in vapour pressure on the formation of solution. Now, by dividing the lowering in vapour pressure with the vapour pressure of the pure solvent, i.e., $(p_A^\circ - p_A)/p_A^\circ$ we get the **relative lowering in vapour pressure**. The above relation also gives an alternative statement of Raoult's law. Thus, the **Raoult's law in its modified form** may be stated as

the relative lowering in vapour pressure of an ideal solution containing the non-volatile solute is equal to the mole fraction of the solute at a given temperature.

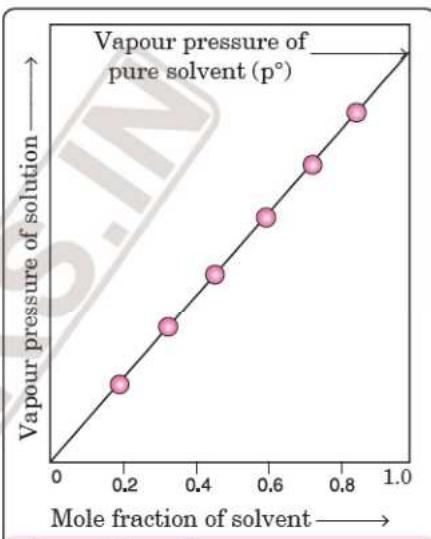


Fig. 9. Plot of vapour pressure of solution containing non-volatile solute versus mole fraction of the solvent.

KEY NOTE

According to latest convention, pressure is represented as p instead of P . Still both abbreviations are commonly used. But in the present text, p is used for pressure.

KEY NOTE

The **difference** and **similarity** between Raoult's law and Henry's law must be noted carefully.

Similarities

- Both Raoult's law and Henry's law apply to volatile component in solution.
- Both laws state that the vapour pressure of one component is proportional to the mole fraction of that component.

Differences

- Raoult's law defines the proportionality constant as the vapour pressure of the pure component, whereas Henry's law defines the proportionality constant as some experimentally determined value (Henry's constant, K_H).

Raoult's law as a special case of Henry's law

Raoult's law may be regarded as a special case of Henry's law. According to Raoult's law, the vapour pressure of a volatile component in given solution is given by the relation :

$$p_A = p_A^\circ x_A$$

where p_A° is the vapour pressure of the pure component, p_A is the vapour pressure in the solution having mole fraction x_A . In the case of solution of a gas in a liquid, the gaseous component is volatile component. Its solubility is governed by Henry law which gives the relation :

$$p = K_H x$$

where p is the pressure of the gas above the solution and x is its mole fraction. K_H is a proportionality constant known as Henry's constant.

The comparison of equations for Raoult's law and Henry's law shows that the partial pressure of the volatile component or gas is directly proportional to its mole fraction in solution. The only difference in the two expressions is the proportionality constant p_A° (in Raoult's law) and K_H (in Henry's law).

Therefore, **Raoult's law becomes a special case of Henry's law in which K_H becomes equal to vapour pressure of the pure component (p_A°)**. Even in the liquid solutions, one of the components may sometimes obey Henry's law over a range of mole fraction.

In that case K_H becomes equal to p_A° . In practice, in solutions in which solute behaves ideally according to Henry's law, the solvent also behaves ideally according to Raoult's law. However, the reverse is not necessarily true and the Raoult's law ideality of the solvent does not mean that the solute must obey Henry's law.

As the solution becomes more and more dilute, and approaches a limit of infinite dilution ($x_2 \longrightarrow 0$) its components behave more ideally. The solvent behaves Raoult's law whereas the solute (minor component) obeys Henry's law for dilute solutions.

IDEAL AND NON-IDEAL SOLUTIONS

The binary liquid-liquid solutions may be classified into two types :

- (1) *Ideal solutions*
- (2) *Non-ideal solutions*

These may be described as follows:

1. Ideal solutions

An ideal solution may be defined as **the solution which obeys Raoult's law exactly over the entire range of concentration**.

Such solutions are formed by mixing the two components which are identical in molecular size, in structure and have almost identical intermolecular forces. In these solutions, the intermolecular interactions between the components (A – B attractions) are of same magnitude as the intermolecular interactions in pure components (A – A and B – B attractions). According to Raoult's law, the partial vapour pressure of two components of the solution may be given as :

$$\begin{aligned} p_A &= p_A^\circ x_A \\ \text{and} \quad p_B &= p_B^\circ x_B \end{aligned}$$

Total pressure p is given by

$$p = p_A + p_B = p_A^\circ x_A + p_B^\circ x_B$$

The ideal solutions have also the following characteristics:

- (i) **Heat change on mixing is zero.** Since there is no change in magnitude of the attractive forces in the two components present, the heat change on mixing i.e. $\Delta_{mixing} H$ in such solutions must be zero.

(ii) Volume change on mixing is zero. In ideal solutions, the volume of the solution is the sum of the volumes of the components before mixing i.e., there is no change in volume on mixing or $\Delta_{mixing}V$ is zero.

For example, when we mix 100 cm³ of benzene with 100 cm³ of toluene, the volume of the solution is found to be exactly 200 cm³. Therefore, there is no change in volume on mixing i.e. $\Delta_{mixing}V = 0$. It has been noticed that the solutions generally tend to become ideal when they are dilute.

The **characteristics** of an ideal solution may be **summed up** as follows :

- (i) It must obey Raoult's law.
- (ii) $\Delta_{mixing}H$ should be zero.
- (iii) $\Delta_{mixing}V$ should be zero.

Examples of ideal solutions. In fact, ideal solutions are quite rare but some solutions are nearly ideal in behaviour at least when they are very dilute. A few examples of ideal solutions are:

- (i) Benzene and toluene
- (ii) *n*-hexane and *n*-heptane
- (iii) Bromoethane and iodoethane
- (iv) Chlorobenzene and bromobenzene.

The graphical behaviour of ideal solution has already been discussed in Fig. 7. Such solutions which obey Raoult's law are called **ideal liquid solutions**.

2. Non-ideal solutions

The solutions which do not obey Raoult's law over the entire range of concentration are called non-ideal solutions.

Therefore, for such solutions

$$p_A \neq p_A^{\circ}x_A \quad \text{and} \quad p_B \neq p_B^{\circ}x_B$$

Thus, the vapour pressure of such solutions is either higher or lower than that predicted by Raoult's law. In non-ideal solutions, there is a noticeable change in volume and heat energy when the two components are mixed. Most of the solutions are non-ideal because they deviate from ideal behaviour to more or less extent. Thus, for **non-ideal solutions**,

- (i) none of the components obey Raoult's law over the entire composition range, i.e., $p_A \neq p_A^{\circ}x_A$ and $p_B \neq p_B^{\circ}x_B$
- (ii) $\Delta_{mixing}V$ is not equal to zero.
- (iii) $\Delta_{mixing}H$ is not equal to zero.

Thus, non-ideal solutions do not obey Raoult's law and are accompanied by change in enthalpy and change in volume during their formation.

Differences between ideal and non-ideal solutions

The main points of differences between ideal and non-ideal solutions are **summed up** below:

Ideal solution	Non-ideal solution
<ol style="list-style-type: none"> The interactions between the components are similar to those in the pure components. There is no enthalpy change on mixing. $(\Delta_{mixing}H = 0)$ There is no volume change on mixing. $(\Delta_{mixing}V = 0)$ Each component obeys Raoult's law at all temperatures and concentrations, i.e., $p_A = p_A^{\circ} \times x_A$ and $p_B = p_B^{\circ} \times x_B$ 	<p>The interaction between the components are different from those of the pure components.</p> <p>There is enthalpy change on mixing. $(\Delta_{mixing}H \neq 0)$</p> <p>There is volume change on mixing. $(\Delta_{mixing}V \neq 0)$</p> <p>Their components do not obey Raoult's law. They show positive and negative deviations from Raoult's law i.e., $p_A \neq p_A^{\circ}x_A$ and $p_B \neq p_B^{\circ}x_B$</p>

Types of Non-ideal Solutions

Non-ideal solutions show positive and negative deviations from the ideal behaviour depending upon their nature.

(i) Non-ideal solutions showing positive deviations from Raoult's law. Consider a binary solution of two components A and B. If the A–B interactions in the solutions are *weaker* than the A–A and B–B interactions in the two liquids forming the solution, then the escaping tendency of A and B types of molecules from the solution becomes more than from pure liquids. As a result, each component of solution has a partial vapour pressure greater than expected on the basis of Raoult's law. The total vapour pressure will be greater than corresponding vapour pressure expected in case of ideal solution of the same composition. This type of behaviour of solution is described as **positive deviations** from Raoult's law. Mathematically, it may be expressed as :

$$P_A > P_A^\circ x_A \text{ and } P_B > P_B^\circ x_B$$

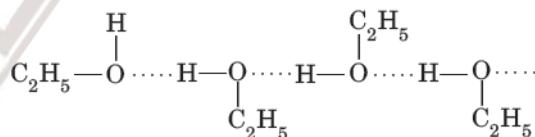
The total vapour pressure,

$$P = P_A + P_B \text{ is always greater than } (P_A^\circ x_A + P_B^\circ x_B)$$

The positive deviations have been shown in Fig. 10, in which dotted lines show the ideal behaviour upon mixing while the thick lines exhibit the actual behaviour. A few examples of solutions showing positive deviations are :

- (i) Ethyl alcohol and cyclohexane
- (ii) Acetone and carbon disulphide
- (iii) Benzene and acetone
- (iv) Carbon tetrachloride and chloroform
- (v) Acetone and ethyl alcohol
- (vi) Ethyl alcohol and water.

Explanation for positive deviations. Let us explain by considering a solution of ethyl alcohol and cyclohexane. In ethyl alcohol, the molecules are held together due to hydrogen bonding as shown below :



When cyclohexane is added to ethyl alcohol, the molecules of cyclohexane tend to occupy the spaces between ethyl alcohol molecules. Consequently, some hydrogen bonds in alcohol molecules break and the attractive forces in alcohol molecules are weakened. The escaping tendency of alcohol and cyclohexane molecules from the solution increases. Consequently, the vapour pressure of the solution is greater than the vapour pressure as expected according to Raoult's law.

In such solutions, $\Delta_{mixing}\text{H}$ and $\Delta_{mixing}\text{V}$ are also not equal to zero as explained below :

(i) $\Delta_{mixing}\text{H}$ is positive because energy is required to break A–A or B–B attractive forces. Therefore, dissolution process is *endothermic*.

(ii) Because of the decrease in the magnitude of intermolecular forces in solutions, the molecules will be loosely held and, therefore, there will be increase in volume on mixing. Thus, $\Delta_{mixing}\text{V}$ will be +ve.

Since the dissolution process is endothermic, *heating will increase the solubility of such a solution*.

(ii) Non-ideal solutions showing negative deviations from Raoult's law. In such solutions, the A–B interactions are *stronger* than the A–A and B–B interactions present in the two liquids forming the solution. Due to stronger A–B interactions, the escaping tendency of A and B types of molecules from the solution becomes less than from pure liquids. Consequently, each component of the solution has a partial vapour pressure less than expected on the basis of Raoult's law. As a result, the total vapour pressure becomes less than

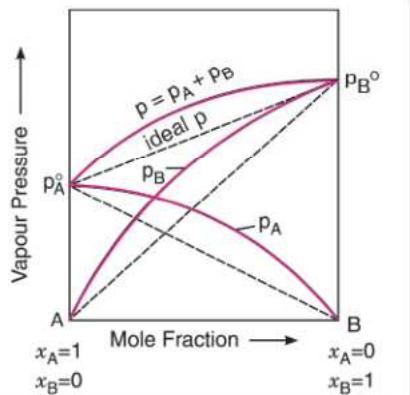


Fig. 10. Positive deviations from ideal behaviour. The dotted lines (----) represent ideal behaviour and solid lines (—) represent actual behaviour.

the corresponding vapour pressure expected in case of ideal solution. The solutions are said to have **negative deviations** from Raoult's law.

Mathematically,

$$p_A < p_A^{\circ}x_A \text{ and } p_B < p_B^{\circ}x_B$$

Thus, the total vapour pressure,

$$p = p_A + p_B \text{ is always less than } (p_A^{\circ}x_A + p_B^{\circ}x_B)$$

The negative deviations have been shown in Fig. 11, in which dotted lines show the ideal behaviour upon mixing while the thick lines show the actual behaviour. A few examples of the solutions showing negative deviations are:

- (i) Acetone and chloroform
- (ii) Chloroform and diethyl ether
- (iii) Chloroform and nitric acid
- (iv) Acetone and aniline
- (v) Water and nitric acid
- (vi) Diethyl ether and chloroform.

Explanation for negative deviations. Let us illustrate by considering a solution of acetone and chloroform. When acetone and chloroform are mixed, there are new attractive forces due to intermolecular hydrogen bonding. Thus, the attractive forces become stronger and the escaping tendency of each liquid from the solution decreases.

Therefore, the vapour pressure of the solution is less than that expected for an ideal solution.

In these solutions also, $\Delta_{mixing}H$ and $\Delta_{mixing}V$ are not equal to zero as explained below :

(i) $\Delta_{mixing}H$ is *negative* because energy is released due to increase in attractive forces. Therefore, *dissolution process is exothermic and heating the solution will decrease solubility*.

(ii) Because of the increase in forces of attraction in the solution, the molecules will be held more tightly. Therefore, there will be decrease in volume on mixing i.e. $\Delta_{mixing}V$ will be negative.

The **main properties** of two types of non-ideal solutions are summed up below :

Solutions having +ve deviation from ideal behaviour	Solutions having -ve deviation from ideal behaviour
<ol style="list-style-type: none"> The interactions between the components are less than in the pure components. $p_A > p_A^{\circ}x_A$ and $p_B > p_B^{\circ}x_B$ $\Delta_{mixing}H = +ve$ Dissolution is endothermic. Heating increases solubility. $\Delta_{mixing}V = +ve$ 	<ol style="list-style-type: none"> The interactions between the components are more than in the pure components. $p_A < p_A^{\circ}x_A$ and $p_B < p_B^{\circ}x_B$ $\Delta_{mixing}H = -ve$ Dissolution is exothermic Heating decreases solubility. $\Delta_{mixing}V = -ve$

Azeotropes or Constant Boiling Mixtures

There are some mixtures of liquids (solutions) which on boiling produce vapour with the same composition as the liquid and boil at a constant temperature. Therefore, such liquid mixtures distil over as if these are pure liquids. In such cases, it is not possible to separate the components by fractional distillation.

The solutions (liquid mixtures) which boil at constant temperature and can distil unchanged in composition are called **azeotropes or azeotropic mixtures** (Greek meaning *boiling without change*).

There are two types of azeotropes depending upon the type of deviations from Raoult's law. These are:

- (i) Minimum boiling azeotropes
- (ii) Maximum boiling azeotropes.

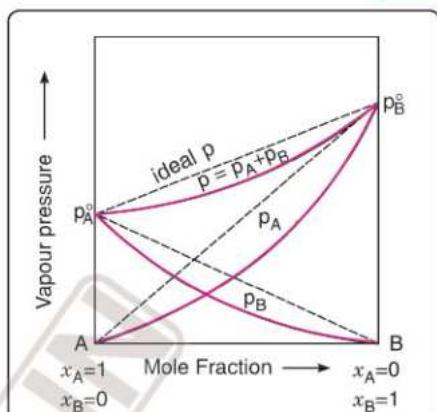
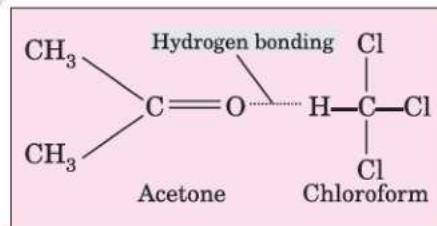


Fig. 11. Negative deviations from ideal behaviour. The dotted lines (----) represent ideal behaviour and solid lines (—) represent actual behaviour.



Competition Plus

Azeotropes are liquid mixtures which distil over as if these are pure liquids. For details, refer **Competition File** (Page 98).

REMEMBER

- Solutions showing **positive deviations** from ideal behaviour form **minimum boiling azeotropes**.
- Solutions showing **negative deviations** from ideal behaviour form **maximum boiling azeotropes**.

R U Curious...

- Pure ethyl alcohol cannot be obtained from rectified spirit (95.6% of alcohol) even by fractional distillation!
- This is because a mixture of 95.6% alcohol and 4.4% water forms an azeotropic i.e., constant boiling mixture. At this stage liquid and vapour have the same composition and therefore, it cannot be further distilled to separate water from ethanol.

(i) Minimum boiling azeotropes: The solutions which show a large positive deviation from Raoult's law form minimum boiling azeotrope at a specific composition. For example, ethanol-water mixtures (obtained by fermentation of sugars) are rich in water. The fractional distillation gives a solution containing approximately 95% by volume of ethanol. Once the composition has been obtained the liquid and vapour have the same composition and therefore, it cannot be further distilled to separate water from ethanol. Other methods of separation have to be used to prepare 100% ethanol.

(ii) Maximum boiling azeotropes: The solutions which show negative deviation from Raoult's law form maximum boiling azeotrope at a specific composition. For example, nitric acid (HNO_3) and water form maximum boiling azeotrope. The azeotrope has the approximate composition 68% nitric acid and 32% water by mass with a boiling point of 393.5 K.

Some common azeotropic mixtures are given below :

Components		Composition (mass % B)	Boiling Point (K)		
A	B	A	B	Azeotrope	
Minimum Boiling Azeotropes					
H_2O	$\text{C}_2\text{H}_5\text{OH}$	95.6	373	351.5	351
H_2O	$n\text{-C}_3\text{H}_7\text{OH}$	72.0	373	370.2	361
CHCl_3	$\text{C}_2\text{H}_5\text{OH}$	6.8	334.2	351.3	332.3
Maximum Boiling Azeotropes					
H_2O	HCl	20.2	373	188	381.6
H_2O	HNO_3	68.0	373	359	393.5
H_2O	HCOOH	77.0	373	374	380.0
CHCl_3	CH_3COCH_3	20.0	334.2	329.1	337.7

It is clear from the above table that in case of minimum boiling azeotrope, the boiling point of the azeotrope is less than the boiling point of either of the pure components. Similarly, in case of maximum boiling azeotrope, the boiling point of azeotrope is more than the boiling point of either of the pure components.

Solving Numerical Problems**FORMULAE AND UNITS**

According to Raoult's law, for a binary solution of components A and B

$$\begin{aligned} p_A &= p_A^\circ x_A \\ p_B &= p_B^\circ x_A \end{aligned}$$

where p_A° and p_A are the vapour pressure of pure component A and its vapour pressure in solution respectively and x_A is its mole fraction in solution. p_B° and p_B are the vapour pressure of pure component B and its vapour pressure in solution respectively and x_B is its mole fraction.

For a solution containing a non-volatile solute,

Vapour pressure of solution = Vapour pressure of solvent in solution, $p_A = p_A^\circ \cdot x_A$
where p_A° is the vapour pressure of pure component and x_A is its mole fraction in solution.

SOLVED EXAMPLES

Example 26.

The vapour pressure of ethyl alcohol at 298 K is 40 mm of Hg. Its mole fraction in a solution with methyl alcohol is 0.80. What is its vapour pressure in solution if the mixture obeys Raoult's law?

Solution : According to Raoult's law,

$$p_A = p_A^\circ x_A$$

Vapour pressure of pure ethyl

$$\text{alcohol } (p_A^\circ) = 40 \text{ mm of Hg}$$

Mole fraction of ethyl alcohol (x_A) = 0.80

Vapour pressure of ethyl alcohol

$$\begin{aligned} \text{in solution } (p_A) &= 40 \times 0.80 \\ &= 32 \text{ mm of Hg.} \end{aligned}$$

Example 27.

An aqueous solution of glucose is made by dissolving 10 g of glucose ($C_6H_{12}O_6$) in 90 g of water at 303 K. If the vapour pressure of pure water at 303 K be 32.8 mm Hg, what would be the vapour pressure of the solution? (A.I.S.B. 2000)

Solution : According to Raoult's law, vapour pressure of the solution,

$$p_A = p_A^\circ x_A$$

where p_A° = vapour pressure of pure water and x_A is the mole fraction of water.

Since solute is non-volatile

$$\begin{aligned} \text{Vapour pressure of solution} &= p_A = p_A^\circ x_A \\ p_A^\circ &= 32.8 \text{ mm Hg} \end{aligned}$$

$$\text{Moles of water} = \frac{90}{18} = 5.0$$

$$\text{Moles of glucose} = \frac{10}{180} = 0.0556$$

$$\text{Mole fraction of water, } x_A = \frac{5.0}{5.0 + 0.0556} = 0.989$$

$$\text{Vapour pressure of solution} = 32.8 \times 0.989$$

$$= 32.44 \text{ mm.}$$

Example 28.

At 298 K, the vapour pressure of pure benzene, C_6H_6 is 0.256 bar and the vapour pressure of pure toluene $C_6H_5CH_3$ is 0.0925 bar. If the mole fraction of benzene in solution is 0.40 (i) what is the total vapour pressure of the solution? (ii) Calculate the composition of the vapour in terms of mole fraction.

(Pb.S.B. 2009, 2010)

Solution : (i) Calculation of total vapour pressure

According to Raoult's law,

Vapour pressure of a component = Vapour pressure of pure liquid \times Mole fraction

Mole fraction of benzene, $x_{\text{benzene}} = 0.40$

Vapour pressure of pure benzene, $p_{\text{benzene}}^\circ = 0.256$ bar

Partial vapour pressure of benzene,

$$p_{\text{benzene}} = 0.256 \times 0.40 = 0.1024 \text{ bar}$$

Mole fraction of toluene, $x_{\text{toluene}} = 1 - 0.40 = 0.60$

Vapour pressure of pure toluene,

$$p_{\text{toluene}}^\circ = 0.0925 \text{ bar}$$

Partial vapour pressure of toluene,

$$p_{\text{toluene}} = 0.0925 \times 0.60 = 0.0555 \text{ bar}$$

Total vapour pressure of solution,

$$p_{\text{total}} = p_{\text{benzene}} + p_{\text{toluene}} = 0.1024 + 0.0555 = 0.158 \text{ bar.}$$

(ii) Calculation of composition of vapour phase

Mole fraction of benzene in vapour phase

$$y_{\text{benzene}} = \frac{p_{\text{benzene}}}{p_{\text{total}}} = \frac{0.1024}{0.158} = 0.648$$

Mole fraction of toluene in vapour phase

$$y_{\text{toluene}} = \frac{0.0555}{0.158} = 0.351$$

Example 29.

Vapour pressure of chloroform ($CHCl_3$) and dichloromethane (CH_2Cl_2) at 298 K are 200 mm Hg and 415 mm Hg respectively.

(i) Calculate the vapour pressure of the solution prepared by mixing 25.5 g of $CHCl_3$ and 40 g of CH_2Cl_2 at 290 K and

(ii) Mole fraction of each component in solution.

N.C.E.R.T. (Pb.S.B. 2009, 2010, Kerala S.B. 2012)

Solution : (i) Molar mass of $CHCl_3$ = $1 \times 12 + 1 \times 1 + 3 \times 35.5$

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

$$\begin{aligned} \text{Molar mass of } CH_2Cl_2 &= 1 \times 12 + 2 \times 1 + 2 \times 35.5 \\ &= 85 \text{ g mol}^{-1} \end{aligned}$$

$$\text{Moles of } CHCl_3 = \frac{25.5 \text{ g}}{119.5 \text{ g mol}^{-1}} = 0.213 \text{ mol}$$

$$\text{Moles of } CH_2Cl_2 = \frac{40 \text{ g}}{85 \text{ g mol}^{-1}} = 0.470 \text{ mol}$$

$$\text{Total number of moles} = 0.213 + 0.470 = 0.683 \text{ mol}$$

$$x_{CHCl_3} = \frac{0.213}{0.683} = 0.312$$

$$x_{CH_2Cl_2} = 1.0 - 0.312 = 0.688$$

$$p_{CHCl_3} = p^\circ CHCl_3 \times x_{CHCl_3}$$

$$= 200 \times 0.312 = 62.4 \text{ mm Hg}$$

$$p_{CH_2Cl_2} = p^\circ CH_2Cl_2 \times x_{CH_2Cl_2}$$

$$= 4.15 \times 0.688 = 288.5$$

$$\begin{aligned} p_{\text{total}} &= 62.4 + 288.5 \\ &= 347.9 \text{ mm Hg} \end{aligned}$$

(ii) Mole fraction in vapour phase

$$y_{CHCl_3} = \frac{p_{CHCl_3}}{p} = \frac{62.4}{347.9} = 0.18$$

$$\begin{aligned} y_{CH_2Cl_2} &= \frac{p_{CH_2Cl_2}}{p} = \frac{288.5}{347.9} \\ &= 0.82. \end{aligned}$$

It may be noted that since CH_2Cl_2 is a more volatile component than CHCl_3 [$p^\circ(\text{CH}_2\text{Cl}_2) = 415 \text{ mm Hg}$ and $p^\circ(\text{CHCl}_3) = 200 \text{ mm Hg}$] and therefore, the vapour phase is also richer in CH_2Cl_2 . Thus, it may be concluded that at equilibrium, vapour phase will be always rich in the component which is more volatile.

Example 30.

Two liquids X and Y on mixing form an ideal solution. The vapour pressure of the solution containing 3 mol of X and 1 mol of Y is 550 mm of Hg. But when 4 mol of X and 1 mol of Y are mixed, the vapour pressure of the solution, thus, formed is 560 mm of Hg. What will be the vapour pressure of the pure X and pure Y at this temperature?

Solution : Let the vapour pressure of X be p_1° and of Y be p_2° and x_1 and x_2 be their mole fractions.

Then according to Raoult's law, the total pressure, p is

$$p = p_1^\circ \cdot x_1 + p_2^\circ \cdot x_2$$

In the first solution,

$$x_1 = \frac{3}{3+1} = 0.75, x_2 = \frac{1}{3+1} = 0.25$$

$$\therefore p_1^\circ \times 0.75 + p_2^\circ \times 0.25 = 550 \text{ mm} \quad \dots(i)$$

In the second solution,

$$x_1 = \frac{4}{4+1} = 0.80, x_2 = \frac{1}{4+1} = 0.20$$

$$\therefore p_1^\circ \times 0.80 + p_2^\circ \times 0.20 = 560 \text{ mm} \quad \dots(ii)$$

Multiply eq. (i) by 4 and eq. (ii) by 5, we get

$$3p_1^\circ + p_2^\circ = 2200 \text{ mm} \quad \dots(iii)$$

$$4p_1^\circ + p_2^\circ = 2800 \text{ mm} \quad \dots(iv)$$

$$\text{Subtracting } -p_1^\circ = -600 \text{ mm}$$

$$\therefore p_1^\circ = 600 \text{ mm of Hg}$$

Substituting in eq. (iii) we get

$$3 \times 600 + p_2^\circ = 2200 \text{ or } p_2^\circ = 2200 - 1800 = 400 \text{ mm Hg}$$

Vapour pressure of pure component X = 600 mm Hg

Vapour pressure of pure component Y = 400 mm Hg

KEY NOTE

Mole fraction of a component in vapour phase may be calculated as :

Mole fraction of component A in vapour phase

$$= \frac{\text{Partial vapour pressure of A in solution}}{\text{Total vapour pressure}}$$

Mole fraction of component B in vapour phase

$$= \frac{\text{Partial vapour pressure of B in solution}}{\text{Total vapour pressure}}$$

Practice Problems

31. The vapour pressure of pure liquid A at 310°C is 0.158 bar. The vapour pressure of this liquid in solution with liquid B is 0.095 bar. Calculate the mole fraction of A in the solution if the mixture obeys Raoult's law.

32. At 293 K, ethyl acetate has vapour pressure of 72.8 torr of Hg and ethyl propionate has vapour pressure of 27.7 torr of Hg. Assuming their mixtures to obey Raoult's law, determine the vapour pressure of a mixture containing 25 g of ethyl acetate and 50 g of ethyl propionate.

33. An aqueous solution containing 28% by weight of a liquid A (molecular mass = 140) has a vapour pressure of 0.210 bar at 37°C . Calculate the vapour pressure of pure liquid (vapour pressure of water at $37^\circ\text{C} = 0.198$ bar).

34. Benzene and toluene form nearly ideal solution. At a certain temperature, the vapour pressure of the pure benzene is 150 torr and of pure toluene is 50 torr. Calculate the vapour pressure of the solution containing equal weights of two substances at this temperature.

35. The vapour pressure of ethanol and methanol are 44.5 and 88.7 mm Hg respectively. An ideal solution is formed at the same temperature by mixing 60 g of ethanol and 40 g of methanol. Calculate the total vapour pressure of the solution and the mole fraction of methanol in the vapour phase.

(Pb.S.B.E. 2009, 2010)

36. Methanol and ethanol forms nearly ideal solution at 300 K. A solution is made by mixing 32 g methanol and 23 g ethanol. Calculate the partial pressure of its constituents and the total pressure of the solution. (at 300 K; $p^\circ(\text{CH}_3\text{OH}) = 90 \text{ mm Hg}$, $p^\circ(\text{C}_2\text{H}_5\text{OH}) = 51 \text{ mm Hg}$).

37. At 20°C , the vapour pressure of pure liquid A is 22 mm Hg and that of pure liquid B is 75 mm Hg. What is the composition of the solution of these two components that has a vapour pressure of 48.5 mm Hg at this temperature (assume ideal behaviour) ?

Answers to Practice Problems

31. 0.601
32. 44.25 torr of Hg
33. 0.448 bar
34. 104.1 torr
35. 66.15 mm Hg, 0.657
36. $p(\text{CH}_3\text{OH}) = 60.3 \text{ mm Hg}$, $p(\text{C}_2\text{H}_5\text{OH}) = 16.8 \text{ mm Hg}$, $p(\text{Total}) = 77.1 \text{ mm Hg}$
37. $x_A = x_B = 0.5$ equal moles of A and B.

38. Two liquids A and B have vapour pressure of 0.658 bar and 0.264 bar respectively. In an ideal solution of the two, calculate the mole fraction of A at which the two liquids have equal partial pressures.
39. The liquids X and Y form ideal solution having vapour pressures 200 and 100 mm Hg respectively. Calculate the mole fraction of component X in vapour phase in equilibrium with an equimolar solution of the two.
40. At a certain temperature, the vapour pressure (in mm Hg) of CH_3OH and $\text{C}_2\text{H}_5\text{OH}$ solution is represented by $P = 119x + 135$ where x is the mole fraction of CH_3OH . What are the vapour pressures of pure components at this temperature?

Answers to Practice Problems

38. 0.286

39. 0.67

40. $p(\text{CH}_3\text{OH}) = 254 \text{ mm Hg}$
 $p(\text{C}_2\text{H}_5\text{OH}) = 135 \text{ mm Hg}$ **Hints & Solutions on page 66****Advanced Level****PROBLEMS****Accelerate Your Potential
(for JEE Advance)**

Problem 5. The mole fraction of X in the vapours in equilibrium with homogeneous mixture of liquids X and Y is 0.42. The vapour pressure of liquids X and Y at the same temperature are 406.5 and 140 torr respectively. Calculate the mole fraction of X in the solution.

Solution According to Raoult's law,

$$p_X = p_X^\circ \times x_X \quad \dots(i)$$

$$p_Y = p_Y^\circ \times x_Y = p_Y^\circ (1 - x_X) \quad \dots(ii)$$

In vapour state, mole fractions of X and Y are :

$$y_X = \frac{p_X}{p_{\text{total}}}$$

$$0.42 = \frac{p_X}{p_{\text{total}}} \quad \text{or } p_X = 0.42 p_{\text{total}} \quad \dots(iii)$$

$$\text{Similarly, } y_Y = \frac{p_Y}{p_{\text{total}}}$$

$$0.58 = \frac{p_Y}{p_{\text{total}}} \quad \text{or } p_Y = 0.58 p_{\text{total}} \quad \dots(iv)$$

Dividing eq. (iii) by eq. (iv),

$$\text{or } \frac{p_X}{p_Y} = \frac{0.42}{0.58} = 0.724 \quad \dots(v)$$

From eq. (i), (ii) and eq. (v),

$$\frac{p_X}{p_Y} = \frac{p_X^\circ \times x_X}{p_Y^\circ \times (1 - x_X)} = 0.724$$

$$\text{or } \frac{406.5 x_X}{140(1 - x_X)} = 0.724$$

$$\text{or } 406.5 x_X = 101.36 - 101.36 x_X$$

$$507.86 x_X = 101.36$$

$$\therefore x_X = 0.20$$

Problem 6. Liquids A and B form ideal solution over the entire range of composition. At temperature T, equimolar binary solution of liquids A and B has vapour pressure 45 torr. At the same temperature, a new solution of A and B having mole fractions x_A and x_B respectively has vapour pressure of 22.5 torr. What is the value of x_A/x_B in the new solution? (Given that the vapour pressure of pure liquid A is 20 torr at temperature T).

(JEE Advance 2018)

Solution For equimolar binary solution of liquids A and B

$$x_A = 0.5, x_B = 0.5 \text{ and } p_A^\circ = 20 \text{ torr}$$

$$p_{\text{total}} = x_A p_A^\circ + x_B p_B^\circ$$

$$45 = 0.5 \times 20 + 0.5 \times p_B^\circ$$

$$0.5 p_B^\circ = 45 - 10 = 35$$

$$\therefore p_B^\circ = 35 \times 2 = 70 \text{ torr}$$

If mole fractions are x_A and x_B for the new solution,

$$22.5 = 20x_A + 70x_B$$

$$22.5 = 20x_A + 70(1-x_A)$$

$$50x_A = 70 - 22.5 = 47.5$$

$$x_A = \frac{47.5}{50} = 0.95$$

$$x_B = 1 - 0.95 = 0.05$$

$$\therefore \frac{x_A}{x_B} = \frac{0.95}{0.05} = 19.00$$

Problem 7. A solution of A and B with 30 mol % A is in equilibrium with its vapour which contains 40 mol % B. Assuming that the solution and the vapour behave ideally, calculate the ratio of vapour pressure of pure A and pure B.

Solution In solution, mol % of A is 30, so that

$$x_A = 0.30, x_B = 0.70$$

In vapour phase, mol % of B is 40, so that

$$y_A = 0.60, y_B = 0.40$$

$$\text{Now, } y_A = \frac{p_A}{\text{total vapour pressure}} = \frac{x_A p_A^\circ}{x_A p_A^\circ + x_B p_B^\circ}$$

$$\text{or } \frac{0.30 p_A^\circ}{0.30 p_A^\circ + 0.70 p_B^\circ} = 0.60 \quad \dots(i)$$

Similarly,

$$y_B = \frac{p_B}{\text{total vapour pressure}} = \frac{x_B p_B^\circ}{x_A p_A^\circ + x_B p_B^\circ}$$

$$\text{or } \frac{0.70 p_B^\circ}{0.30 p_A^\circ + 0.70 p_B^\circ} = 0.40 \quad \dots(ii)$$

Dividing eq. (i) by eq. (ii):

$$\frac{0.30 p_A^\circ}{0.70 p_B^\circ} = \frac{0.60}{0.40}$$

$$\text{or } \frac{p_A^\circ}{p_B^\circ} = \frac{0.60}{0.40} \times \frac{0.70}{0.30} = 3.5$$

Conceptual Questions

2

- Q.1. What happens to vapour pressure of water if a tablespoon of sugar is added to it ?**
Ans. Addition of non-volatile solute lowers the vapour pressure of solvent (water).
- Q.2. Why is the time saved when cooking is done in a pressure cooker ?** (J.K.S.B. 2013)
Ans. At higher pressure over the liquid (due to weight of the pressure cooker lid), the liquid boils at higher temperature. Therefore, cooking occurs faster.
- Q.3. Why is the vapour pressure of a liquid constant at a constant temperature ?**
Ans. Vapour pressure is the pressure of the vapour at equilibrium state when rate of evaporation becomes equal to rate of condensation. Equilibrium constant does not change at a particular temperature and, therefore, vapour pressure remains constant.
- Q.4. Two liquids A and B are mixed and the resulting solution is found to be cooler. What do you conclude about deviation from ideal behaviour ?**
Ans. The solution shows positive deviation from ideal behaviour.
- Q.5. Can we separate the components of azeotropic mixture by distillation ?**
Ans. No, we cannot separate the components of an azeotropic mixture by distillation because at a particular composition, both the components boil at the same temperature.
- Q.6. Mixing of acetone with chloroform takes place with reduction in volume. What type of deviation from Raoult's law is shown in this case ?**
Ans. The solution has negative deviation from Raoult's law because decrease in volume indicates strong forces of interaction between the molecules in solution.
- Q.7. Why is liquid ammonia bottle first cooled in ice before opening it ?**
Ans. At room temperature, the vapour pressure of liquid ammonia is very high. On cooling vapour pressure decreases. Therefore, the liquid ammonia will not splash out.
- Q.8. Two liquid A and B boil at 145°C and 190°C respectively. Which of them has higher vapour pressure at 80°C ?** (D.S.B. 2006)
Ans. Lower the boiling point, more volatile it is. Therefore, liquid A will have higher vapour pressure at 80°C.
- Q. 9. A and B liquids on mixing produce a warm solution. Which type of deviation from Raoult's law is there ?** (C.B.S.E. Sample Paper 2011)
Ans. Negative deviation.
- Q. 10. A solution of chloroform and acetone is an example of maximum boiling azeotrope. Why ?** (C.B.S.E. Sample Paper 2012)
Ans. The solution of chloroform and acetone has lower vapour pressure than ideal solution because of stronger interactions between chloroform and acetone molecules. As a result, total vapour pressure becomes less than the corresponding ideal solution of same composition (i.e., negative deviations). Therefore, the boiling points of solutions are increased and form maximum boiling azeotropes.
- Q. 11. The dissolution of ammonium chloride in water is an endothermic process. What is the effect of temperature on its solubility?**
Ans. The solubility increases with rise in temperature (Le Chatelier's principle).

COLLIGATIVE PROPERTIES

The dilute solutions of non-volatile solutes exhibit certain characteristic properties which do not depend upon the nature of the solute but depend only on the number of particles (molecules or ions) of the solute i.e., on the molar concentration of the solute. These are called **colligative properties** (colligative, from Latin : *co* means together, *ligare* means to bind). Thus,

the properties of the solutions which depend only on the number of solute particles but not on the nature of the solute are called **colligative properties**.

The four important colligative properties are :

- (i) Relative lowering in vapour pressure
- (ii) Elevation in boiling point
- (iii) Depression in freezing point
- (iv) Osmotic pressure.

RELATIVE LOWERING IN VAPOUR PRESSURE

We have already studied that when a non-volatile solute is added to a solvent, the vapour pressure of the solution decreases. Let x_A be the mole fraction of the solvent, x_B be the mole fraction of the solute and p_A° be the vapour pressure of the pure solvent and p be the vapour pressure of solution.

Since solute is non-volatile, there will be no contribution of solute to the vapour pressure and the vapour pressure of the solution will be only due to the solvent. Therefore, the vapour pressure of the solution (p) will be equal to the vapour pressure of the solvent (p_A), over the solution, i.e.,

$$p = p_A$$

But, according to Raoult's law, the vapour pressure of solvent is equal to the product of its vapour pressure in pure state and its mole fraction,

$$\begin{aligned} p_A &= p_A^\circ x_A \\ \text{or} \quad p &= p_A = p_A^\circ x_A \end{aligned} \quad \dots(13)$$

Since x_A is always less than one, the vapour pressure of the solution is always less than p_A° i.e., vapour pressure of the pure solvent.

The lowering in vapour pressure is:

$$\begin{aligned} \Delta p_A &= p_A^\circ - p_A \\ &= p_A^\circ - p_A^\circ x_A \\ &= p_A^\circ (1 - x_A) \end{aligned}$$

or

But $1 - x_A = x_B$ so that

$$\begin{aligned} \Delta p_A &= p_A^\circ x_B \\ \Delta p_A &= x_B \\ p_A^\circ & \end{aligned}$$

Thus,

$$\frac{\Delta p_A}{p_A^\circ} = \frac{p_A^\circ - p_A}{p_A^\circ} = x_B \quad \dots(14)$$

where, $p_A^\circ - p_A$ (difference in vapour pressure of pure solvent and solution) represents the lowering in vapour pressure on the formation of solution and $(p_A^\circ - p_A)/p_A^\circ$ gives the relative lowering in vapour pressure. Thus, the **relative lowering in vapour pressure of an ideal solution containing the non-volatile solute is equal to the mole fraction of the solute at a given temperature.**

It may be noted that in a solution containing several non-volatile solutes, the lowering in vapour pressure depends on the sum of the mole fractions of different solutes.

Relative lowering of vapour pressure — a colligative property. According to Eq. 14, the relative lowering in vapour pressure depends only on the molar concentration of the solute (mole fraction) and is independent of its nature. Therefore, *relative lowering in vapour pressure is a colligative property*.

Determination of Molar Mass of a Solute from Relative Lowering in Vapour Pressure

Molar mass of a non-volatile solute can be calculated from relative lowering in vapour pressure. A known mass of the solute is dissolved in a known quantity of solution and relative lowering in vapour pressure is measured experimentally. According to Raoult's law, the relative lowering in vapour pressure on the addition of a non-volatile solute to the solvent is:

$$\frac{p_A^\circ - p_A}{p_A^\circ} = x_B$$

Suppose w_A and w_B are the weights of the solvent and solute respectively and M_A and M_B are their corresponding molar masses. Then,

$$\text{Mole fraction of solute, } x_B = \frac{n_B}{n_A + n_B}$$

where n_A and n_B are the moles of the solvent and the solute respectively and

$$n_A = \frac{w_A}{M_A}, \quad n_B = \frac{w_B}{M_B}$$

$$\therefore x_B = \frac{\frac{w_B}{M_B}}{\frac{w_A}{M_A} + \frac{w_B}{M_B}}$$

KEY NOTE

Colligative properties of dilute solutions are also called **democratic properties**. This is because just as in democracy, it is only the number of persons which count. In the same way, it is the number of particles (irrespective of their nature) which counts. This means that if two solutions contain equal number of solute particles of A and B (i.e., molar concentration is same) then the two solutions will have same colligative properties irrespective of the nature of A and B. In other words, the relative lowering in vapour pressure, elevation in boiling point, etc. will be same for the two solutions. The colligative properties are very useful to determine the molar mass, commonly called molecular weight of the non-volatile solutes.

WATCH OUT !

It must be remembered that only **relative lowering in vapour pressure is a colligative property**. Vapour pressure or lowering in vapour pressure are not colligative properties.

Competition Plus

Relative lowering in vapour pressure is measured by Ostwald Walker dynamic method. For detail, refer **Competition File (Page 98).**

Therefore, relative lowering in vapour pressure is

$$\frac{p_A^\circ - p_A}{p_A^\circ} = \frac{w_B / M_B}{w_A / M_A + w_B / M_B}$$

For dilute solutions, n_B is very small in comparison to n_A ($n_B \ll n_A$) so that n_B can be neglected in the denominator,

$$n_A + n_B \approx n_A$$

Thus,

$$\begin{aligned} \frac{p_A^\circ - p_A}{p_A^\circ} &= \frac{n_B}{n_A} = \frac{w_B / M_B}{w_A / M_A} \\ \therefore \quad \frac{p_A^\circ - p_A}{p_A^\circ} &= \frac{w_B \times M_A}{w_A \times M_B} \end{aligned} \quad \dots(15)$$

$$\text{or } M_B = \frac{w_B \times M_A}{w_A \times \left(\frac{p_A^\circ - p_A}{p_A^\circ} \right)} \quad \dots(16)$$

Thus, the molar mass of the solute can be determined if the other quantities, w_A , w_B , M_A and relative lowering in vapour pressure $\left(\frac{p_A^\circ - p_A}{p_A^\circ} \right)$ are known.

Solving Numerical Problems

FORMULAE AND UNITS

According to Raoult's law,
relative lowering in vapour pressure,

$$\left(\frac{p_A^\circ - p_A}{p_A^\circ} \right) = x_B$$

$$\text{or } = \frac{n_B}{n_A + n_B} \approx \frac{n_B}{n_A}$$

and molecular mass of non-volatile solute,

$$M_B = \frac{w_B \times M_A}{w_A \left(\frac{p_A^\circ - p_A}{p_A^\circ} \right)}$$

SOLVED EXAMPLES

Example 31.

Vapour pressure of water at 20°C is 17.5 mm of Hg and lowering of vapour pressure of a sugar solution is 0.061 mm of Hg. Calculate

- (i) relative lowering of vapour pressure
- (ii) vapour pressure of the solution
- (iii) mole fraction of sugar and water.

Solution : (i) Calculation of relative lowering of vapour pressure

Vapour pressure of water (p_A°) = 17.5 mm of Hg

Lowering of vapour pressure ($p_A^\circ - p_A$) = 0.061

\therefore Relative lowering of vapour pressure,

$$\frac{p_A^\circ - p_A}{p_A^\circ} = \frac{0.061}{17.5} = 0.00348$$

(ii) Calculation of vapour pressure of solution

p = Vapour pressure of solvent – Lowering in vapour pressure

$$= 17.5 - 0.061 = 17.439 \text{ mm of Hg}$$

(iii) Calculation of mole fraction of sugar and water

Mole fraction of sugar, x_B (solute)

$$\frac{p_A^\circ - p_A}{p_A^\circ} = x_B$$

Here

$$\frac{p_A^\circ - p_A}{p_A^\circ} = 0.00348$$

\therefore Mole fraction of sugar, x_B = 0.00348

$$\begin{aligned} \text{Mole fraction of water, } x_A &= 1 - x_B = 1 - 0.00348 \\ &= 0.9965. \end{aligned}$$

SOLUTIONS

□ Example 32.

The vapour pressure of pure benzene at a certain temperature is 0.850 bar. A non-volatile, non-electrolyte solid weighing 0.50 g is added to 39.0 g of benzene (molar mass 78 g mol⁻¹). The vapour pressure of the solution, then is 0.845 bar. What is the molar mass of the solid substance?

N.C.E.R.T. (Meghalaya S.B. 2014, H.P.S.B. 2014, Kerala S.B. 2016)

Solution : According to Raoult's law

$$\frac{p_A^\circ - p_A}{p_A^\circ} = x_B = \frac{w_B \times M_A}{M_B \times w_A} \text{ (for dilute solution)}$$

$w_B = 0.50 \text{ g}$, $w_A = 39.0 \text{ g}$, $p_A = 0.845 \text{ bar}$, $p_A^\circ = 0.850 \text{ bar}$

$$\frac{0.850 - 0.845}{0.850} = \frac{0.5 \times 78}{39.0 \times M_B}$$

$$\frac{0.005}{0.850} = \frac{0.5 \times 78}{39.0 \times M_B}$$

$$\text{or } M_B = \frac{0.5 \times 78 \times 0.850}{0.005 \times 39.0} = 170 \text{ g mol}^{-1}.$$

□ Example 33.

Calculate the mass of a non-volatile solute (molecular mass = 40), which should be dissolved in 114 g octane to reduce its vapour pressure to 80%.

N.C.E.R.T. (Pb.S.B. 2008, Assam S.B. 2017)

Solution : The vapour pressure is reduced to 80% on the addition of a non-volatile solute so that

$$\frac{p_A^\circ - p_A}{p_A^\circ} = \frac{100 - 80}{100} = \frac{1}{5} = 0.2$$

Now, according to Raoult's law

$$\frac{p_A^\circ - p_A}{p_A^\circ} = x_B$$

Let mass of non-volatile solute to be added = $x \text{ g}$

$$\therefore \frac{p_A^\circ - p_A}{p_A^\circ} = \frac{x}{\frac{114}{40} + x} = \frac{x}{\frac{114}{40} + \frac{x}{40}}$$

(Molar mass of octane = 114)

$$0.2 = \frac{x/40}{1+x/40}$$

$$\therefore 0.2 \left(1 + \frac{x}{40}\right) = \frac{x}{40}$$

$$\text{or } 0.2 = \frac{x}{40} - \frac{0.2x}{40}$$

$$\therefore 0.2 = \frac{0.8x}{40 \text{ g}}$$

$$\text{or } x = 10 \text{ g}$$

∴ Mass of solute to be added = 10 g.

□ Example 34.

Calculate the vapour pressure of an aqueous solution containing 5% by mass of urea (NH_2CONH_2) at 298 K. The vapour pressure of water at 298 K is 23.75 mm Hg.

(Assam S.B. 2015)

Solution : A 5% aqueous solution of urea means that out of 100 g of solution, urea is 5 g and water is 95 g.

Weight of solute (urea), $w_B = 5 \text{ g}$;

Weight of solvent (water), $w_A = 95 \text{ g}$

Molar mass of urea $M_B = 60$,

Molar mass of water $M_A = 18$

Vapour pressure of water, $p_A^\circ = 23.75 \text{ mm Hg}$;

Vapour pressure of solution, $p_A = ?$

According to Raoult's law,

$$\frac{p_A^\circ - p_A}{p_A^\circ} = \frac{w_B M_A}{w_A M_B}$$

$$\text{or } \frac{23.75 - p_A}{23.75} = \frac{5 \times 18}{95 \times 60}$$

$$\text{or } 23.75 - p_A = \frac{5 \times 18 \times 23.75}{95 \times 60} = 0.375$$

$$\text{or } p_A = 23.75 - 0.375 = 23.375$$

∴ Vapour pressure of solution = 23.375 mm Hg.

□ Example 35.

A solution containing 30 g of a non-volatile solute in 90 g water has a vapour pressure of 2.8 kPa at 298 K. Further 18 g of water is added to solution, the new vapour pressure becomes 2.9 kPa at 298 K. Calculate
(i) Molecular mass of solute.
(ii) Vapour pressure of water at 298 K. **N.C.E.R.T.**

Solution : $w_B = 30 \text{ g}$, $w_A = 90 \text{ g}$, $p_A = 2.8 \text{ kPa}$

According to Raoult's law,

$$\frac{p_A^\circ - p_A}{p_A^\circ} = x_B \approx \frac{\frac{w_B}{M_B}}{\frac{w_A}{M_A} + \frac{w_B}{M_B}} \approx \frac{w_B \times M_A}{M_B \times w_B}$$

$$\therefore \frac{p_A^\circ - 2.8}{p_A^\circ} = \frac{30}{M_B} \times \frac{18}{90}$$

$$1 - \frac{2.8}{p_A^\circ} = \frac{6}{M_B}$$

$$\text{or } \frac{2.8}{p_A^\circ} = 1 - \frac{6}{M_B}$$

$$\text{or } \frac{2.8}{p_A^\circ} = \frac{M_B - 6}{M_B} \quad \dots(i)$$

Similarly, $w_B = 30 \text{ g}$, $w_A = 90 + 18 = 108 \text{ g}$, $p_A = 2.9 \text{ kPa}$

$$\therefore \frac{p_A^\circ - 2.9}{p_A^\circ} = \frac{30}{M_B} \times \frac{18}{108}$$

$$1 - \frac{2.9}{p_A^\circ} = \frac{5}{M_B}$$

$$\text{or } \frac{2.9}{p_A^\circ} = 1 - \frac{5}{M_B}$$

$$\text{or } \frac{2.9}{p_A^\circ} = \frac{M_B - 5}{M_B} \quad \dots(ii)$$

Dividing eq. (i) by eq. (ii) we get

$$\frac{2.8}{2.9} = \frac{M_B - 6}{M_B - 5}$$

$$2.8 M_B - 14 = 2.9 M_B - 17.4$$

$$2.9 M_B - 2.8 M_B = 17.4 - 14$$

$$0.1 M_B = 3.4$$

$$\therefore M_B = 34 \text{ g mol}^{-1}$$

Substituting the value of M_B in eqn. (i) we get

$$\frac{2.8}{p_A^\circ} = \frac{34 - 6}{34} = \frac{28}{34}$$

$$28 p_A^\circ = 2.8 \times 34$$

$$p_A^\circ = 3.4 \text{ kPa.}$$

Practice Problems

41. 30 g of urea ($M = 60 \text{ g mol}^{-1}$) is dissolved in 846 g of water. Calculate the vapour pressure of water for this solution if vapour pressure of pure water at 298 K is 23.8 mm Hg. (A.I.S.B. 2017)
42. The vapour pressure of water is 12.3 kPa at 300 K. Calculate vapour pressure of 1 molar solution of a solute in it.
43. The vapour pressure of water at 20°C is 17.5 mm Hg. A solution of sucrose (molar mass = 342) is prepared by dissolving 68.4 g in 1000 g of water. Calculate
 - (i) relative lowering of vapour pressure
 - (ii) vapour pressure of solution. (Pb.S.B. 2004)
44. The vapour pressure of pure benzene at a certain temperature is 262 bar. At the same temperature the vapour pressure of a solution containing 2 g of non-volatile, non-electrolytic solid in 100 g of benzene is 256 bar. What is the molecular mass of the solid ? (H.P.S.B. 2011)
45. The vapour pressures of pure liquids A and B are 450 mm and 700 mm of Hg respectively at 350 K. Calculate the composition of liquid mixture if total vapour pressure is 600 mm of Hg. Also find the composition of the mixture in vapour phase. (CBSE Sample Paper 2010, Assam S.B. 2015)
46. The vapour pressure of a 5% aqueous solution of a non-volatile organic substance at 373 K is 745 mm. Calculate the molar mass of the solute. (Vapour pressure of water at 373 K = 760 mm Hg). (Jharkhand S.B. 2012, Manipur S.B. 2017)
47. At 25°C, the vapour pressure of pure water is 23.76 mm of Hg and that of an aqueous dilute solution of urea is 22.98 mm of Hg. Calculate the molality of the solution.
48. What mass of a non-volatile solute, urea (NH_2CONH_2) need to be dissolved in 100 g of water in order to decrease the vapour pressure of water by 25% ? What will be the molality of the solution ?
49. Urea forms an ideal solution in water. Determine the vapour pressure of an aqueous solution containing 10% by mass of urea at 40°C. (Vapour pressure of water at 40°C = 55.3 mm of Hg) (A.I.S.B. 2006, Nagaland S.B. 2015)
50. The vapour pressure of water at 293 K is 0.0231 bar and the vapour pressure of a solution of 108.24 g of a compound in 1000 g of water at the same temperature is 0.0228 bar. Calculate the molar mass of the solute.

Answers to Practice Problems

41. 23.55 mm Hg
42. 12.08 kPa
43. (i) 0.0036 (ii) 17.437 mm of Hg
44. 68.12 g mol⁻¹
45. 0.4, 0.6, 0.3, 0.7
46. 48 g mol⁻¹
47. 1.83 m
48. 111 g, 18.5 m
49. 53.46 mm Hg
50. 150.0.

Hints & Solutions on page 66

ELEVATION IN BOILING POINT

The boiling point of a liquid is the **temperature at which its vapour pressure becomes equal to the atmospheric pressure**. We have learnt that the vapour pressure of the solution containing non-volatile solute is less than that of the solvent. Therefore, the solution has to be heated to a higher temperature so that its vapour pressure becomes equal to the atmospheric pressure. Thus, the boiling point of the solution is always higher than that of the pure solvent.

For example, vapour pressure of water is 1.013 bar (or 1 atm) at 373 K. Therefore, water boils at 373 K because its vapour pressure at this temperature becomes equal to one atmospheric pressure which is 1.013 bar. The vapour pressure of an aqueous solution of sucrose is less than 1.013 bar at 373 K and therefore, the solution will not boil at 373 K. In order to make the solution to boil, its temperature must be increased so that its vapour pressure becomes

equal to 1.013 bar (1 atm). Thus, boiling point of a solution is always higher than the boiling point of the pure solvent in which the solution is prepared.

The elevation in boiling point on the addition of a non-volatile solute to a solvent can be easily illustrated graphically. The vapour pressure of the pure solvent or solution increases with rise in temperature. The variation of vapour pressure of the solvent and solution at different temperatures is shown in Fig. 12. The curve AB gives the vapour pressure for the pure solvent and the curve CD gives the vapour pressure for the solution at different temperatures. The curve CD representing the vapour pressure of the solution at different temperatures lies below the curve AB which corresponds to the vapour pressure of the pure solvent. This is because of the fact that the vapour pressure of the solution is less than that of the pure solvent at all temperatures.

It is clear from the figure that the vapour pressure of the pure solvent becomes equal to atmospheric pressure at X (corresponding to temperature T_b°) while the vapour pressure of the solution becomes equal to atmospheric pressure at Y (corresponding to temperature T_b'). Thus, the boiling point of the pure solvent is T_b° while that of the solution is T_b' . Since T_b' is greater than T_b° there is an elevation or increase in boiling temperature of the solution as compared to that of the solvent.

Mathematically, elevation in boiling point, ΔT_b may be expressed as :

$$\Delta T_b = T_b - T_b'$$

It has been found out experimentally that the elevation in the boiling point (ΔT_b) of a solution is proportional to the molal concentration of the solution, i.e.,

$$\frac{\Delta T_b}{m} \propto m \quad \text{or} \quad \Delta T_b = K_b m \quad \dots(17)$$

where m is the molality of the solution and represents moles of solute in 1 kg of solvent and K_b is called **molal boiling point elevation constant** or **molal boiling point constant** or **ebullioscopic constant**.

$$\text{If } m = 1 \\ \text{then } \Delta T_b = K_b$$

Thus, **molal boiling point elevation constant**, K_b , is defined as **the elevation in boiling point for 1 molal solution i.e., a solution containing 1 gram mole of solute dissolved in 1000 g of the solvent**.

Elevation in boiling point — a colligative property. From Eq. (17), as K_b is constant, so that

$$\Delta T_b \propto m$$

Thus, **elevation in boiling point is directly proportional to the molal concentration of the solute (i.e., number of molecules) and therefore, it is a colligative property**.

The K_b values for some common solvents are given in Table 3.

Table 3. Molal boiling point elevation constants (K_b) for some solvents.

Solvent	b.p. (K)	K_b (K m^{-1})
Water (H_2O)	373.15	0.52
Ethanol ($\text{C}_2\text{H}_5\text{OH}$)	351.5	1.20
Benzene (C_6H_6)	353.3	2.53
Chloroform (CHCl_3)	334.4	3.63
Ether ($\text{C}_4\text{H}_{10}\text{O}$)	307.8	2.02
Carbon tetrachloride (CCl_4)	350.0	5.03
Carbon disulphide (CS_2)	319.4	2.34
Acetic acid (CH_3COOH)	391.1	2.93
Cyclohexane (C_6H_{12})	353.74	2.79

Determination of Molar Mass of Solute from Elevation in Boiling Point Temperature

Let w_B gram of a non-volatile solute is dissolved in w_A grams of the solvent and M_B is the molar mass of the solute.

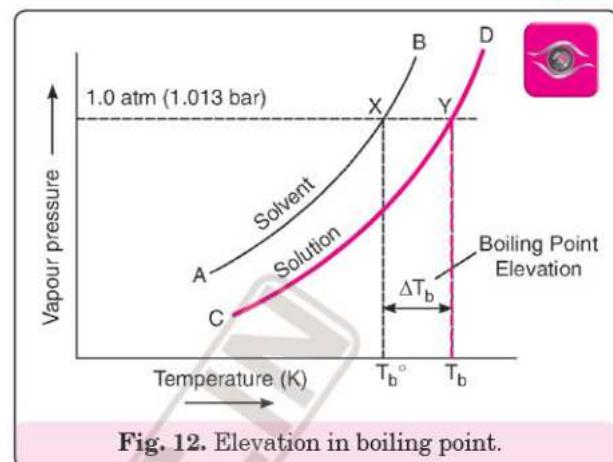


Fig. 12. Elevation in boiling point.

The units of K_b are degree/molality, i.e. K m^{-1} or ${}^\circ\text{C m}^{-1}$ or K kg mol^{-1}

NOTE

K_b can be calculated from molar enthalpy of vaporisation as :

$$K_b = \frac{M R T_b^2}{\Delta_{\text{vap}} H \times 1000}$$

where M is a molar mass of solvent, T_b is the boiling point of the solvent, R is gas constant and $\Delta_{\text{vap}} H$ is the molar enthalpy of vaporisation of the solvent.

For example, latent heat of vaporisation is 2.257 kJ g^{-1} for water. Its molal elevation constant can be calculated as :

$$K_b = \frac{M R T_b^2}{\Delta_{\text{vap}} H \times 1000}$$

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$M = 18 \text{ g mol}^{-1}$$

$$T_b = 373 \text{ K}$$

$$\Delta_{\text{vap}} H = 2.257 \times 18 \times 10^3 \text{ J mol}^{-1}$$

$$K_b = \frac{18 \times 8.314 \times (373)^2}{2.257 \times 18 \times 10^3 \times 1000}$$

$$= 0.512 \text{ K kg mol}^{-1}$$

WATCH OUT !

It must be remembered that **elevation in boiling point is a colligative property**, but boiling point is not a colligative property.

Therefore, the molality, m of the solution is :

$$m = \frac{\text{Moles of solute} \times 1000}{\text{Wt. of solvent in grams}}$$

$$\text{where moles of solute} = \frac{w_B}{M_B}$$

$$m = \frac{w_B \times 1000}{M_B \times w_A}$$

Substituting the value of m in the relation (Eq. 17)

$$\Delta T_b = K_b m$$

$$\text{we get, } \Delta T_b = \frac{K_b \times w_B \times 1000}{M_B \times w_A} \quad \dots(18)$$

Thus, molar mass of solute,

$$M_B = \frac{K_b \times w_B \times 1000}{\Delta T_b \times w_A}$$

From the above relation, molar mass of the solute can be calculated knowing the values of other quantities.

Solving Numerical Problems**FORMULAE AND UNITS**

Elevation in boiling point

$$\Delta T_b = K_b \times m$$

m = molality of solution, K_b = Molal elevation in boiling point

$$\text{or } \Delta T_b = \frac{1000 \times K_b \times w_B}{w_A \times M_B}$$

where M_B = Molecular mass of solute

w_A = Weight of solvent

w_B = Weight of solute

and molecular mass of solute,

$$M_B = \frac{1000 \times K_b \times w_B}{w_A \times \Delta T_b}$$

SOLVED EXAMPLES**Example 36.**

Molal elevation constant for benzene is 2.52 K/m . A solution of some organic substance in benzene boils at 0.126°C higher than benzene. What is the molality of the solution?

Solution : The elevation in boiling point on dissolving a solute is :

$$\Delta T_b = K_b m$$

$$\Delta T_b = 0.126^\circ, K_b = 2.52 \text{ K/m}$$

$$\therefore m = \frac{\Delta T_b}{K_b} = \frac{0.126}{2.52} = 0.05$$

∴ Molality of solution = **0.05 m**.

Example 37.

The boiling point of benzene is 353.23 K . When 1.80 g of a non-volatile solute was dissolved in 90 g of benzene, the boiling point is raised to 354.11 K . Calculate the molar mass of the solute.

(K_b for benzene is $2.53 \text{ K kg mol}^{-1}$)

N.C.E.R.T.

(Kerala S.B. 2013, Mizoram S.B. 2015,
Pb. S.B. 2017, Karnataka S.B. 2018)

Solution : Molar mass of a substance can be calculated as

$$M_B = \frac{K_b \times w_B \times 1000}{\Delta T_b \times w_A}$$

$$K_b = 2.53 \text{ K kg mol}^{-1}, w_B = 1.80 \text{ g}, w_A = 90 \text{ g}$$

$$\Delta T_b = 354.11 - 353.23 = 0.88 \text{ K}$$

$$\therefore M_B = \frac{2.53 \times 1.80 \times 1000}{90 \times 0.88} = 57.5 \text{ g mol}^{-1}$$

Example 38.

A solution containing 0.730 g of camphor (molar mass = 152) in 36.8 g of acetone (b.p. 56.30°C) boils at 56.55°C . A solution of 0.564 g of an unknown compound in the same weight of solvent boils at 56.46°C . Calculate the molar mass of the unknown compound.

Solution : In this problem, the value of K_b is not given.

The first data is used to calculate K_b which is used to calculate the molar mass from the second data.

(i) Calculation of K_b for acetone

$$K_b = \frac{\Delta T_b \times M_B \times w_A}{w_B \times 1000}$$

$$\begin{aligned}\Delta T_b &= 56.55 - 56.30 = 0.25^\circ\text{C}, M_B = 152 \\ w_B &= 0.730 \text{ g}, w_A = 36.8 \text{ g} \\ \therefore K_b &= \frac{0.25 \times 152 \times 36.8}{0.736 \times 1000} = 1.92 \text{ K m}^{-1}\end{aligned}$$

(ii) Calculation of molar mass of unknown compound

$$M_B = \frac{K_b \times 1000 \times w_B}{\Delta T_b \times w_A}$$

$$\begin{aligned}K_b &= 1.92 \text{ Km}^{-1}, \Delta T_b = 56.46 - 56.30 \\ &= 0.16^\circ\text{C} \\ w_B &= 0.564 \text{ g}, w_A = 36.8 \text{ g},\end{aligned}$$

$$M_B = \frac{1.92 \times 1000 \times 0.564}{0.16 \times 36.8} = 183.9 \text{ g mol}^{-1}.$$

Example 39.

On dissolving 3.24 g of sulphur in 40 g of benzene, boiling point of solution was higher than that of benzene by 0.81 K. K_b value for benzene is 2.53 K kg mol $^{-1}$. What is the molecular formula of sulphur?

(Atomic mass of sulphur = 32 g mol $^{-1}$). (D.S.B. 2000)

Solution : Let us first calculate the molar mass of sulphur,

$$M_B = \frac{K_b \times 1000 \times w_B}{\Delta T_b \times w_A}$$

$$K_b = 2.53 \text{ K kg mol}^{-1}, w_B = 3.24 \text{ g}, w_A = 40 \text{ g}, \Delta T_b = 0.81 \text{ K}$$

$$\therefore M_B = \frac{2.53 \times 1000 \times 3.24}{0.81 \times 40} = 253$$

Let the molecular formula of sulphur = S_x

$$\begin{aligned}\text{Atomic mass of sulphur} &= 32 \\ \text{Molecular mass} &= 32 \times x\end{aligned}$$

$$\text{or } 32x = 253$$

$$\text{or } x = 7.91 \approx 8$$

$$\therefore \text{Molecular formula of sulphur} = S_8.$$

Example 40.

What would be the molar mass of a compound if 6.21 g of it dissolved in 24.0 g of chloroform form a solution that has a boiling point of 68.04°C. The boiling point of pure chloroform is 61.7°C and the boiling point elevation constant, K_b for chloroform is 3.63°C/m.

(D.S.B. 2011)

Solution : Elevation in boiling point,

$$\Delta T_b = 68.04 - 61.7 = 6.34^\circ\text{C}$$

$$\text{Mass of substance, } w_B = 6.21 \text{ g,}$$

$$\text{Mass of chloroform, } w_A = 24.0 \text{ g}$$

$$K_b = 3.63^\circ\text{C/m}$$

$$K_b = \frac{\Delta T_b \times M_B \times w_A}{w_B \times 1000}$$

or

$$\begin{aligned}M_B &= \frac{K_b \times w_B \times 1000}{\Delta T_b \times w_A} \\ &= \frac{3.63 \times 6.21 \times 1000}{6.34 \times 24} \\ &= 148.15 \text{ g mol}^{-1}.\end{aligned}$$

Example 41.

A solution of glycerol ($C_3H_8O_3$) in water was prepared by dissolving some glycerol in 500 g of water. This solution has a boiling point of 100.42°C while pure water boils at 100°C. What mass of glycerol was dissolved to make the solution?

(K_b for water = 0.512 K kg mol $^{-1}$)

(D.S.B. 2012, A.I.S.B. 2012, P.b.S.B. 2013)

Solution : Elevation in boiling point

$$\Delta T_b = \frac{K_b \times 1000 \times w_B}{w_A \times M_B}$$

$$\begin{aligned}\Delta T_b &= 100.42 - 100 = 0.42^\circ\text{C}, w_A = 500 \text{ g}, w_B = ?, K_b = 0.512 \text{ K kg mol}^{-1} \\ M_B &= 3 \times 12 + 8 \times 1 + 3 \times 16 = 92\end{aligned}$$

$$0.42 = \frac{0.512 \times 1000 \times w_B}{500 \times 92}$$

$$\begin{aligned}\text{or } w_B &= \frac{0.42 \times 500 \times 92}{0.512 \times 1000} \\ &= 37.73 \text{ g}\end{aligned}$$

Mass of glycerol to be added = 37.73 g

Example 42.

A solution prepared by dissolving 1.25 g of oil of winter green (methyl salicylate) in 99.0 g of benzene has a boiling point of 80.31 °C. Determine the molar mass of this compound. (B.P. of pure benzene = 80.10 °C and K_b for benzene = 2.53 °C kg mol $^{-1}$)

(D.S.B. 2010)

Solution : $\Delta T_b = \frac{K_b \times 1000 \times w_B}{M_B \times w_A}$

$$M_B = \frac{K_b \times 1000 \times w_B}{\Delta T_b \times w_A}$$

$$K_b = 2.53 \text{ } ^\circ\text{C kg mol}^{-1},$$

$$w_A = 99.0 \text{ g}, w_B = 1.25 \text{ g}$$

$$\Delta T_b = 80.31 - 80.10 = 0.21 \text{ } ^\circ\text{C}$$

$$M_B = \frac{2.53 \times 1000 \times 1.25}{0.21 \times 99.0}$$

$$= 152.1 \text{ g mol}^{-1}$$

Example 43.

18 g of glucose, $C_6H_{12}O_6$ (molar mass = 180 g mol $^{-1}$) is dissolved in 1 kg of water in a sauce pan. At what temperature will this solution boil?

(K_b for water = 0.52 K kg mol $^{-1}$, boiling point of pure water = 373.15 K).

N.C.E.R.T. (D.S.B. 2013, P.b.S.B. 2016)

Solution : $\Delta T_b = \frac{K_b \times 1000 \times w_B}{w_A \times M_B}$

$$w_B = 18 \text{ g}, w_A = 1000 \text{ g}, M_B = 180,$$

$$K_b = 0.52 \text{ K m}^{-1}$$

$$\therefore \Delta T_b = \frac{0.52 \times 1000 \times 18}{1000 \times 180} = 0.052 \text{ K}$$

Boiling point of solution = 373.15 + 0.052 = 373.202 K.

Answers to Practice Problems

51. 128.25 g mol⁻¹
 52. 146.6 g mol⁻¹
 53. 373.202 K
 54. 150 g mol⁻¹
 55. 96.54 g mol⁻¹
 56. 253 g mol⁻¹
 57. 1.28°C
 58. 53.06 g mol⁻¹

Hints & Solutions on page 66

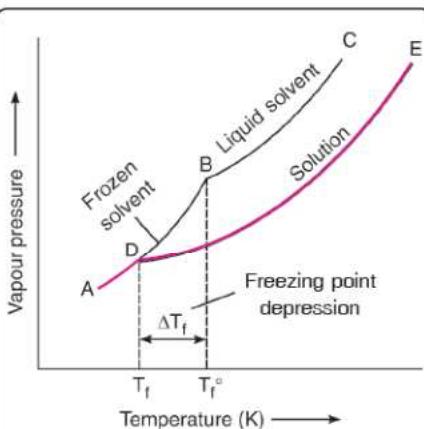


Fig. 18. Depression in freezing point.

K_f can be calculated from molar enthalpy of fusion by the relation :

$$K_f = \frac{MRT_f^2}{\Delta_{fus}H \times 1000}$$

where M is the molar mass of the solvent. T_f is the freezing point and $\Delta_{fus}H$ is the molar enthalpy of fusion of the solvent.

For example, latent heat of fusion of ice is 6.0 kJ mol⁻¹. Its molal depression constant can be calculated as :

$$K_f = \frac{MRT_f^2}{\Delta_f H \times 1000}$$

$$\Delta_{fus}H = 6.0 \times 10^3 \text{ J mol}^{-1}, T_f = 273 \text{ K}$$

$$\therefore K_f = \frac{18 \times 8.314 \times (273)^2}{6.0 \times 10^3 \times 1000}$$

$$= 1.86 \text{ K m}^{-1}$$

Practice Problems

51. A solution containing 8 g of a substance in 100 g of diethyl ether boils at 36.86°C, whereas pure ether boils at 35.60°C. Determine molecular mass of the solute (For ether $K_b = 2.02 \text{ K kg mol}^{-1}$). (A.I.S.B. 2008)
52. The boiling point of a solution containing 1.5 g of dichlorobenzene in 100 g of benzene was higher by 0.268°C. Calculate the molar mass of dichlorobenzene (K_b for benzene = 2.62 degree/molal).
53. 18 g of glucose, $C_6H_{12}O_6$, is dissolved in 1 kg of water in a sauce pan. At what temperature will the water boil. K_b for water is 0.52 K kg mol⁻¹ and boiling point of water is 373.15 K. (N.C.E.R.T. (Pb.S.B. 2008)
54. The boiling point of water (100°C) becomes 100.52°C if 3 g of a non-volatile solute is dissolved in 20 ml of it. Calculate the molar mass of the solute (K_b for water = 0.52 Km⁻¹).
55. A solution containing 0.513 g of naphthalene (molar mass = 128) in 50 g of CCl_4 gives a boiling point elevation of 0.402°C, while a solution of 0.625 g of an unknown solute gives a boiling point elevation of 0.650°C. Find the molar mass of the unknown solute.
56. 10 gram of a non-volatile solute when dissolved in 100 gram of benzene raises its boiling point by 1°. What is the molecular mass of the solute? (K_b for benzene = 2.53 K mol⁻¹). (Pb.S.B. 2016, Meghalaya S.B. 2016)
57. What elevation in boiling point of alcohol is to be expected when 5 g of urea (molar mass = 60) are dissolved in 75 g of it? The molal elevation constant for alcohol is 1.15°C.
58. A solution containing 12.5 g of a non-electrolyte substance in 175 g of water gave boiling point elevation of 0.70 K. Calculate the molar mass of the substance. (K_b for water = 0.52 K kg mol⁻¹). (H.P.S.B. 2010, 2013, Pb.S.B. 2012)

DEPRESSION IN FREEZING POINT

We know that at the freezing point of a solvent, the solid and the liquid are in equilibrium. This is only possible if they have the same vapour pressure. Thus, the freezing point is *the temperature at which the solid and the liquid states of the substance have the same vapour pressure*. It has been observed that when a non-volatile solute is added to a solvent, the freezing point of the solution is always lower than that of the pure solvent. This may be illustrated graphically as shown in Fig. 13.

In the figure, the curve BC gives vapour pressure of the pure solvent. We know that the addition of a non-volatile solute lowers the vapour pressure and the curve DE gives the vapour pressure curve for the solution at different temperatures. The curve AB corresponds to the vapour pressure of the solid at different temperatures.

The temperature corresponding to the point B where the solid and liquid solvent meet (*i.e.*, solid and liquid states have the same vapour pressure) represents the freezing point temperature of pure solvent ($T_f^°$). The temperature corresponding to the point D where the solid solvent and liquid solution meet (*i.e.*, solid and liquid states have the same vapour pressure) represents the freezing point temperature of the solution (T_f).

Since T_f is less than $T_f^°$, this shows that the freezing temperature of the solution is less than that of pure solvent and the depression in freezing temperature (ΔT_f) is given as :

$$\Delta T_f = T_f^° - T_f$$

It has been determined experimentally that the depression in freezing point of a solution is proportional the molal concentration of the solution *i.e.*,

$$\Delta T_f \propto m \\ = K_f m \quad \dots(19)$$

The units of K_f are degree/molality i.e. K m^{-1} , $^\circ\text{C m}^{-1}$ or K kg mol^{-1} where K_f is the **molal freezing point depression constant**. It is also called **molal cryoscopic constant**.

If

$$m = 1 \\ \Delta T_f = K_f$$

Thus, molal freezing point depression constant is defined as the depression in freezing point for 1 molal solution i.e., a solution containing 1 gram mole of solute dissolved in 1000 g of solvent.

Depression in freezing point—a colligative property. From Eq. (18) as K_f constant,

$$\Delta T_f \propto m$$

Thus, the depression in freezing point temperature is directly proportional to the molal concentration of the solute (i.e., number of molecules) and therefore, it is a colligative property.

The K_f values of some common solvents are given in Table 4.

Table 4. Molal freezing point depression constant (K_f) for some solvents.

Solvent	Freezing point (K)	K_f (K m ⁻¹)
Water (H ₂ O)	273.0	1.86
Ethanol (C ₂ H ₅ OH)	155.7	1.99
Benzene (C ₆ H ₆)	278.6	5.12
Chloroform (CHCl ₃)	209.6	4.79
Carbon tetrachloride (CCl ₄)	250.5	31.8
Carbon disulphide (CS ₂)	164.2	3.83
Ether (C ₄ H ₁₀ O)	156.9	1.79
Cyclohexane (C ₆ H ₁₂)	279.5	20.0
Acetic acid (CH ₃ COOH)	290.0	3.90

Determination of Molar Mass of Solute from Depression in Freezing Point Temperature

The depression in freezing point temperature (ΔT_f) is useful in determining the molar mass of the solute (M_B). To calculate the molar mass of an unknown non-volatile compound, a known mass of it is dissolved in a known mass of a solvent and depression in its freezing point (ΔT_f) is determined.

Let wt. of the solute = w_B g

Wt. of solvent = w_A g

Molar mass of the solute = M_B

$$\text{Molality of solution } m = \frac{w_B \times 1000}{M_B \times w_A}$$

By substituting the value of m in the relation $\Delta T_f = K_f m$, we have

$$\Delta T_f = \frac{K_f \times w_B \times 1000}{w_A \times M_B}$$

$$\therefore M_B = \frac{K_f \times w_B \times 1000}{\Delta T_f \times w_A} \quad \dots(20)$$

All other values being given, the molar mass of the solute can be calculated.

Solving Numerical Problems

FORMULAE AND UNITS

Depression in freezing point

$$\Delta T_f = K_f \times m$$

m = molality of solution and K_f = molal depression in freezing point

$$\text{or } \Delta T_f = \frac{K_f \times w_B \times 1000}{w_A \times M_B}$$

where M_B = molecular mass of solute

w_A = weight of solvent

w_B = weight of solute

and molecular mass of solute

$$M_B = \frac{K_f \times 1000 \times w_B}{w_A \times \Delta T_f}$$

The units of K_f are degree/molality i.e., K m⁻¹ or °C m⁻¹ or K kg mol⁻¹.

KEY NOTE

Molal elevation constant (K_b) and molal freezing point depression constant (K_f) have characteristic values for different solvents. These are expressed as degree/molal i.e., K/m. For example, for water $K_f = 1.86$ degree/molal. It means that for 1 molal solution of a substance in water, the freezing point will be lowered by 1.86°. Thus, K_f stands for 1 molal solution. Similarly for water, $K_b = 0.52$ K/m. However, sometimes K_f and K_b are also expressed as mol per 100 g; i.e., K/mol per 100 g. The values in latter case are 10 times the value expressed as K/m. For example, K_b for water = 0.52 K/m or 5.2 K/mol per 100 g. For using the relations given in Eqs. 3.16 to 3.19, it should be used as K/m only.

● **Anti-freeze solutions.** Water is used in radiators of vehicles. If the vehicle is to be used in places where the temperature is less than zero then water would freeze in the radiators. To avoid this problem, certain substances are used in radiators so that water does not freeze at low temperature in radiators. These are called **anti-freeze solutions**. Ethylene glycol in water is commonly used in car radiators which lowers the freezing point of water. Freezing point can be lowered to the desired extent by changing the amount of ethylene glycol.

● In cold countries, common salt (NaCl) or calcium chloride (CaCl₂) are used to **clear snow on the roads**. This is because they depress the freezing point of water to such an extent that water cannot freeze to form ice. Hence, it melts off easily at the prevailing temperature.

SOLVED EXAMPLES

Example 44.

45 g of ethylene glycol ($C_2H_6O_2$) is mixed with 600 g of water. Calculate

- the freezing point depression
- the freezing point of the solution

(K_f for water = 1.86 K kg ml⁻¹)

N.C.E.R.T. (H.P.S.B 2014, 2015, Pb.S.B. 2017)

Solution : (i) $\Delta T_f = \frac{K_f \times w_B \times 1000}{w_A \times M_B}$

$w_A = 600$ g, $w_B = 45$ g, $K_f = 1.86$ K kg mol⁻¹

$M_B = 2 \times 12 + 6 \times 1 + 2 \times 16 = 62$ mol⁻¹

$$\therefore \Delta T_f = \frac{1.86 \times 45 \times 1000}{600 \times 62}$$

$$= 2.25 \text{ K}$$

∴ Freezing point depression = 2.25 K

(ii) Freezing point of aqueous solution = $273.15 - 2.25$
= 270.90 K

Example 45.

Addition of 0.643 g of a compound to 50 mL of benzene (density 0.879 g/mL) lowers the freezing point from 5.51°C to 5.03°C. If K_f for benzene is 5.12 K kg mol⁻¹, calculate the molar mass of the compound.

(Pb.S.B. 2014, 2016, Meghalaya S.B. 2015)

Solution : The molar mass, M_B is calculated as :

$$M_B = \frac{K_f \times w_B \times 1000}{w_A \times \Delta T_f}$$

$$w_B = 0.643 \text{ g},$$

$$w_A = (50 \text{ mL}) \times (0.879 \text{ g/mL}) \\ = 43.95 \text{ g}$$

$$K_f = 5.12 \text{ K m}^{-1},$$

$$\Delta T_f = 5.51 - 5.03 = 0.48^\circ\text{C}$$

$$M_B = \frac{5.12 \times 0.643 \times 1000}{43.95 \times 0.48} \\ = 156.06.$$

Example 46.

The molal freezing point depression constant of benzene (C_6H_6) is 4.90 K kg mol⁻¹. Selenium exists as a polymer of the type Se_x . When 3.26 g of selenium is dissolved in 226 g of benzene, the observed freezing point is 0.112°C lower than for pure benzene. Deduce the molecular formula of selenium. (Atomic mass of Se = 78.8 g mol⁻¹) (A.I.S.B. 2002, D.S.B. 2002)

Solution : The molar mass M_B is calculated as :

$$M_B = \frac{K_f \times w_B \times 1000}{w_A \times \Delta T_f}$$

$$\Delta T_f = 0.112^\circ\text{C},$$

$$w_A = 226 \text{ g},$$

$$w_B = 3.26 \text{ g},$$

$$K_f = 4.90 \text{ Km}^{-1}$$

$$M_B = \frac{4.90 \times 3.26 \times 1000}{226 \times 0.112} \\ = 632 \text{ g mol}^{-1}$$

Now, molecular mass of Se_x = $x \times 78.8$

$$632 = x \times 78.8$$

$$x = \frac{632}{78.8} = 8$$

∴ Molecular formula of selenium = Se_8 .

Example 47.

1.02 g of urea when dissolved in 98.5 g of certain solvent decreases its freezing point by 0.211 K. 1.60 g of unknown compound when dissolved in 86.0 g of the same solvent depresses the freezing point by 0.34 K. Calculate the molar mass of the unknown compound. (Molar mass of urea = 60 g mol⁻¹).

Solution : Let us first calculate K_f .

$$\Delta T_f = \frac{K_f \times w_B \times 1000}{w_A \times M_B}$$

For urea solution,

$$w_B = 1.02 \text{ g}, w_A = 98.5 \text{ g}, \Delta T_f = 0.211 \text{ K}$$

$$0.211 = \frac{K_f \times 1.02 \times 1000}{98.5 \times 60}$$

$$\therefore K_f = \frac{0.211 \times 98.5 \times 60}{1.02 \times 1000} = 1.22 \text{ Km}^{-1}$$

Now, molar mass of unknown compound can be calculated as:

$$\Delta T_f = \frac{K_f \times w_B \times 1000}{w_A \times M_B}$$

$$\text{or } M_B = \frac{K_f \times w_B \times 1000}{w_A \times \Delta T_f}$$

$$w_B = 1.60 \text{ g}, w_A = 86.0 \text{ g}, \Delta T_f = 0.34 \text{ K}, K_f = 1.22 \text{ Km}^{-1}$$

$$\therefore M_B = \frac{1.22 \times 1.60 \times 1000}{86.0 \times 0.34} \\ = 66.76 \text{ g mol}^{-1}$$

Example 48.

Ethylene glycol (molar mass = 62 g mol⁻¹) is a common automobile antifreeze. Calculate the freezing point of a solution containing 12.4 g of this substance in 100 g of water. Would it be advisable to keep this substance in car radiator during summer?

(K_f for water = 1.86 Km⁻¹ and K_b for water = 0.512 Km⁻¹) (C.B.S.E. Sample Paper 2007)

Solution :

Moles of ethylene glycol

$$= \frac{12.4}{62} = 0.2 \text{ mol}$$

$$\text{Molality} = \frac{0.2}{100} \times 1000 = 2 \text{ m}$$

Freezing point depression

$$\Delta T_f = K_f \times m \\ = 1.86 \times 2 = 3.72 \text{ K}$$

Freezing point of aqueous solution

$$= 273.15 - 3.72 = 269.43 \text{ K}$$

Boiling point elevation of solution

$$\begin{aligned}\Delta T_b &= K_b \times m \\ &= 0.52 \times 2 = 1.04 \text{ K}\end{aligned}$$

Boiling point of solution
 $= 373.15 + 1.04 = 374.19 \text{ K}$

Since boiling point is higher than room temperature in summer, it is advisable to keep this substance in the car radiator during summer.

Example 49.

Two elements A and B form compounds having molecular formula AB_2 and AB_4 . When dissolved in 20 g of benzene, 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 the atomic mass of A and B.

N.C.E.R.T. (A.I.S.B. 2004, Uttarakhand S.B. 2012)

Solution : Let us first calculate molar masses of AB_2 and AB_4 .

For AB_2 compound

$$\begin{aligned}M_B &= \frac{K_f \times w_B \times 1000}{w_A \times \Delta T_f} \\ \Delta T_f &= 2.3 \text{ K}, w_B = 1.0 \text{ g}, w_A = 20.0 \text{ g}\end{aligned}$$

$$\begin{aligned}K_f &= 5.1 \text{ K kg mol}^{-1} \\ M_{AB_2} &= \frac{5.1 \times 1.0 \times 1000}{20.0 \times 2.3} = 110.87\end{aligned}$$

$$\therefore M_{AB_2} = 110.87$$

For AB_4 compound

$$\begin{aligned}\Delta T_f &= 1.3 \text{ K}, w_B = 1.0 \text{ g}, w_A = 20.0 \text{ g} \\ M_{AB_4} &= \frac{5.1 \times 1.0 \times 1000}{20.0 \times 1.3} = 196.5 \\ \therefore M_{AB_4} &= 196.15\end{aligned}$$

Let a is the atomic mass of A and b is the atomic mass of B, then

$$M_{AB_2} = a + 2b = 110.87 \quad \dots(i)$$

$$M_{AB_4} = a + 4b = 196.15 \quad \dots(ii)$$

Subtracting eqn. (ii) from eqn. (i)

$$-2b = -85.28$$

$$\therefore b = 42.64$$

Substituting the value of b in eqn (i)

$$a + 2 \times 42.64 = 110.87$$

$$a = 110.87 - 85.28 = 25.59$$

Atomic mass of A = 25.59

Atomic mass of B = 42.64.

Practice Problems

59. A 10% solution (by mass) of sucrose in water has freezing point of 269.15 K. Calculate the freezing point of 10% glucose in water, if freezing point of pure water is 273.15 K.

Given : (Molar mass of sucrose = 342 g mol^{-1})

(Molar mass of glucose = 180 g mol^{-1}) (A.I.S.B. 2017, D.S.B. 2017)

60. Calculate the mass of a compound (molar mass = 256 g mol^{-1}) to be dissolved in 75 g of benzene to lower its freezing point by 0.48 K ($K_f = 5.12 \text{ K kg mol}^{-1}$) (D.S.B. 2014)

61. A solution containing 18 g of a non-volatile solute in 200 g of H_2O freezes at 272.07 K. Find the molecular mass of the solute. ($K_f = 1.86 \text{ K m}^{-1}$) (Meghalaya S.B. 2018)

62. 1.00 g of non-electrolyte solute dissolved in 50 g of benzene lowered the freezing point of benzene by 0.40 K. Find the molar mass of the solute. (K_f for benzene = 5.12 K kg mol^{-1}). (Mizoram S.B. 2013, A.I.S.B. 2013)

63. When 2.56 g of sulphur was dissolved in 100 g of CS_2 , the freezing point lowered by 0.383 K. Calculate the formula of sulphur (S_x). (K_f for CS_2 = 3.83 K kg mol^{-1} , Atomic mass of sulphur = 32 g mol^{-1}) (D.S.B. 2016)

64. What mass of ethylene glycol (molar mass = 62.0 g mol^{-1}) must be added to 5.50 kg of water to lower the freezing point of water from 0°C to -10.0°C? (K_f for water = 1.86 K kg mol^{-1}). (A.I.S.B. 2010)

65. Two aqueous solutions containing respectively 7.5 g urea (molar mass = 60) and 42.75 g substance X in 100 g of water freeze at the same temperature. Calculate the molecular weight of X.

66. When 30.0 g of a non-volatile solute having the empirical formula CH_2O are dissolved in 800 g of water, the solution freezes at -1.16°C. What is the molecular formula of the solute? (K_f for water = 1.86 K m^{-1}).

Answers to Practice Problems

59. 265.55 K

60. 1.8 g

61. 155 g mol^{-1}

62. 256 g mol^{-1}

63. S_8

64. 1.833 kg

65. 342 g mol^{-1}

66. $\text{C}_2\text{H}_4\text{O}_2$

Hints & Solutions on page 66

67. In winter, the normal temperature in a Himalayan's valley was found to be -10°C . Is a 30% by mass of aqueous solution of ethylene glycol (molar mass = 62) suitable for car radiator ? (K_f for water = 1.86 K/m) (Pb.S.B. 2011)
68. An aqueous solution freezes at 272.07 K, while pure water freezes at 273 K. Determine the molality and boiling point of the solution.
(Given K_f for water = 1.86 K/m, K_b = 0.512 K/m).

(Hr. S.B. 2006, Mizoram S.B. 2015)

69. A solution of urea in water has a boiling point 101.128°C . Calculate the freezing point of the same solution. Molal constant for water, K_f and K_b are 1.86°C and 0.512°C respectively. (Pb.S.B. 2006)
70. Ethylene glycol (molar mass = 62 g mol⁻¹) is used as an antifreeze for water to be used in car radiators in cold places. How much ethylene glycol should be added to 1kg of water to prevent it from freezing at -10°C ? [K_f for water = 1.86 K kg mol⁻¹] (Nagaland S.B. 2018)

Answers to Practice Problems

67. It is suitable because water freezes at -12.86°C
68. 0.5 m, 373.256 K
69. -4.1°C
70. 333.3 g

Hints & Solutions on page 66

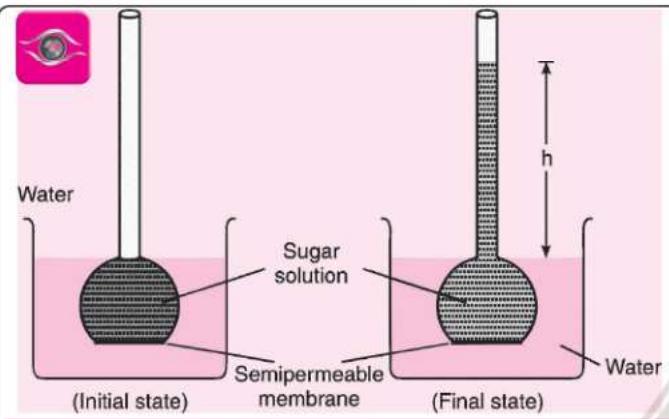


Fig. 14. Process of osmosis and measurement of osmotic pressure in a thistle funnel.

OSMOSIS AND OSMOTIC PRESSURE

Osmotic pressure is another colligative property. Before we discuss osmotic pressure let us try to understand osmosis and its difference from diffusion.

Osmosis. The phenomenon of osmosis was studied for the first time by *Abbe Nollet* in 1748. Let us consider an aqueous solution of sugar placed in an inverted thistle funnel having a *semipermeable membrane* (SPM) such as animal bladder or parchment paper, attached to its bottom. The thistle funnel is lowered into a beaker containing water. The membrane is such that it allows only the molecules of the solvent and not of the solute to pass through it. In other words, the membrane is permeable only to solvent molecules. Thus, there will be movement of water molecules from pure solvent into the solution. As a result, water passes into the thistle funnel and level of solution in the thistle funnel rises gradually (Fig. 14). This process is called **osmosis**. Thus, *the phenomenon of the flow of solvent through a semipermeable membrane from pure solvent to the solution* is called **osmosis**.

Osmosis can also take place between the solutions of different concentrations. In such cases, the solvent molecules move from the **less concentrated solution (low solute concentration) to a more concentrated solution (higher solute concentration)** through a semipermeable membrane.

Difference between osmosis and diffusion. Although both diffusion and osmosis involve the movement of the molecules, still they differ in the following respects:

KEY NOTE

Osmosis is very common phenomenon which we observe in nature or at home. For example, raw mangoes shrivel when pickled in brine (salt water), wilted flowers revive when placed in fresh water, blood cells collapse when suspended in saline water. If we look into these processes carefully, we notice one thing common in all. All these substances are bound by membranes which occur in nature in plants and animals.

Osmosis	Diffusion
<ol style="list-style-type: none"> The process of osmosis takes place through a semi-permeable membrane. The osmosis involves the movement of the solvent molecules only. In osmosis, molecules of solvent move from a region of lower concentration of solution into a region of higher concentration. Osmosis is limited to solutions only. Osmosis can be stopped or reversed by applying additional pressure on the higher concentration side. 	<p>No semi-permeable membrane is needed for the diffusion process.</p> <p>In diffusion, both the solute and the solvent molecules can move.</p> <p>In diffusion, the molecules move from a region of higher concentration into the region of lower concentration.</p> <p>Diffusion is common in gases as well as in liquids.</p> <p>It cannot be stopped or reversed.</p>

Semipermeable membrane. We have pointed out that a semipermeable membrane is one which allows only the solvent and not the solute to pass through it. Nature has provided many such membranes both in plants and animals for specific functions e.g., pig's bladder or parchment. These can also be synthetic such as cellophane membrane, etc. But these are rather not particularly useful in the laboratory due to their imperfect nature. Consequently, they can be even artificially prepared. One such membrane is the film of gelatinous precipitates of cupric ferrocyanide, $\text{Cu}_2[\text{Fe}(\text{CN})_6]$. These membranes appear to be continuous sheets or films, yet they contain a network of submicroscopic holes or pores. Small solvent molecules like water can pass through these holes but bigger molecules like solute cannot pass through these holes. These types of membranes are called semipermeable membranes (SPM).

Demonstration of osmosis

Take two eggs. Remove the outer hard shell of the eggs by dissolving in dilute HCl. Place one egg in distilled water [Fig. 15 (a)] and the other egg in a saturated sodium chloride solution [Fig. 15 (b)]. After a few minutes, it will be observed that the egg placed in water swells [Fig. 15 (b)] whereas the other placed in salt solution shrinks [Fig. 15 (c)]. This curious observation can be explained on the basis of process of osmosis. The skin of the egg acts as a semipermeable membrane. In the first case, the concentration of water (solvent) is higher outside the egg. Therefore, pure water enters into egg due to osmosis and the egg swells. On the other hand, the water comes out of egg material when placed in a saturated solution of sodium chloride due to higher concentration of water (solvent) inside the egg. Therefore, the egg shrinks.

Osmotic pressure

We have studied that when an aqueous solution of sugar is placed in an inverted thistle funnel and separated from pure water with the help of a semipermeable membrane, there will be osmosis of water molecules into the solution of sugar. As a result, the level of solution in the stem of the funnel will rise and an additional hydrostatic pressure will be exerted on the solution. This hydrostatic pressure will tend to oppose the inflow of solvent into the funnel. The level of solution will continue rising till a particular height. At this stage, equilibrium is reached and the hydrostatic pressure of the liquid exactly balances the tendency of the liquid to pass inward through the semipermeable membrane. Thus, there will be no more osmosis taking place.

The equilibrium hydrostatic pressure on the solution due to osmosis of the pure solvent into it is a measure of osmotic pressure.

Alternatively, to understand the concept of osmotic pressure, consider an apparatus shown in Fig. 16. It consists of two vessels connected by a semipermeable membrane. These two compartments are fitted with water-tight frictionless pistons. Let us take solution in one compartment and pure solvent in the other compartment. Due to osmosis, there will be flow of solvent into the solution compartment through the semipermeable membrane. As a result, the piston on the solution side will tend to move outwards. To stop this movement of piston outwards, we have to apply pressure on the solution side. This pressure just sufficient to stop osmosis will be equal to the osmotic pressure. Thus, **osmotic pressure** may be defined as

the minimum excess pressure which must be applied to a solution to prevent the passage of solvent into it through a semipermeable membrane.

Thus, osmotic pressure is the pressure applied to the solution to prevent osmosis. It is generally denoted by π .

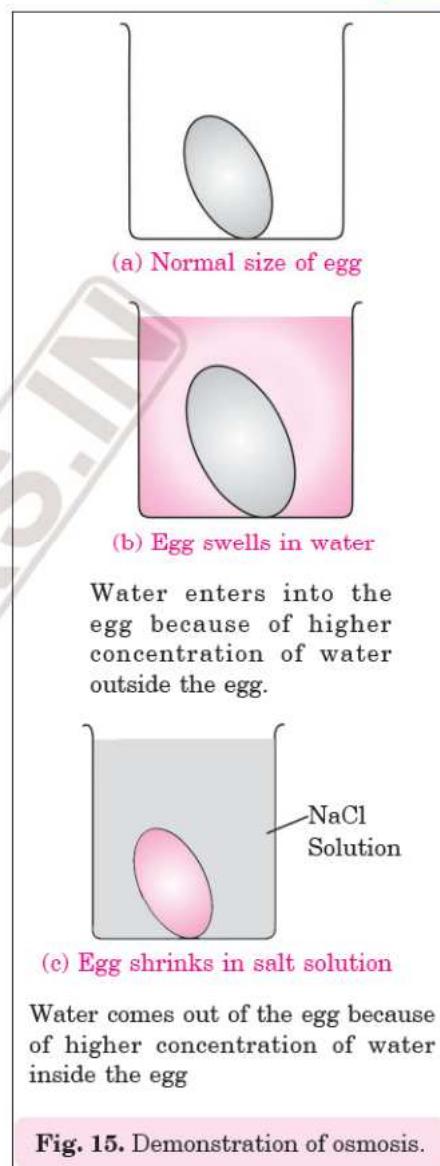


Fig. 15. Demonstration of osmosis.

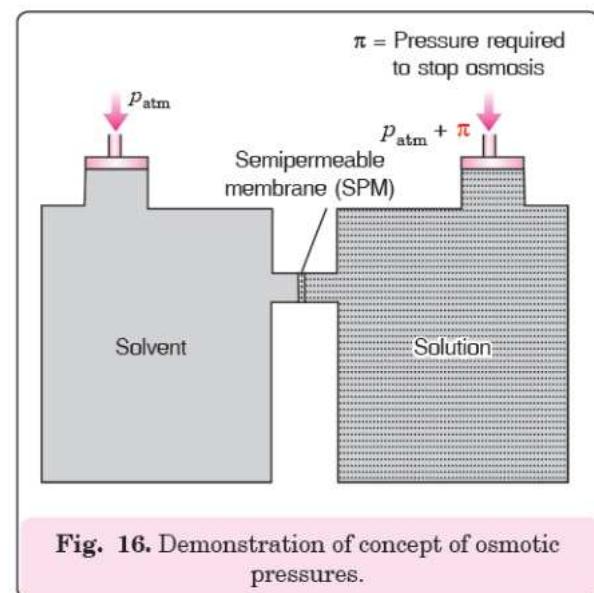


Fig. 16. Demonstration of concept of osmotic pressures.

Osmotic pressure — a Colligative Property

Van't Hoff (1887) observed that for dilute solutions, the osmotic pressure (π) is given as :

$$\pi = cRT$$

where c is the molar concentration of the solution (molarity), T is the temperature and R is the gas constant.

For a solution, at a given temperature, both R and T are constant

$$\therefore \pi \propto c$$

Since osmotic pressure depends upon the molar concentration of solution, therefore, it is a colligative property.

Experimental Measurement of Osmotic Pressure

Berkeley and Hartley's Method. The principle of this method is to apply external pressure on the solution by putting weight on the piston just sufficient to prevent the osmosis of the solvent into it. The apparatus consists of a porous pot containing copper ferrocyanide deposited on its walls which acts as a semipermeable membrane. It is fitted into a bronze cylinder to which is fitted a piston and a pressure gauge (Fig. 17). The porous pot is fitted with a water reservoir on one side and a capillary indicator on the other side. Water is put in the porous cell while the bronze cylinder is filled with the solution, the osmotic pressure of which is to be measured. Water placed in the porous pot tends to pass into the solution through the semipermeable membrane with the result that the level in the capillary indicator moves downwards. External pressure is now applied on the piston so that the water level in the capillary indicator tube remains constant. This pressure which is equal to the osmotic pressure is read from the pressure gauge.

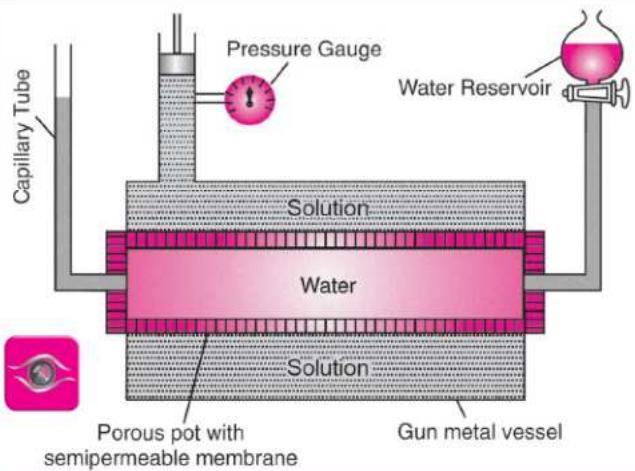


Fig. 17. Berkely and Hartley apparatus for measuring osmotic pressure.

Determination of Molar Mass from Osmotic Pressure

According to Van't Hoff equation,

$$\pi = cRT$$

But

$$c = \frac{n}{V}$$

where n is the number of moles of solute dissolved in V litre of the solution.

\therefore

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

or

$$\pi V = nRT \quad \dots(21)$$

This equation is called Van't Hoff equation for dilute solutions.

The number of moles of solute n may be given as $\frac{w_B}{M_B}$. Here w_B is the weight of the solute and M_B is its molar mass.

Substituting the value of n in the above expression,

$$\pi = \frac{w_B RT}{VM_B} \text{ or } M_B = \frac{w_B RT}{V\pi}$$

Thus, the molar mass of the solute, M_B , can be calculated.

Conditions for Getting Accurate Value of Molar Mass

(i) The solute must be non-volatile.

(ii) The solution must be dilute, i.e., concentration of the solution in the solution should not be more than 5%.

(iii) The solute should not undergo either dissociation or association in the solution.

Biological significance of osmosis

Osmosis plays a significant role in the absorption of water by the plants which is taken in by the roots. The absorption of water by plants from the soil through the roots and its movement to different parts of plants is due to the process of osmosis. Plants and animal bodies are composed of very large number of cells. The cells contain a fluid (called cell sap) and the walls of the cells are made up of living cytoplasmic membrane which acts as a semipermeable membrane.

If the cell comes in contact with water or some dilute solution whose osmotic pressure is less than that of cell sap present in the cell, there will be a tendency of water to enter into the cell through the cell wall. This causes swelling or rupture of the cell, a process known as **hemolysis**. On the other hand, if the cell comes in contact with a solution of higher osmotic pressure than that of cell sap present in the cell, the water from the cell will go out resulting shrinkage of the cell. This shrinking of the cells is called **plasmolysis**.

The membranes of plants and animal bodies allow water to pass through but block the passage of the enzymes and proteins that have been synthesised in the cell. The cell saps have generally higher osmotic pressure and, therefore, when the cells come in contact with water, there is tendency of water to enter into the cell due to osmosis. Therefore, the osmosis process helps the plants to absorb soil water and push it up to the stem and other parts of the plants and trees. Plants which grow in marshy lands have more concentrated saps which develop an osmotic pressure of the order of twenty five atmospheres. Thus, the plant may absorb excess of water from the soil which might cause bursting of root hair. Ultimately the plant decays. The addition of fertilizer may raise the osmotic pressure of the soil water. Consequently, the cell sap is not in a position to absorb excessive water and the decay of the plant is thus, checked.

The use of salt and sugar as preservatives in pickles and jams has its basis in preventing growth of fungi and bacteria by osmosis.

Isotonic solutions

We know that different solutions have different vapour pressures. Consequently their osmotic pressures must also be different. When two such solutions are separated by a semipermeable membrane, the solvent molecules flow from the solution of lower osmotic pressure towards solution of higher osmotic pressure. This continues till both the solutions attain the same osmotic pressure. At this stage, there is no further osmosis.

The solutions having same osmotic pressure at the same temperature are called isotonic solutions or isosmotic solutions.

From the equation, $\pi = cRT$, it is clear that if two solutions have same concentrations, they must have same osmotic pressure at the same temperature. Thus, **solutions of equimolar concentrations at the same temperature have same osmotic pressure, i.e., are isotonic**.

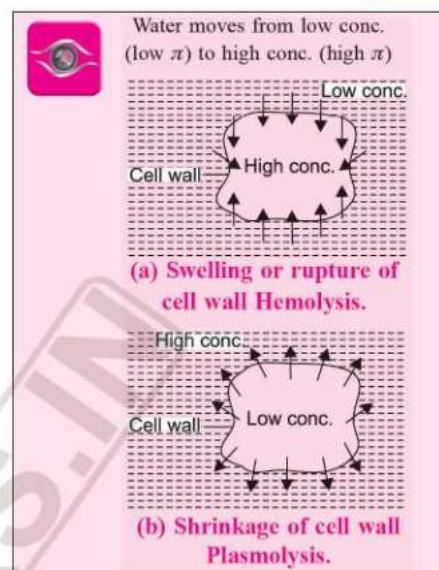
Hypertonic and hypotonic solutions

If a solution has more osmotic pressure than some other solution, it is called **hypertonic**. For example, 0.1 M urea solution exerts higher osmotic pressure than 0.05 M sucrose solution. Hence, 0.1 M urea solution is hypertonic to 0.05 M sucrose solution.

On the other hand, a solution having less osmotic pressure than the other solution is called **hypotonic**. For example, 0.05 M sucrose solution exerts lower osmotic pressure than 0.1 M urea solution. Therefore, 0.05 M sucrose solution is hypotonic to 0.1 M urea solution.

Thus, **a hypertonic solution will be more concentrated with respect to other solution and a hypotonic solution will be less concentrated with respect to other solution**.

It is quite interesting to note that a 0.91% (mass/volume) solution of sodium chloride (known as saline water) is isotonic with fluids inside human red blood cells (RBC). In this solution, the corpuscles neither swell nor shrink. Therefore, the medicines are mixed with saline water before being injected into the veins. Therefore, normal saline water is quite safe to inject intravenously.



Learning Plus

The **osmotic pressure** method is widely used for measuring the molecular masses of proteins, polymers and other macromolecules. It is regarded as one of the most suitable methods. The other methods such as depression in freezing point or elevation in boiling point cannot be used because of the following reasons:

(i) The changes (ΔT_f or ΔT_b) observed in other methods based on colligative properties are very small (e.g., for substances having molar mass of 10^6 g mol^{-1} , the ΔT_f or ΔT_b are only 0.0001K). These cannot be easily measured. On the other hand, osmotic pressure of the order of 10^{-3} atm can be easily measured in terms of mm of Hg.

(ii) Elevation in boiling point method for these biological molecules such as proteins is not suitable because these molecules are not stable at higher temperatures. The osmotic pressure method has the advantage because it can be measured at room temperature.

□ Thus, **osmotic pressure method is used for measuring molecular masses of proteins, polymers and other macromolecules** because

- (i) it can be measured around room temperature
- (ii) osmotic pressure values are larger and measurable even for dilute solutions.
- (iii) Molarity of the solution is used instead of molality.

R U Curious....

- Salt water fish die when they are suddenly transferred to a fresh water aquarium!
- Osmosis tries to equalise the concentration of water in the solution; both in the cells of the fish and the surrounding water. Water from aquarium passes through the cell membranes causing them to expand and get ruptured.

R U Curious....

- A person suffering from high blood pressure is advised to take minimum quantity of common salt!
- The osmotic pressure increases with the amount of solute. Since the body fluid contains Na^+ and Cl^- ions and if we take more salt, the concentration of these ions will increase leading to high osmotic pressure. The high osmotic pressure may cause rupture of the cells. Therefore, the patients suffering from high blood pressure are advised to take less of common salt.

However, the solutions having concentration more or less than 0.91% (mass/volume) are not safe as explained below:

(i) A pure sodium chloride solution with salt concentration less than 0.91% (mass/volume) is said to be **hypotonic** solution. When red blood cells are placed in this solution, water flows into the cells and they swell or burst.

(ii) A pure sodium chloride solution with salt concentration more than 0.91% (mass/volume) is said to be **hypertonic** solution. When red blood cells are placed in this solution, water flows out of the cells and they shrink or collapse due to loss of water by osmosis.

People taking a lot of salt or salty food experience water retention in tissue cells and intercellular spaces because of osmosis. The swelling or puffiness is called **edema**. When red blood cells are placed in this solution, water comes out of the cells and they shrink.

Osmosis can also explain some other commonly occurring processes :

(i) Carrots which have become limp because of water loss into the atmosphere can be placed into the water which makes them firm again. Water will move into them through osmosis.

(ii) A raw mango placed in concentrated salt solution (brine) loses water due to osmosis and shrivels into pickle.

(iii) Wilted flowers revive when placed in fresh water due to osmosis.

(iv) The preservation of meat by salting and fruits by adding sugar protects against bacterial action. A bacterium on salted meat or candid fruit loses water due to osmosis, shrivels and ultimately dies.

Reverse osmosis and desalination of sea water. The process of osmosis can be reversed if a pressure larger than the osmotic pressure is applied on the solution side. As a result, the solvent starts moving from solution towards the pure solvent through the semipermeable membrane. *This process of movement of solvent through a semipermeable membrane from the solution to the pure solvent by applying excess pressure on solution side is called reverse osmosis.*

A variety of polymer membranes are available these days for desalination of sea water. The pressure needed for reverse osmosis are generally quite high and workable porous membrane is a film of cellulose acetate placed over a suitable support. Cellulose acetate membrane is permeable to water but impermeable to impurities and other ions present in sea water. These days many countries meet their water requirement from desalination plants.

Desalination of sea water. The reverse osmosis process can be used for desalination of sea water for getting drinking water. A schematic set up for the process is shown in Fig. 18. If no pressure were applied to the salt water solution, osmosis would transfer water into the solution as shown in Fig. 18 (a). When a pressure greater than osmotic pressure is applied on the salt water side of a semipermeable membrane the pure water flows from the salt water side to pure water side through the semipermeable membrane. As a result, water is squeezed out of sea water as shown in Fig. 18 (b). Thus, the pure water is obtained which does not contain dissolved undesirable salts.

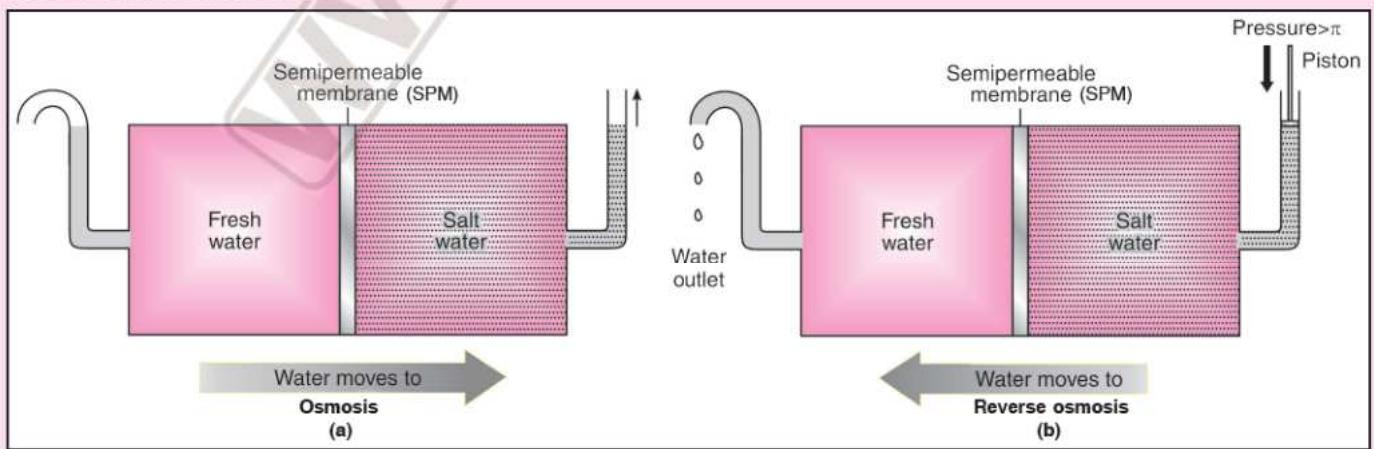


Fig. 18. Desalination of water (a) Osmosis and (b) Reverse osmosis.

Colligative Properties of Solutions Containing Mixture of Solutes

Since colligative properties depend on the total number of particles, therefore, these will depend on the number of molecules from different solutes present. These become :

- Relative lowering in vapour pressure

$$\frac{\Delta p}{p^\circ} = \frac{\sum m_i \times M_i}{1000}$$

where m_i is the molality of each solute and M_i is its molar mass.

- Elevation in boiling point

$$\Delta T_b = K_b \sum m_i$$

- Depression in freezing point

$$\Delta T_f = K_f \sum m_i$$

- Osmotic pressure

$$\pi = (\Sigma c_i) RT$$

where c_i is the molarity of each solute.

Solving Numerical Problems

FORMULAE AND UNITS

Van't Hoff equation

$$\pi = cRT$$

$$\text{or } \pi = \frac{nRT}{V}$$

where π = Osmotic pressure (in atmospheres)

n = number of moles,

V = volume (in litres)

c = concentration in moles per unit volume

T = absolute temperature,

R = $0.082 \text{ L atm mol}^{-1} \text{ K}^{-1}$

and molecular mass of solute

$$M_B = \frac{w_B RT}{V \times \pi}$$

w_B = Weight of solute,

M_B = molecular mass of solute

For isotonic solutions, osmotic pressures are equal. Since $\pi = cRT$ so at the same temperature, concentration are equal for isotonic solutions.

SOLVED EXAMPLES

□ **Example 50.**

200 cm³ of an aqueous solution of a protein contains 1.26 g of the protein. The osmotic pressure of such a solution at 300 K is found to be 2.57×10^{-3} bar. Calculate the molar mass of the protein. ($R = 0.083 \text{ L bar mol}^{-1} \text{ K}^{-1}$)

N.C.E.R.T.

(Hr. S.B. 2012, Pb.S.B. 2012, 2014, H.P.S.B. 2015)

Solution : According to Van't Hoff equation,

$$\pi = cRT = \frac{n}{V} RT = \frac{w_B RT}{M_B V}$$

$$M_B = \frac{w_B RT}{\pi V}$$

$$V = 200 \text{ cm}^3 = 0.20 \text{ L}, w_B = 1.26 \text{ g}, T = 300 \text{ K}$$

$$R = 0.083 \text{ L bar K}^{-1} \text{ mol}^{-1}, \pi = 2.57 \times 10^{-3} \text{ bar}$$

$$\therefore M_B = \frac{1.26 \text{ g} \times 0.083 \text{ L bar K}^{-1} \text{ mol}^{-1} \times 300 \text{ K}}{2.57 \times 10^{-3} \text{ bar} \times 0.20 \text{ L}}$$

$$= 61039 \text{ g mol}^{-1}$$

$$T = 300 \text{ K and } R = 0.083 \text{ L bar K}^{-1} \text{ mol}^{-1}$$

$$\pi = \frac{1.71 \times 0.083 \times 300}{342 \times 0.5} = 0.249 \text{ bar.}$$

□ **Example 52.**

Calculate the osmotic pressure of a solution obtained by mixing 100 mL of 3.4 percent solution of urea (mol. mass = 60) and 100 mL of 1.6 percent solution of cane sugar (mol. mass = 342) at 293 K.

$$(R = 0.083 \text{ L bar K}^{-1} \text{ mol}^{-1})$$

Solution : After mixing the volume of the solution = 200 mL.

(i) **Osmotic pressure of urea**

$$w_B = 3.4 \text{ g}, V = 200 \text{ mL} = 0.2 \text{ L}, T = 293 \text{ K},$$

$$M_B = 60, R = 0.083 \text{ L bar mol}^{-1} \text{ K}^{-1}$$

$$\pi = \frac{w_B RT}{M_B V}$$

$$\text{or } \pi = \frac{3.4 \times 0.083 \times 293}{60 \times 0.2} = 6.89 \text{ bar}$$

(ii) **Osmotic pressure of cane sugar**

$$w_B = 1.6 \text{ g}, V = 200 \text{ mL} = 0.2 \text{ L}, T = 293 \text{ K}, M_B = 342, R = 0.083 \text{ L bar mol}^{-1} \text{ K}^{-1}$$

$$\pi = \frac{w_B RT}{M_B V}$$

$$\text{or } \pi = \frac{1.6 \times 0.083 \times 293}{342 \times 0.2} = 0.57 \text{ bar}$$

Since the dilute solution behave like ideal gases, the total osmotic pressure will be equal to the sum of the partial osmotic pressure (similar to Dalton's law of partial pressure of gases).

$$\therefore \pi = 6.89 + 0.57 = 7.46 \text{ bar.}$$

□ **Example 51.**

If 1.71 g of sugar (molar mass = 342) are dissolved in 500 cm³ of a solution at 300 K, what will be its osmotic pressure?

$$(R = 0.083 \text{ L bar K}^{-1} \text{ mol}^{-1}) \quad (\text{Mizoram S.B. 2014})$$

Solution : According to Van't Hoff equation,

$$\pi = cRT = \frac{n}{V} RT = \frac{w_B RT}{M_B V}$$

$$w_B = 1.71 \text{ g}, V = \frac{500}{1000} \text{ L} = 0.5 \text{ L}$$

NOTE

This problem can be solved by first calculating the total number of moles of urea and sugar because the colligative properties are independent of the nature of the solute.

$$\text{Moles of urea} = \frac{3.4}{60} = 0.0567,$$

$$\text{Moles of sucrose} = \frac{1.6}{342} = 0.00472$$

$$\begin{aligned}\text{Total moles} &= 0.0567 + 0.0047 \\ &= 0.0614\end{aligned}$$

$$V = 200 \text{ mL} = 0.2 \text{ L}$$

$$\begin{aligned}\pi &= \frac{0.0614}{0.2} \times 0.083 \times 298 \\ &= 7.46 \text{ bar}\end{aligned}$$

Example 53.

36 g of glucose dissolved per litre of the solution has an osmotic pressure of 4.98 bar at 300 K. If the osmotic pressure of the solution is 1.52 bar at the same temperature, what would be its concentration?

N.C.E.R.T.

Solution : According to Van't Hoff equation,

$$\pi = cRT$$

$$c_1 = \frac{36}{180} \text{ M}, \pi_1 = 4.98 \text{ bar}$$

and

$$c_2 = ? \quad \pi_2 = 1.52 \text{ bar}$$

$$\therefore 4.98 \text{ bar} = \frac{36}{180} RT \quad \dots(i)$$

$$1.52 \text{ bar} = c_2 RT \quad \dots(ii)$$

Dividing eqn. (ii) by eqn. (i),

$$\frac{c_2}{36} \times 180 = \frac{1.52}{4.98}$$

$$\therefore c_2 = \frac{1.52}{4.98} \times \frac{36}{180} = 0.061 \text{ M}$$

∴ Concentration of second solution = 0.061 M.

Example 54.

A solution of an organic compound was prepared by dissolving 6.8 g in 100 g of water. Calculate the osmotic pressure of this solution at 298 K when boiling point of solution is 100.11°C. Given K_b for water = 0.52 K m^{-1} and $R = 0.082 \text{ litre atm K}^{-1} \text{ mol}^{-1}$.

(Hr.S.B. 2005)

Solution : Molecular mass can be calculated from boiling point data as :

$$M_B = \frac{K_b \times w_B \times 1000}{\Delta T_b \times w_A}$$

$$w_B = 6.8 \text{ g}, w_A = 100 \text{ g}, K_b = 100.11 - 100 = 0.11 \text{ K m}^{-1}$$

$$\therefore M_B = \frac{0.52 \times 6.8 \times 1000}{0.11 \times 100} = 321.45$$

Now

$$\pi = \frac{nRT}{V}, n = \frac{6.8}{321.45}$$

$$V = 100 \text{ g} \approx 100 \text{ ml} = 0.1 \text{ L},$$

$$R = 0.082 \text{ L atm mol}^{-1} \text{ K}^{-1}$$

$$T = 298 \text{ K}$$

$$\pi = \frac{6.8 \times 0.082 \times 298}{321.45 \times 0.1}$$

$$= 5.17 \text{ atm.}$$

Example 55.

A solution prepared by dissolving 8.95 mg of a gene fragment in 35.0 mL of water has an osmotic pressure of 0.335 torr at 25°C. Assuming the gene fragment is a non-electrolyte, determine its molar mass.

(D.S.B. 2011, A.I.S.B. 2011)

Solution : Mass of gene fragment = 8.95 mg
= $8.95 \times 10^{-3} \text{ g}$

$$\text{Volume of water} = 35.0 \text{ mL} = 35.0 \times 10^{-3} \text{ L}$$

$$\text{Osmotic pressure, } \pi = 0.335 \text{ torr} = 0.335/760 \text{ atm}$$

$$\text{Temperature} = 25^\circ\text{C} = 273 + 25 = 298 \text{ K}$$

$$\pi = \frac{w_B RT}{M_B \times V}$$

$$\frac{0.335}{760} = \frac{8.95 \times 10^{-3} \times 0.0821 \times 298}{M_B \times 35.0 \times 10^{-3}}$$

$$M_B = \frac{8.95 \times 10^{-3} \times 0.0821 \times 298 \times 760}{0.335 \times 35.0 \times 10^{-3}}$$

$$= 14193.3 \text{ g mol}^{-1} \text{ or} \\ 1.42 \times 10^4 \text{ g mol}^{-1}.$$

Example 56.

A solution containing 15 g urea (molar mass = 60 g mol⁻¹) per litre of solution in water has the same osmotic pressure (isotonic) as a solution of glucose (molar mass = 180 g mol⁻¹) in water. Calculate the mass of glucose present in one litre of its solution.

(A.I.S.B. 2014, Kerala S.B. 2018)

Solution : For isotonic solutions,

$$\pi(\text{urea}) = \pi(\text{glucose})$$

$$\pi(\text{urea}) = \frac{nRT}{V} = \frac{15}{60} \times \frac{RT}{1}$$

$$\pi(\text{glucose}) = \frac{nRT}{V} = \frac{w}{180} \times \frac{RT}{1}$$

Now

$$\frac{15}{60} RT = \frac{w}{180} RT$$

∴

$$w = \frac{15 \times 180}{60} = 45 \text{ g}$$

Practice Problems

71. A solution of sucrose (molar mass = 342 g mol⁻¹) is prepared by dissolving 68.4 g of it per litre of solution. What is the osmotic pressure at 300 K ?
72. Osmotic pressure of a solution containing 3.5g of dissolved protein per 50cc of a solution is 25 mm (Hg) at 37°C. Calculate the molar mass of protein.
(Manipur S.B. 2014)
73. The osmotic pressure of a solution containing 0.2 g of a substance (moar mass = 176) in 302 ml of solution was found to be 4.1 atmosphere at 15.5°C. Calculate the value of solution constant.
74. Calculate the osmotic pressure of a solution obtained by mixing 100 ml of 1.5% solution of urea (molar mass = 60) and 100 ml of 3.42% of cane sugar (molar mass = 342) at 20°C.
(R = 0.82 litre atm K⁻¹ mol⁻¹).
75. Three grams of non-volatile solute when dissolved in a litre of water shows an osmotic pressure of 2 bar at 300 K. Calculate the molar mass of the solute.
(R = 0.083 L bar K⁻¹ mol⁻¹).
76. Calculate the osmotic pressure of a solution containing 10 gram each of glucose (C₆H₁₂O₆) and sucrose (C₁₂H₂₂O₁₁) in 1000 cm³ of the solution at 25°C.
(R = 0.083 L bar K⁻¹ mol⁻¹)
77. A solution containing 10.2 g of glycerine per litre is found to be isotonic with a 2% solution of glucose. Calculate the molar mass of glycerine (molar mass of glucose = 180).
(Mizoram S.B. 2016)
78. A 5% solution of cane sugar (molar mass = 342) is isotonic with 0.877% solution of urea. Calculate the molar mass of urea.
(Uttarakhand S.B. 2014, Nagaland S.B. 2016)
79. What is the concentration of solution of sucrose (molar mass = 342) which is isotonic with a solution containing 6 g of urea per litre ?
80. Osmotic pressure of a solution containing 7 g of a protein per 100 cm³ of solution is 3.3 × 10⁻² bar at 37°C. Calculate the molar mass of protein.
81. A solution of an organic compound is prepared by dissolving 68.4 g in 1000 g of water. Calculate the molecular mass of the compound and osmotic pressure of the solution at 293 K when elevation in boiling point is 0.104 and K_b for water is 0.52 Km⁻¹.
(Hr.S.B. 2005)
82. A solution of an organic compound is prepared by dissolving 34.2 g in 500 g of water. Calculate the molecular mass of the compound and freezing point of the solution. Given that K_b for water = 0.52 K m⁻¹, b.pt. of solution = 100.14°C, K_f for water = 1.87 Km⁻¹.
(Hr.S.B. 2005)
83. The average osmotic pressure of human blood is 7.7 atm at 40°C.
(a) What would be the total concentration of various solutes in the blood ?
(b) Assuming the concentration to be essentially the same as the molality, calculate the freezing point of blood (K_f for water = 1.86°C m⁻¹).
84. The osmotic pressure of blood is 8.21 atm at 37°C. How much glucose should be used per litre for an intravenous injection that is isotonic with blood ?
85. 600 mL of aqueous solution containing 2.5 g of a protein shows an osmotic pressure of 25 mm Hg at 27°C. Determine the relative molecular mass of protein.
(Tripura S.B. 2016)

Answers to Practice Problems

71. 4.92 atm.
72. 54159.7
73. 0.0821 litre atm/mol/degree
74. 4.20 atm.
75. 37.35 g mol⁻¹
76. 2.10 bar
77. 91.8
78. 59.99 g mol⁻¹
79. 34.2 g L⁻¹
80. 54579
81. 342, 4.80 atm
82. 342, - 0.374°C
83. 0.30 mol L⁻¹, - 0.558 °C
84. 58.06 g
85. 3119.8 g mol⁻¹

Hints & Solutions on page 66

Advanced Level

PROBLEMS

Problem 8. How many grams of sucrose (molecular mass 342) should be dissolved in 100 g water in order to produce a solution having difference between the boiling point and freezing point equal to 105°?

$$(K_b = 0.512 \text{ Km}^{-1}, K_f = 1.86 \text{ Km}^{-1})$$

Solution w_{solvent} = 100g, w_{sucrose} = ?

$$T_b - T_f = 105^\circ$$

$$\text{Now, } \Delta T_b = K_b \cdot m$$

$$\text{Boiling point of solution, } T_b = 100 + \Delta T_b$$

$$\text{or } T_b = 100 + K_b \cdot m \quad \dots(i)$$

Accelerate Your Potential
(for JEE Advance)

$$\Delta T_f = K_f \cdot m$$

Freezing point of solution, $T_f = 0 - \Delta T_f$

or $T_f = 0 - K_f \times m \quad \dots(ii)$

Subtracting eq. (ii) from eq. (i)

$$T_b - T_f = 100 + K_b \times m - (0 - K_f \times m)$$

$$105 = 100 + K_b \times m + K_f \times m$$

$$105 = 100 + 0.512 \times m + 1.86 \times m$$

$$2.372 m = 5$$

or $m = \frac{5}{2.372} = 2.108$

Now, $m = \frac{w_{\text{sucrose}} \times 1000}{M_{\text{sucrose}} \times w_{\text{solvent}}}$

$$\therefore 2.108 = \frac{w_{\text{sucrose}} \times 1000}{342 \times 100}$$

$$\therefore w_{\text{sucrose}} = \frac{2.108 \times 342 \times 100}{1000} = 72.09 \text{ g}$$

Problem 9. If boiling points of an aqueous solution containing a non-volatile solute is 100.15°C . What is its freezing point? Given latent heat of fusion and vaporisation of water are 80 cal g^{-1} and 540 cal g^{-1} respectively.

Solution For a given aqueous solution

$$\Delta T_f = K_f \times m \quad \dots(i)$$

$$\Delta T_b = K_b \times m \quad \dots(ii)$$

$$K_f = \frac{RT_f^2}{1000 l_f} \quad \text{and} \quad \dots(iii)$$

$$K_b = \frac{RT_b^2}{1000 l_v} \quad \dots(iv)$$

Dividing eq. (iii) by eq. (iv)

$$\frac{K_f}{K_b} = \frac{T_f^2 \times l_v}{T_b^2 \times l_f}$$

$$\therefore \frac{\Delta T_f}{\Delta T_b} = \frac{T_f^2 \times l_v}{T_b^2 \times l_f}$$

$$T_f = 0 + 273 = 273 \text{ K}$$

$$T_b = 100 + 273 = 373 \text{ K}$$

$$l_f = 80 \text{ cal g}^{-1}, l_v = 540 \text{ cal g}^{-1}$$

$$\Delta T_b = 100.15 - 100 = 0.15$$

$$\therefore \frac{\Delta T_f}{0.15} = \frac{273 \times 273 \times 540}{373 \times 373 \times 80}$$

$$\text{or } \Delta T_f = \frac{273 \times 273 \times 540}{373 \times 373 \times 80} \times 0.15 = 0.542$$

$$\therefore T_f = 0 - 0.542 = -0.542^\circ\text{C}.$$

Problem 10. A very small amount of non-volatile solute (that does not dissociate) is dissolved in 56.8 cm^3 of benzene (density 0.889 g cm^{-3}). At room temperature, vapour pressure of this solution is 98.88 mm Hg while that of benzene is 100 mm Hg . Find the molality of this solution. If the freezing temperature of this solution is 0.73 degree lower than that of benzene, what is the value of molal freezing point depression constant of benzene?

Solution For very dilute solutions,

$$\frac{p^o - p}{p^o} = x_B (x_B = \text{mole fraction of substance})$$

$$\therefore \frac{100 - 98.88}{100} = x_B$$

$$\text{Now, } x_B = \frac{n_B}{n_A + n_B} = \frac{n_B}{n_A} \quad (\text{for dilute solution})$$

$$= \frac{n_B}{w_A} \times M_A \quad \dots(i)$$

$$\text{Molality, } m = \frac{n_B \times 1000}{w_A} \quad \dots(ii)$$

Dividing equation (i) by eq. (ii)

$$\frac{x_B}{m} = \frac{M_A}{1000}$$

or $m = \frac{x_B \times 1000}{M_A}$

$$\therefore m = \frac{0.0112 \times 1000}{78} = 0.1436$$

$$\Delta T_f = K_f \times m$$

$$\text{or } K_f = \frac{\Delta T_f}{m} = \frac{0.73}{0.1436} = 5.08 \text{ Km}^{-1}.$$

Problem 11. Calculate the amount of ice that will separate out on cooling a solution containing 50 g of ethylene glycol in 200 g of water to -9.3°C . (K_f for water = 1.86 K m^{-1})

Solution Let us calculate the amount of water present in the solution.

$$\Delta T_f = \frac{K_f \times 1000 \times w_B}{M_B \times w_A}$$

or $w_A = \frac{K_f \times 1000 \times w_B}{M_B \times \Delta T_f}$

$$\Delta T_f = 0 - (-9.3) = 9.3^\circ$$

$$\therefore w_A = \frac{1.86 \times 1000 \times 50}{62 \times 9.3} = 161.29 \text{ g}$$

$$\begin{aligned} \text{Amount of ice separated from } 200 \text{ g of water} \\ &= 200 - 161.29 = 38.71 \text{ g.} \end{aligned}$$

Problem 12. At 10°C , the osmotic pressure of urea solution is 500 mm Hg . The solution is diluted and the temperature is raised to 25°C , when the osmotic pressure is found to be 105.3 mm Hg . Calculate the extent of dilution.

Solution For initial solution,

$$\pi = \frac{500}{760} \text{ atm, } T = 273 + 10 = 283 \text{ K}$$

Let volume of solution is V_1

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

$$\frac{500}{760} = \frac{n}{V_1} \times R \times 283 \quad \dots(i)$$

After dilution, let the volume becomes V_2 and temperature is raised to 25°C .

$$\pi = \frac{105.3}{760} \text{ atm, } T = 273 + 25 = 298 \text{ K}$$

$$\frac{105.3}{760} = \frac{n}{V_2} \times R \times 298 \quad \dots(ii)$$

Dividing eq. (i) by eq. (ii)

$$\frac{500}{105.3} = \frac{V_2}{V_1} \times \frac{283}{298}$$

$$\text{or } \frac{V_2}{V_1} = \frac{500 \times 298}{105.3 \times 283} = 5$$

∴ The solution was diluted 5 times.

Problem 13. Hundred grams of a 5 m urea solution are cooled to -6°C . What amount of urea will separate out? ($K_f = 1.86 \text{ K m}^{-1}$).

Solution Molality of solution at -6°C

$$\Delta T_f = K_f m$$

$$\text{or } m = \frac{\Delta T_f}{K_f} = \frac{6}{1.86} = 3.23 \text{ mol kg}^{-1}$$

5 m solution of urea means that 5 moles or $5 \times 60 \text{ g}$ of urea are present in 1000 g of solvent or $(1000 + 5 \times 60) \text{ g}$ of solution, so that

SOLUTIONS

(1000 + 300) g of solution contain urea = 300 g

$$\begin{aligned} 100 \text{ g of solution contain urea} &= \frac{300}{1300} \times 100 \\ &= 23.08 \text{ g} \\ \text{Mass of water in the solution} &= 100 - 23.08 \\ &= 76.92 \text{ g} \end{aligned}$$

When urea separates out, mass of water does not change. At -6°C , the molality is 3.23 mol kg^{-1} . Let

us calculate the amount of urea to make the molality 3.23 mol kg^{-1} .

1000 g of water contain urea = $60 \times 3.23 \text{ g}$

$$\begin{aligned} 76.92 \text{ g of water contain urea} &= \frac{60 \times 3.23 \times 76.92}{1000} \\ &= 14.91 \text{ g} \end{aligned}$$

$$\begin{aligned} \text{Mass of urea separated} &= 23.08 - 14.91 \\ &= 8.17 \text{ g} \end{aligned}$$

ABNORMAL MOLAR MASSES : ELECTROLYTIC SOLUTIONS

We have discussed in the previous sections that the colligative properties help us to calculate the molar masses of solutes. But in some cases, the molar masses determined by these methods do not agree with the expected or theoretical values. The accurate values of molar masses can be obtained only if the following two conditions are satisfied.

1. The solutions should be dilute

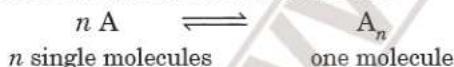
The solutions used for measuring colligative properties must not be too concentrated. In the concentrated solutions, the particles begin to interact with each other as well as with the solvent. As a result, the vapour pressure and therefore, other colligative properties depend upon the nature of the solute and not just on the number of solute particles.

2. The solute must not dissociate or associate in solution

The equations derived for measuring the colligative properties are for **non-electrolyte solutes** which do not undergo any dissociation or association in the solution. However, discrepancies in determination of molar mass arise when the solutes dissociate or associate on dissolving in a solvent. This is because due to the association or the dissociation of the solute molecules in the solution, the number of molecules undergo a change. Therefore, **abnormal molar masses** are obtained as discussed below:

1. Association of solute particles

In certain solvents, generally non-polar, the solute molecules undergo association *i.e.*, two, three or even more molecules exist in combination with each other to form bigger molecules. For example, suppose n simple molecules combine to form an associated molecule as :



Therefore, the total number of molecules in solution become less than the number of molecules of the substance added and, therefore, **colligative properties will be lower**. Since the *colligative properties are inversely proportional to the molar mass of the solute, the molar masses in such cases will be greater than the theoretical values*. For example, in benzene solvent, both ethanoic acid (acetic acid) and benzoic acid exist as dimers as :



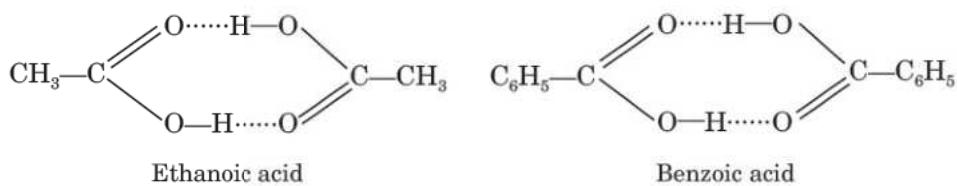
Ethanoic acid Dimer



Benzoic acid Dimer

The molar masses of ethanoic acid and benzoic acid have been found to be nearly 120 and 244 which are about double than their normal values of 60 and 122 respectively. The association of solute molecules in a solution is generally due to the hydrogen bonding between these molecules. For example, benzoic acid and ethanoic acid (acetic acid) exist as dimers due to the formation of hydrogen bonds as shown ahead:

Colligative property of an electrolyte solution is always greater than that of a non-electrolyte solution of the same molar concentration because of the dissociation of the electrolyte.



2. Dissociation of solute molecules

Molecules of electrolytes (acids, bases and salts) dissociate or ionise in a solvent to give two or more particles. For example, AB dissociates to give double number of particles as



Consequently, the total number of particles increases in solution and, therefore, the *colligative properties of such solutions will be large. Since colligative properties are inversely proportional to molar mass, the observed molar mass will be less than the theoretical value.* For example, KCl dissociates to give K^+ and Cl^- ions.



This means that if we dissolve 1 mol of KCl (74.5 g) in water, we expect 1 mol of K^+ and 1 mol of Cl^- ions to be produced in the solution. Therefore, there would be 2 mol of particles in the solution instead of 1 mol. Consequently, the colligative properties would also be about double than expected. For example, if we ignore interionic attractions, 1 mol of KCl in 1 kg of water would be expected to increase the boiling point by $2 \times 0.52\text{ K}$ ($K_b = 0.52\text{ Km}^{-1}$) = 1.04 K. Obviously, the molar mass of the salt must be about half of its normal value i.e., 37.25.

Van't Hoff Factor

In 1886, Van't Hoff introduced a factor called Van't Hoff factor, '*i*' to express the extent of association or dissociation of solutes in solution. Van't Hoff factor is defined as

the ratio of the normal molar mass to the observed molar mass (or abnormal molar mass) of the solute, i.e.,

$$i = \frac{\text{Normal molar mass}}{\text{Observed (or abnormal) molar mass}}$$

- In case of association, observed molar mass being more than the normal, the factor '*i*' has a value less than 1.
- In case of dissociation, the Van't Hoff factor is more than 1 because the observed molar mass has a lesser value.
- In case of solutes which do not undergo any association or dissociation in a solvent, the Van't Hoff factor '*i*' will be equal to 1 because the observed and normal molar masses will be same.

Since the molar masses are inversely proportional to the colligative property, Van't Hoff factor may also be defined as:

the ratio of the observed value of colligative property to the normal value of the colligative property.

$$\text{i.e., } i = \frac{\text{Observed value of colligative property}}{\text{Normal value of colligative property}}$$

Inclusion of Van't Hoff factor (*i*) modifies the equations for colligative properties as follows:

$$\text{Relative lowering in vapour pressure, } \frac{\Delta p}{p^\circ} = i x_{\text{solute}}$$

$$\text{Elevation in boiling point, } \Delta T_b = i K_b m$$

$$\text{Depression in freezing point, } \Delta T_f = i K_f m$$

$$\text{Osmotic pressure, } \pi = i cRT$$

REMEMBER

- The normal value of colligative property is the theoretically calculated value assuming no association or dissociation and abnormal value of colligative property is the experimentally determined value.
- For solutes which do not undergo association or dissociation, $i = 1$
- For solutes undergoing association, $i < 1$
- For solutes undergoing dissociation, $i > 1$

The Van't Hoff factor is given for some strong electrolytes in Table 5.

Table 5. Values of Van't Hoff factor at various concentrations for some common strong electrolytes.

Electrolyte	Value of i			' i ' for complete dissociation
	0.1 m	0.01 m	0.001 m	
NaCl	1.87	1.94	1.97	2.0
KCl	1.85	1.94	1.98	2.0
MgSO ₄	1.21	1.53	1.82	2.0
K ₂ SO ₄	2.32	2.70	2.84	3.0

It is clear from the table that values of ' i ' for KCl, NaCl and MgSO₄ approaches 2 (expected for complete dissociation) as the solution becomes very dilute. Similarly, the ' i ' value approaches 3 (for complete dissociation) for K₂SO₄ as the solution becomes very dilute.

Van't Hoff Factor and Extent of Dissociation or Association in an Electrolytic Solution

Van't Hoff factor can be used to calculate the extent of dissociation or association in terms of degree of dissociation or association of a substance in solution.

(i) **Degree of dissociation.** It is defined as *the fraction of total substance that undergoes dissociation into ions, i.e.,*

$$\text{Degree of dissociation} = \frac{\text{No. of moles of the substance dissociated}}{\text{Total number of moles of the substance taken}}$$

Suppose a molecule of an electrolyte gives m ions after dissociation. Then if we start with 1 mole of the solute, and α is the degree of dissociation, then at equilibrium :

$$\text{Number of moles of solute left undissociated} = 1 - \alpha$$

$$\text{Number of moles of ions formed} = m\alpha$$

$$\text{Total number of moles of particles} = 1 - \alpha + m\alpha$$

$$\text{Van't Hoff factor } i = \frac{\text{Observed number of moles of solute}}{\text{Normal number of moles of solute}}$$

$$i = \frac{1 - \alpha + m\alpha}{1}$$

$$1 - \alpha + m\alpha = i$$

$$\text{or } \alpha(m - 1) = i - 1$$

$$\alpha = \frac{i - 1}{m - 1}$$

$$\text{But } i = \frac{\text{Normal molar mass}}{\text{Observed molar mass}}$$

Knowing the value of ' i ' from observed molar mass and normal molar mass, degree of dissociation, α can be calculated.

For the electrolytes of the type AB, such as KCl, NaCl, etc., the number of particles in solution *i.e.*, $m = 2$

$$\therefore \alpha = i - 1$$

For the electrolytes of the type AB₂ like CaCl₂, Ba(NO₃)₂ etc., the value of $m = 3$, so that

$$\alpha = \frac{i - 1}{2}$$

(ii) **Degree of association.** It is defined as *the fraction of total number of molecules which combine to form associated molecules, i.e.*

$$\text{Degree of association} = \frac{\text{No. of moles of the substance associated}}{\text{Total number of moles of substance taken}}$$

For example, suppose n simple molecules of the solute associate to form the associated molecule A_n .

$$nA = A_n$$

If we start with 1 mole of A and α is the degree of association, the concentration of the species after association is :

$$[A_n] = \alpha/n$$

$$[A] = (1 - \alpha)$$

$$\text{Total number of moles after association} = 1 - \alpha + \alpha/n$$

Thus, the colligative properties will correspond to $(1 - \alpha + \alpha/n)$ mole particles rather than one mole of particles.

Van't Hoff factor, ' i ' is

$$i = \frac{\text{Observed number of moles of solute particles}}{\text{Number of moles of solute particles assuming no association}}$$

$$i = \frac{1 - \alpha + \alpha/n}{1}$$

$$i = 1 + \alpha(1/n - 1)$$

$$\text{or } \alpha(1/n - 1) = i - 1$$

$$\text{or } \alpha = \frac{i - 1}{1/n - 1}$$

$$\text{But } i = \frac{\text{Normal molar mass}}{\text{Observed molar mass}}$$

Thus, knowing ' n ' the number of simple molecules which combine to give associated molecule, observed molar mass, degree of association (α) can be calculated.

Solving Numerical Problems

FORMULAE AND UNITS

Van't Hoff factor

$$i = \frac{\text{Observed colligative property}}{\text{Normal colligative property}} = \frac{\text{Normal molecular mass}}{\text{Observed molecular mass}} = \frac{\text{No. of particles after dissociation or association}}{\text{No. of particles without dissociation or association}}$$

- (i) If observed colligative property < normal colligative property or observed molecular mass > normal molecular mass
⇒ the solute is associated.
- (ii) If observed colligative property > normal colligative property or observed molecular mass < normal molecular mass
⇒ the solute is dissociated.

Calculation of degree of dissociation or association

- Calculate Van't Hoff factor using above relations.
- Write dissociation or association equation. Starting with 1 mole and assuming α to be degree of dissociation or association, calculate the actual number of particles. Then

$$i = \frac{\text{Actual number of particles}}{1}$$

Equate i from above two steps and calculate α ; the degree of dissociation or association.

SOLVED EXAMPLES

Example 57.

Calculate the boiling point of solution when 2 g of Na_2SO_4 ($M = 142 \text{ g mol}^{-1}$) was dissolved in 50 g of water, assuming Na_2SO_4 undergoes complete ionization. (K_b for water = $0.52 \text{ K kg mol}^{-1}$)

(A.I. S.B. 2016)

$$\text{Solution: } \Delta T_b = \frac{i \times K_b \times w_B \times 1000}{M_B \times w_A}$$

Weight of solute, $w_B = 2 \text{ g}$

Molar mass = 142 g mol^{-1}

Weight of solvent = 50 g

$$K_b = 0.52 \text{ Km}^{-1}$$

Na_2SO_4 undergoes complete ionization as:



One mole of Na_2SO_4 gives 3 mole particles and therefore,
 $i = 3$

$$\therefore \Delta T_b = \frac{3 \times 0.52 \times 2 \times 1000}{142 \times 50} = 0.439$$

$$\text{Boiling point of solution} = 373 + 0.439 \\ = 373.439 \text{ K}$$

SOLUTIONS

Example 58.

Calculate the amount of CaCl_2 (molar mass = 111 g mol⁻¹) which must be added to 500 g of water to lower its freezing point by 2K, assuming CaCl_2 is completely dissociated. (K_f for water = 1.86 K kg mol⁻¹)

(A.I.S.B. 2015).

Solution: CaCl_2 undergoes complete dissociation as:



One mole of CaCl_2 will give 3 mole particles and therefore, the value of i will be equal to 3.

$$\begin{aligned}\Delta T_f &= i K_f \times m \\ &= \frac{i \times K_f \times w_B \times 1000}{M_B \times w_A}\end{aligned}$$

$K_f = 1.86 \text{ K kg mol}^{-1}$, $w_A = 500 \text{ g}$, $w_B = ?$, $\Delta T_f = 2 \text{ K}$, $i = 3$, $M_B = 111 \text{ g mol}^{-1}$

$$2 = \frac{3 \times 1.86 \times w_B \times 1000}{111 \times 500}$$

$$\therefore w_B = \frac{2 \times 111 \times 500}{3 \times 1.86 \times 1000} = 19.89 \text{ g}$$

Example 59.

At 25°C, 3 g of a solute A in 100 mL of an aqueous solution gave an osmotic pressure of 2.5 atmosphere. What is the nature of solute (associated or dissociated) if its normal molar mass is 246?

Solution : Normal molar mass of solute = 246

The molar mass may be calculated as:

$$\pi = cRT = \frac{nRT}{V} = \frac{w_B RT}{M_B V}$$

$$\text{or } M_B = \frac{w_B RT}{\pi V}$$

$w_B = 3.0 \text{ g}$, $V = 100 \text{ ml} = 0.1 \text{ L}$, $\pi = 2.5 \text{ atm}$,

$$R = 0.082 \text{ L atm mol}^{-1} \text{ K}^{-1}$$

$$M_B = \frac{3 \times 0.082 \times 298}{2.5 \times 0.1} = 293.$$

This means that the solute has abnormal behaviour in solution. Since observed molar mass is more than the normal value (246) the solute exists as **associated** in solution.

Example 60.

A solution containing 0.5 g of KCl dissolved in 100 g of water freezes at -0.24°C. Calculate the percentage ionization of the salt. (K_f for water = 1.86 Km⁻¹).

(C.B.S.E. Sample Paper 2007)

Solution : Let us first calculate the observed molar mass as :

$$M_B = \frac{K_f \times w_B \times 1000}{\Delta T_f \times w_A}$$

$w_B = 0.5 \text{ g}$, $w_A = 100 \text{ g}$, $\Delta T_f = 0 - (-0.24) = 0.24^\circ$, $K_f = 1.86$

$$\therefore M_B = \frac{1.86 \times 0.5 \times 1000}{0.24 \times 100} = 38.75$$

Normal molar mass of $\text{KCl} = 39 + 35.5 = 74.5$

Van't Hoff factor,

$$i = \frac{\text{Normal molar mass}}{\text{Observed molar mass}} = \frac{74.5}{38.75} = 1.92$$

KCl ionizes as :

If α is the degree of ionization, then



Initial moles 1 0 0

Moles after dissociation $1 - \alpha$ α α

Total number of moles after dissociation = $1 - \alpha + \alpha + \alpha = 1 + \alpha$

$$i = \frac{\text{Observed moles of solute}}{\text{Normal moles of solute}} = \frac{1 + \alpha}{1}$$

$$\therefore \frac{1 + \alpha}{1} = 1.92 \quad \text{or} \quad 1 + \alpha = 1.92$$

$$\text{or} \quad \alpha = 1.92 - 1 = 0.92$$

Percentage ionization = 92%.

Example 61.

2 g of benzoic acid ($\text{C}_6\text{H}_5\text{COOH}$) dissolved in 25 g of benzene shows a depression in freezing point equal to 1.62 K. Molar depression constant for benzene is 4.9 K kg mol⁻¹. What is the percentage association of acid if it forms double molecules (dimer) in solution?

N.C.E.R.T. (Pb. S.B. 2009)

Solution : Let us first calculate observed molar mass,

$$M_B = \frac{K_f \times w_B \times 1000}{\Delta T_f \times w_A}$$

$$w_B = 2 \text{ g}$$
, $w_A = 25 \text{ g}$, $\Delta T_f = 1.62 \text{ K}$

$$K_f = 4.9 \text{ K kg mol}^{-1}$$

$$M_B = \frac{4.9 \times 2 \times 1000}{1.62 \times 25} = 241.98 \text{ g mol}^{-1}$$

Observed molar mass = 241.98 mol⁻¹

Normal molar mass of $\text{C}_6\text{H}_5\text{COOH}$

$$= 7 \times 12 + 6 \times 1 + 2 \times 16 = 122 \text{ g mol}^{-1}$$

Benzoic acid associates as :



If α is the degree of association

Initial moles 1 0

Moles after association $1 - \alpha$ $\alpha/2$

Total moles after association = $1 - \alpha + \alpha/2 = 1 - \alpha/2$

$$i = \frac{\text{Normal molar mass}}{\text{Observed molar mass}} = \frac{122}{241.98} = 0.504$$

$$\text{Now } i = \frac{1 - \frac{\alpha}{2}}{1} = 0.504$$

$$-\frac{\alpha}{2} = 0.504 - 1$$

$$-\frac{\alpha}{2} = -0.496$$

$$\alpha = 0.496 \times 2 = 0.992$$

Thus, degree of association of benzoic acid in benzene = 99.2%.

Example 62.

A solution containing 3.100 g of BaCl_2 in 250 g of water boils at 100.083°C. Calculate the Van't Hoff factor and molality of BaCl_2 in this solution. (K_b for water = 0.52 Km⁻¹, molar mass of BaCl_2 = 208.3 g mol⁻¹)

(A.I.S.B. 2001)

Solution : Molality of the solution,

$$m = \frac{w_B \times 1000}{M_B \times w_A}$$

$$w_B = 3.100 \text{ g}$$
, $w_A = 250 \text{ g}$, $M_B = 208.3$

$$m = \frac{3.100 \times 1000}{208.3 \times 250} = 0.05952$$

Now, let us calculate normal elevation in boiling point,

$$\Delta T_b = K_b \times m \\ = 0.05952 \times 0.52 = 0.03095$$

Observed elevation in boiling point,

$$\Delta T_b = 100.083 - 100 = 0.083^\circ\text{C} \\ i = \frac{\text{Observed } \Delta T_b}{\text{Normal } \Delta T_b} = \frac{0.083}{0.03095} = 2.68.$$

Example 63.

The freezing point of a solution containing 0.3 g of acetic acid in 30.0 g of benzene is lowered by 0.45°. Calculate Van't Hoff factor. (K_f for benzene = 5.12 K kg mol⁻¹). (A.I.S.B. 2001)

Solution : Let us first calculate observed molar mass

$$M_B = \frac{K_f \times w_B \times 1000}{\Delta T_f \times w_A}$$

$w_B = 0.3$ g, $w_A = 30.0$ g, $\Delta T_f = 0.45^\circ$, $K_f = 5.12$ K kg mol⁻¹

$$\therefore M_B = \frac{5.12 \times 0.3 \times 1000}{0.45 \times 30} = 113.8$$

Normal molar mass = 60

$$\text{Now } i = \frac{\text{Normal molar mass}}{\text{Observed molar mass}} = \frac{60}{113.8} = 0.527.$$

Example 64.

A solution contains 0.8960 g of K_2SO_4 in 500 mL solution. Its osmotic pressure is found to be 0.690 atm at 27°C. Calculate the value of Van't Hoff factor. (At. mass K = 39.0, S = 32, O = 16, R = 0.082 atm mol⁻¹ K⁻¹). (A.I.S.B. 2001)

Solution : Let us first calculate observed molar mass,

$$M_B = \frac{w_B \times R \times T}{\pi \times V}$$

$w_B = 0.8960$ g, $V = 500$ mL = 0.5 L

$R = 0.082$ L atm mol⁻¹ K⁻¹, $\pi = 0.690$ atm, $T = 300$ K

$$M_B = \frac{0.8960 \times 0.082 \times 300}{0.690 \times 0.5} = 63.9$$

Normal molar mass = $2 \times 39 + 32 + 4 \times 32 = 174$

$$\text{Van't Hoff factor, } i = \frac{\text{Normal molar mass}}{\text{Observed molar mass}} \\ = \frac{174}{63.9} = 2.72.$$

Example 65.

0.6 mL of acetic acid (CH_3COOH) having density 1.06 g mL⁻¹ is dissolved in 1 litre of water. The depression in freezing point observed for this strength of acid was 0.0205°C. Calculate the Van't Hoff factor and dissociation constant of the acid. [N.C.E.R.T.]

$$\text{Solution : Moles of acetic acid} = \frac{0.6 \text{ mL} \times 1.06 \text{ g mL}^{-1}}{60 \text{ g mol}} \\ = 0.016 \text{ mol}$$

[M (CH_3COOH) = 60]

Mass of water = 1000 mL × 1 g mL⁻¹ = 1000 g

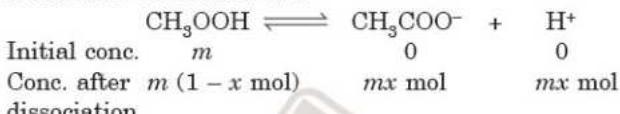
$$\text{Molality} = \frac{0.0106}{1000 \text{ g}} \times 1000 = 0.0106 \text{ mol kg}^{-1}$$

$$\text{Now, } \Delta T_f = K_f \times m \\ = 1.86 \text{ K kg mol}^{-1} \times 0.0106 \text{ mol kg}^{-1} \\ = 0.0197 \text{ K}$$

Observed freezing point depression = 0.0205 K

$$\text{Van't Hoff factor} = \frac{\text{Observed freezing point}}{\text{Calculated freezing point}} \\ = \frac{0.0205 \text{ K}}{0.0197 \text{ K}} = 1.041$$

Acetic acid dissociates as :



Total moles of particles = $m(1-x + x + x) = m(1+x)$

$$i = \frac{m(1+x)}{m} = 1.041 \\ \therefore x = 0.041$$

∴ Degree of dissociation = 0.041

$$[CH_3COOH] = m(1-x) = 0.0106 \times (1-0.041) = 0.0102$$

$$[CH_3COO^-] = mx = 0.0106 \times 0.041 = 4.35 \times 10^{-4}$$

$$[H^+] = mx = 4.35 \times 10^{-4}$$

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} \\ = \frac{(4.35 \times 10^{-4})(4.35 \times 10^{-4})}{0.0102} \\ = 1.86 \times 10^{-5}.$$

Example 66.

Calculate the freezing point depression expected for 0.0711 m aqueous solution of Na_2SO_4 . If this solution actually freezes at -0.320°C, what would be the value of Van't Hoff factor? (K_f for water is 1.86°C mol⁻¹) (D.S.B. 2009)

Solution: Freezing point depression,

$$\Delta T_f = K_f \times m \\ K_f = 1.86^\circ\text{C mol}^{-1}, m = 0.0711 \\ \Delta T_f = 1.86 \times 0.0711 = 0.132^\circ \\ \text{Observed freezing point} = 0 - (-0.320) = 0.320^\circ$$

$$\text{Van't Hoff factor} = \frac{\text{Observed freezing point}}{\text{Calculated freezing point}} \\ = \frac{0.320}{0.132} = 2.42$$

Example 67.

What mass of $NaCl$ (molar mass = 58.5 g mol⁻¹) must be dissolved in 65.0 g of water to lower the freezing point by 7.50 °C? The freezing point depression constant, K_f , for water is 1.86 K kg mol⁻¹. Assume Van't Hoff factor for $NaCl$ is 1.87. (A.I.S.B. 2011)

$$\Delta T_f = i \frac{K_f \times 1000 \times w_B}{w_A \times M_B} \\ i = 1.87$$

$$K_f = 1.86 \text{ K kg mol}^{-1}, \\ w_A = 65.0 \text{ g}, M_B = 58.5, \Delta T_f = 7.50^\circ\text{C} \\ 7.50 = 187 \times \frac{1.86 \times 1000 \times w_B}{65.0 \times 58.5} \\ w_B = \frac{7.50 \times 65.0 \times 58.5}{1.87 \times 1.86 \times 1000} \\ = 8.2 \text{ g.}$$

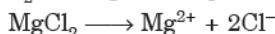
SOLUTIONS

□ Example 68.

Calculate the freezing point of solution when 1.9 g of $MgCl_2$ ($M = 95 \text{ g mol}^{-1}$) was dissolved in 50 g of water, assuming $MgCl_2$ undergoes complete ionization. (K_f for water = $1.86 \text{ K kg mol}^{-1}$) (D.S.B. 2016)

$$\text{Solution : } \Delta T_f = \frac{i \times K_f \times w_B \times 1000}{M_B \times w_A}$$

$w_B = 1.9 \text{ g}$, $w_A = 50 \text{ g}$, $M_B = 95 \text{ g mol}^{-1}$, $K_f = 1.86 \text{ Km}^{-1}$
 $MgCl_2$ undergoes complete ionization as



$$i = 3$$

$$\therefore \Delta T_f = \frac{3 \times 1.86 \times 1.9 \times 1000}{95 \times 50} \\ = 2.232 \text{ K}$$

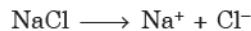
Freezing point of solution = $273 - 2.232 = 270.768 \text{ K}$

□ Example 69.

Calculate the boiling point of a solution prepared by adding 15.00 g of $NaCl$ to 250.0 g of water. (K_b for water = $0.512 \text{ K kg mol}^{-1}$ and molar mass of $NaCl$ = 58.44 g mol^{-1}). (D.S.B. 2011)

$$\text{Solution : } \Delta T_b = \frac{iK_b \times 1000 \times w_2}{w_1 \times M_2}$$

$NaCl$ dissociates as :



$$i = 2$$

$w_2 = 15.0 \text{ g}$, $w_1 = 250.0 \text{ g}$, $M_2 = 58.44 \text{ g mol}^{-1}$

$$\therefore K_b = 0.512 \text{ K kg mol}^{-1}$$

$$\therefore \Delta T_b = \frac{2 \times 0.512 \times 1000 \times 15.0}{250.0 \times 58.44} \\ = 1.05^\circ\text{C}$$

∴ Boiling point of solution = $100 + 1.05 = 101.05^\circ\text{C}$

□ Example 70.

A 1.00 molal solution of trichloroacetic acid (CCl_3COOH) is heated to its boiling point. The solution has the boiling point of 100.18°C . Determine the Van't Hoff factor for trichloroacetic acid (K_b for water = $0.512 \text{ K kg mol}^{-1}$). (D.S.B. 2012)

Solution : Observed boiling point elevation, $\Delta T_b = 100.18 - 100.0 = 0.18^\circ\text{C}$

Practice Problems

86. Decinormal solution of $NaCl$ developed an osmotic pressure of 4.6 atm at 300 K. Calculate the degree of dissociation.
87. Calculate the freezing point of a one molar aqueous solution (density 1.04 g L^{-1}) of KCl . (K_f for water = 1.86 kg mol^{-1} , atomic masses of K = 39, Cl = 35.5).
88. Calculate the boiling point of a one molar aqueous solution of KBr (density 1.06 gm L^{-1}). (K_b for water = 0.52 kg mol^{-1} , atomic masses : K = 39, Br = 80).
89. Calculate the amount of sodium chloride (electrolyte) which must be added to one kilogram of water so that the freezing point is depressed by 3K. Give K_f for water = $1.86 \text{ K kg mol}^{-1}$. (Nagaland S.B. 2017).
90. Phenol associates in benzene to form a dimer ($C_6H_5OH_2$). The freezing point of a solution containing 5 g of phenol in 250 g of benzene is lowered by 0.70°C . Calculate the degree of association of phenol in benzene. (K_f for benzene = 5.12 K m^{-1}) (Pb. S.B. 2009)

Molality of solution = 1.00 m
Calculated boiling point elevation,

$$\Delta T_b(\text{calc.}) = K_b \times m \\ = 0.512 \times 1 = 0.512$$

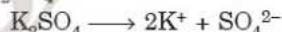
Van't Hoff factor, i

$$= \frac{\text{Observed boiling point elevation}}{\text{Calculated boiling point elevation}} \\ = \frac{0.18}{0.512} = 0.351.$$

□ Example 71.

Determine the osmotic pressure of a solution prepared by dissolving $2.5 \times 10^{-2} \text{ g}$ of K_2SO_4 in $2L$ of water at 25°C , assuming that it is completely dissociated. ($R = 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}$, Molar mass of K_2SO_4 = 174 g mol^{-1}). (D.S.B. 2013)

Solution : Since K_2SO_4 dissociates completely,



One mole of K_2SO_4 will give 3 mole particles and therefore, the value of i is 3.

Osmotic pressure, $\pi = icRT$

$$= i \frac{w_B}{M_B \times V} RT \\ = 2.5 \times 10^{-2} \text{ g}, V = 2.0 \text{ L}, M_B = 174 \\ R = 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1} \\ \therefore \pi = \frac{3 \times 2.5 \times 10^{-2} \times 0.0821 \times 298}{174 \times 2.0} \\ = 5.27 \times 10^{-3} \text{ atm.}$$

□ Example 72.

3.9 g of benzoic acid dissolved in 49 g of benzene shows a depression in freezing point of 1.62 K . Calculate the van't Hoff factor and predict the nature of solute (associated or dissociated). [Given: Molar mass of benzoic acid = 122 g mol^{-1} , K_f for benzene = $4.9 \text{ K kg mol}^{-1}$] (D.S.B. 2015)

Solution: $\Delta T_f = iK_f \times m$

$$= \frac{i \times K_f \times w_B \times 1000}{M_B \times w_A}$$

$$1.62 = \frac{i \times 4.9 \times 3.9 \times 1000}{122 \times 49}$$

$$\text{or } i = \frac{1.62 \times 122 \times 49}{4.9 \times 3.9 \times 1000} = 0.506$$

Since i is less than one, the solute is associated.

Answers to Practice Problems

86. 87%

87. -3.852°C

88. 101.106°C

89. 47.151

90. 72%

Hints & Solutions on page 66

91. 1.5 g of $\text{Ba}(\text{NO}_3)_2$ dissolved in 100 g of water shows a depression in freezing point equal to 0.28°C . What is the percentage dissociation of the salt? (K_f for water = 1.86 K/m and molar mass of $\text{Ba}(\text{NO}_3)_2$ = 261). (Pb.S.B. 2004, 2009)
92. Calculate the difference between the boiling points of 0.2 m Na_2SO_4 and 0.5 m glucose assuming complete dissociation of Na_2SO_4 . (K_b for water = 0.52 K m^{-1})
93. The freezing point of a solution containing 0.2 g of acetic acid in 20.0 g of benzene is lowered by 0.45°C . Calculate the degree of association of acetic acid in benzene. (K_f for benzene = $5.12 \text{ K mol}^{-1} \text{ kg}$) (Pb.S.B. 2004)
94. Calculate the normal freezing point of a sample of sea water containing 3.8% NaCl and 0.12% MgCl_2 by mass. (K_f for water = 1.86 K m^{-1})
95. Calculate the molality of NaCl solution whose elevation in boiling point is equal to the depression in freezing point of 0.25 m sodium carbonate solution in water assuming complete dissociation of salts. ($K_f = 1.86 \text{ K m}^{-1}$, $K_b = 0.52 \text{ K m}^{-1}$).
96. 0.01 m aqueous solution of $\text{K}_3[\text{Fe}(\text{CN})_6]$ freezes at -0.062°C . What is the apparent percentage of dissociation? (K_f for water = $1.86 \text{ K kg mol}^{-1}$) (Pb. S.B. 2002)
97. Calculate the amount of KCl which must be added to 1 kg of water so that the freezing point is depressed by 2K . (K_f for water = $1.86 \text{ K kg mol}^{-1}$) (D.S.B. 2012).
98. An aqueous solution containing 4.9 g of a solute dissolved in 500 mL of the solution shows an osmotic pressure of 2.1 atmosphere at 27°C . What is the nature of the solute (associated or dissociated, if the molar mass of the solute is 57 a.m.u.)? (Hr. S.B. 2006)
99. 0.01 M solutions of KCl and BaCl_2 are prepared in water. The freezing point of KCl is found to be -2°C . What freezing point would you expect for BaCl_2 solution assuming both KCl and BaCl_2 to be completely ionized?
100. Calculate the freezing point of an aqueous solution containing 10.50 g of MgBr_2 in 200 g of water. (Molar mass of MgBr_2 = 184, K_f for water = $1.86 \text{ K kg mol}^{-1}$) (D.S.B. 2011)

Answers to Practice Problems

91. 81%
92. 0.052
93. 94.6%
94. -2.58°C
95. 1.34 m
96. 77.7 %
97. 40.05 g
98. Associated solute
99. -3°C
100. -1.59°C

Hints & Solutions on page 66

Advanced Level

PROBLEMS

Accelerate Your Potential
(for JEE Advance)

Problem 14. A 1.2% solution (wt. /volume) of NaCl is isotonic with 7.2% solution (wt./ volume) of glucose (molar mass = 180). Calculate the degree of dissociation of NaCl solution.

Solution Let us first calculate observed molar mass of NaCl.

For isotonic solutions,

$$\pi(\text{NaCl}) = \pi(\text{urea})$$

$$\text{and } \pi = \frac{wRT}{MV}$$

Osmotic pressure of NaCl,

$$\pi(\text{NaCl}) = \frac{1.2 RT}{M \times 0.1}$$

Osmotic pressure of urea,

$$\pi(\text{urea}) = \frac{7.2 RT}{180 \times 0.1}$$

$$\text{Now, } \frac{1.2 RT}{M \times 0.1} = \frac{7.2 RT}{180 \times 0.1}$$

$$\text{or } M = \frac{180 \times 1.2}{7.2} = 30$$

Normal molar mass of NaCl = 58.5

$$i = \frac{\text{Normal molar mass}}{\text{Observed molar mass}} = \frac{58.5}{30} = 19.5$$

NaCl dissociates as :



If α is the degree of dissociation

$$\begin{array}{ccc} \text{Initial moles} & 1 & 0 \\ \text{Moles after dissociation} & 1 - \alpha & \alpha & \alpha \end{array}$$

$$\text{Total moles after dissociation} = 1 - \alpha + \alpha + \alpha = 1 + \alpha$$

$$i = \frac{\text{Moles of solute after dissociation}}{\text{Normal moles of solute}} = \frac{1 + \alpha}{1}$$

$$\text{Now, } \frac{1 + \alpha}{1} = 1.95 \\ \alpha = 1.95 - 1 = 0.95.$$

Problem 15. To 500 cm^3 of water, $3.0 \times 10^{-3} \text{ kg}$ of acetic acid is added. If 23% of acetic acid is dissociated, what will be the depression in freezing point? K_f and density of water are $1.86 \text{ K kg mol}^{-1}$ and 0.997 g cm^{-3} respectively.

Solution Volume of water = 500 cm^3

$$\text{Density of water} = 0.997 \text{ g cm}^{-3}$$

$$\text{Wt. of water} = \text{Volume} \times \text{Density}$$

$$= 500 \times 0.997 = 498.5 \text{ g}$$

$$\text{Moles of acetic acid} = \frac{3.0 \times 10^{-3} \times 1000}{60} \\ (\text{mol. wt. of } \text{CH}_3\text{COOH} = 60) \\ = 0.05$$

$$\text{Molality} = \frac{\text{Moles of acetic acid}}{\text{Wt. of water}} \times 1000 \\ = \frac{0.05 \times 1000}{498.5} = 0.1003$$

Acetic acid dissociates in water as:



Initial moles 1 0 0

If α is the degree of dissociation,

1 - α α α

Total moles after dissociation = $1 - \alpha + \alpha + \alpha = 1 + \alpha$

$$\text{Van't Hoff factor, } i = \frac{\text{Moles after dissociation}}{\text{Normal moles}}$$

$$= \frac{1 + \alpha}{1}$$

$$\alpha = 23\% = 0.23$$

$$\therefore i = \frac{1 + 0.23}{1} = 1.23$$

Now, $\Delta T_f = i K_f m$

$$= 1.23 \times 1.86 \times 0.1003 = 0.229$$

Depression in freezing point = 0.229°.

Problem 16. The freezing point of a 0.08 molal solution of NaHSO_4 is -0.372°C . Calculate the dissociation constant for the reaction:



(K_f for water = 1.86 Km^{-1})

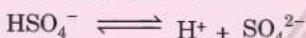
Solution NaHSO_4 dissociates as:



Since the concentration of NaHSO_4 is 0.08 m,

$$[\text{Na}^+] = 0.8 \text{ m}, \text{HSO}_4^- = 0.08 \text{ m}$$

Now, HSO_4^- also dissociates as:



If α is the degree of dissociation, then after dissociation at equilibrium,

$$[\text{HSO}_4^-] = 0.08(1 - \alpha)$$

$$[\text{H}^+] = 0.8\alpha, [\text{SO}_4^{2-}] = 0.08\alpha$$

Total concentration of all ions (i.e., Na^+ , H^+ , HSO_4^- and SO_4^{2-})

$$= 0.08 + 0.08(1 - \alpha) + 0.08\alpha + 0.08\alpha \\ = 0.16 + 0.08\alpha$$

$$\therefore \text{Van't Hoff factor } i = \frac{0.16 + 0.08\alpha}{0.08} = 2 + \alpha$$

Now, $\Delta T_f = i K_f \times m$

$$= i \times 1.86 \times 0.08 = 0.1488i$$

$$\Delta T_f = 0 - (-0.372) = 0.372$$

$$\text{or } 0.372 = 0.1488i$$

$$\text{o } i = \frac{0.372}{0.1488} = 2.5$$

$$\text{Thus, } 2 + \alpha = 2.5 \text{ or } \alpha = 0.5$$

Dissociation constant for the reaction is

$$K = \frac{[\text{H}^+][\text{SO}_4^{2-}]}{\text{HSO}_4^-}$$

$$[\text{H}^+] = 0.08 \times 0.5 = .04, [\text{HSO}_4^-] = 0.08(1 - 0.5) = .04, [\text{SO}_4^{2-}] = 0.08 \times 0.5 = 0.04 \\ K = \frac{(0.04)(0.04)}{(0.04)} = 4.0 \times 10^{-2}.$$

Problem 17. A storage battery contains a solution of H_2SO_4 38% by weight. At this concentration van't Hoff factor is 2.50. At what temperature, will the battery content freeze? (K_f for water = 1.86 Km^{-1})

Solution Weight of $\text{H}_2\text{SO}_4(w_B) = 38 \text{ g}$

Weight of water (w_A) = $100 - 38 = 62 \text{ g}$

Calculated ΔT_f ,

$$\Delta T_f = \frac{1000 \times K_f \times w_B}{w_A \times M_B} \\ = \frac{1000 \times 1.86 \times 38}{62 \times 98} = 11.633^\circ$$

Van't Hoff factor, $i = \frac{\text{Observed } \Delta T_f}{\text{Calculated } \Delta T_f}$

$$\therefore \text{Observed } \Delta T_f = i \times \text{Calculated } \Delta T_f \\ = 2.5 \times 11.633 = 29.08^\circ$$

$$\therefore \text{Freezing point of battery contents} = 273 - 29.08 \\ = 243.92 \text{ K.}$$

Problem 18. A certain mass of a substance when dissolved in 100 g of benzene lowers the freezing point by 1.06°C . The same mass of solute dissolved in 100 g water lowers the freezing point by 1.15°C . If the substance has normal molecular weight in benzene and is completely dissociated in water, into how many ions does it dissociate in water? K_f for water and benzene are 1.86 and $5.12 \text{ K kg mol}^{-1}$ respectively.

Solution ΔT_f is given as :

$$\Delta T_f = \frac{K_f \times 1000 \times w_B}{M_B \times 100}$$

Since the given solute behaves as normal in C_6H_6 and dissociates in water.

$$i = \frac{M(\text{normal})}{M(\text{observed})} = \frac{M(\text{in benzene})}{M(\text{in water})}$$

$$\text{In } \text{C}_6\text{H}_6 \quad 1.06 = \frac{5.12 \times 1000 \times w_B}{M(\text{in benzene}) \times 100} \quad \dots(i)$$

$$\text{In water} \quad 1.15 = \frac{1.86 \times 1000 \times w_B}{M(\text{in water}) \times 100} \quad \dots(ii)$$

Dividing equation (ii) by eq. (i)

$$\frac{M(\text{in benzene})}{M(\text{in water})} = \frac{1.15 \times 5.12}{1.06 \times 1.86} = 2.99$$

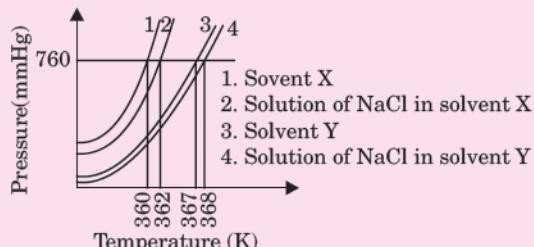
$$\text{or } i = 2.99 \approx 3$$

Since the solute is completely dissociated, $\alpha = 1$, the solute is ionised into three ions in water. If solute is A_xB_y .

$$\text{A}_x\text{B}_y = x\text{A}^+ + y\text{B}^-$$

$$x + y = 3.$$

Problem 19. The plot given below shows P-T curves (where P is the pressure and T is the temperature) for two solvents X and Y and isomolar solutions of NaCl in these solvents. NaCl completely dissociates in both the solvents.



On addition of equal number of moles of a nonvolatile solute S in equal amount (in kg) of these solvents, the elevation of boiling point of solvent X is three times that of solvent Y. Solute S is known to undergo dimerization in these solvents. If the degree of dimerization is 0.7 in solvent Y, then what is the degree of dimerization in solvent X?

(JEE Advance 2018)

Solution When NaCl is solute,

$$\begin{aligned} i &= 2 \\ \Delta T_b &= i \times K_b \times m \end{aligned}$$

For solvent X

$$\begin{aligned} \Delta T_b &= 362 - 360 = 2 \text{ K (from graph)} \\ 2 &= 2 \times (K_b)_X \times m \quad \dots(i) \end{aligned}$$

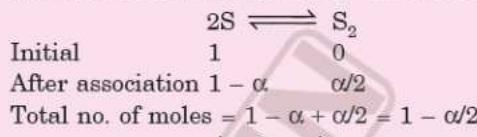
For solvent Y

$$\begin{aligned} \Delta T_b &= 368 - 367 = 1 \text{ K (from graph)} \\ 1 &= 2 \times (K_b)_Y \times m \quad \dots(ii) \end{aligned}$$

Dividing (i) by (ii)

$$\frac{(K_b)_X}{(K_b)_Y} = 2$$

Now for solute S, which dimerizes in both solvents



$$(\Delta T_b)_X = (1 - \alpha/2) (K_b)_X \times m \quad \dots(iii)$$

$$(\Delta T_b)_Y = \left(1 - \frac{0.7}{2}\right) (K_b)_Y \times m = 0.65 (K_b)_Y \times m \quad \dots(iv)$$

Elevation in boiling point in solvent X and Y

$$\frac{(\Delta T_b)_X}{(\Delta T_b)_Y} = 3 \text{ (Given)}$$

Dividing eq. (iii) by (iv) for same concentration,

$$3 = \frac{1 - \alpha/2}{0.65} \times \frac{(K_b)_X}{(K_b)_Y}$$

$$3 = \frac{1 - \alpha/2}{0.65} \times 2$$

$$1 - \alpha/2 = \frac{3 \times 0.65}{2} = 0.975$$

$$-\alpha/2 = 0.975 - 1 = -0.025$$

$$\text{or } \alpha = 0.05$$

add on

Conceptual Questions

3

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QA

- Q.1.** (i) Out of 1 M glucose and 2 M glucose, which one has a higher boiling point and why?
(ii) What happens when the external pressure applied becomes more than the osmotic pressure of solution?

- Ans.** (i) The elevation in boiling point is a colligative property and depends upon the number of moles of solute added. Higher the concentration of solute added, higher will be the elevation in boiling point. Thus, 2M glucose solution has higher boiling point than 1M glucose solution.
(ii) When the external pressure applied becomes more than the osmotic pressure of the solution, then the solvent molecules from the solution pass through the semipermeable membrane to the solvent side. This process is called reverse osmosis.

- Q.1.** Blood cells are isotonic with 0.9% sodium chloride solution. What happens if we place blood cells in a solution containing
(i) 1.2% sodium chloride solution?
(ii) 0.4% sodium chloride solution?

(A.I.S.B. 2016)

- Ans.** (i) 1.2% sodium chloride solution is hypertonic with respect to 0.9% sodium chloride solution or blood cells. When blood cells are placed in this solution, water flows out of the cells and they shrink due to loss of water by osmosis.
(ii) 0.4% sodium chloride solution is hypotonic with respect to 0.9% sodium chloride solution or blood cells. When blood cells are placed in this solution, water flows into the cells and they swell.

- Q.3.** What will happen if pressure greater than osmotic pressure is applied on the solution separated by a semipermeable membrane from the solvent?

Ans. It will result into reverse osmosis i.e., there will be net flow of the solvent from the solution to the solvent.

- Q.4.** Will the elevation in boiling point be same if 0.1 mole of sodium chloride or 0.1 mole of sugar is dissolved in 1 L of water?

- Ans.** The elevation in boiling point of 0.1 mole of NaCl and 0.1 mole of sugar dissolved in water will not be same. Elevation in boiling point is a colligative property and depends upon the number of solute particles. NaCl is ionic and give more number of particles due to ionisation than sugar which consists of molecules.
- Q.5. When dehydrated fruits and vegetables are placed in water, they slowly swell and return to original form. Why? Would a temperature increase accelerate the process? Explain.**
- Ans.** The cell walls of fruits and vegetables are semipermeable. The liquid inside the cells in the dried fruits and vegetables is more concentrated. When these dried fruits and vegetables are placed in water, water enters the fruits and vegetables due to osmosis and they swell and return to their original form. Since the increase in temperature increases the osmotic pressure ($\pi \propto T$), hence the process gets accelerated by increase in temperature.
- Q.6. Why is great care taken in intravenous injection to have comparable concentration of solutions to be injected to that of blood plasma?** (Pb. S.B. 2016)
- Ans.** During intravenous injections, the concentrations of the solution to be injected should be comparable to blood plasma. If the solution is less concentrated, its osmotic pressure will be low. The water will try to move into the red blood cells through the cell walls. As a result, cells will swell and burst. On the other hand, if the solution is more concentrated, the water in the cells will try to move outside the cell to the more concentrated solution by osmosis. This causes cells to shrink and consequently cease to function.
- Q.7. Which colligative property is preferred for the molar mass determination of macromolecules?**
- Ans.** Osmotic pressure measurement is preferred over all other colligative properties because
 - (i) even in dilute solutions, the osmotic pressure values are appreciably high and can be measured accurately.
 - (ii) osmotic pressure can be measured at room temperature. On the other hand, elevation in boiling point is measured at high temperature where the solute may decompose. The depression in freezing point is measured at low temperatures.
- Q.8. Will the depression in freezing point be same or different if 0.1 mole of sugar or 0.1 mole of glucose is dissolved in one litre of water?**
- Ans.** The depression in freezing point will be same in both the solutions because both are non-electrolytes and give same number of solute particles.
- Q.9. Outer hard shells of two eggs are removed. One of the eggs is placed in pure water and the other is placed in saturated solution of sodium chloride. What will be observed and why? (Pb. S.B. 2016)**
- Ans.** The egg placed in water will swell due to osmosis of pure water into the egg. On the other hand, the egg placed in saturated solution of NaCl will shrink due to osmosis of water out of the egg. This is because osmosis always occurs from higher concentration of solvent to lower concentration of solvent.
- Q.10. Are equimolar solutions of sodium chloride and urea isotonic? Why?** (J.K.S.B. 2013)
- Ans.** Sodium chloride gets dissociated to two ions (Na^+ and Cl^-) and exerts almost double osmotic pressure than urea (which is non-electrolyte).
- Q.11. Why is it advised to add ethylene glycol to water in a car radiator while driving in a hill station?**
- Ans.** Ethylene glycol lowers the freezing point of water and, therefore, it does not freeze in a hill station.
- Q.12. Sodium chloride solution freezes at lower temperature than water but boils at higher temperature than water. Explain.**
- Ans.** Freezing point of a liquid depresses on the addition of a non-volatile solute and therefore, a solution of sodium chloride freezes at lower temperature than freezing point of water. On the other hand, there is elevation in boiling point on the addition of a non-volatile solute and consequently boiling point of sodium chloride solution is more than that of water.
- Q.13. What is de-icing agent? How does it function?**
- Ans.** Common salt acts as a de-icing agent because it lowers the freezing point of water to such an extent that it does not freeze to form ice. Hence, it is used to clear snow from roads.
- Q.14. Why is camphor preferred as a solvent for measuring the molecular mass of naphthalene by Rast method?**
- Ans.** Camphor has a large K_f value (39.8%) and therefore, causes large depression in melting point of solution with very small amount of solute (naphthalene).
- Q.15. When mercuric iodide is added to an aqueous solution of KI the freezing point is raised. Why?** (C.B.S.E. Sample Paper 2007)

Ans. HgI_2 forms a complex with KI and therefore, the number of particles in solution decreases.



As a result, the depression in freezing point is less and hence the freezing point increases.

Q.16. Arrange the following in increasing order of freezing point:

0.2 M NaOH, 0.2M Na_2CO_3 , 0.1M AgNO₃, 0.1M $(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}$.

Ans. 0.2M $\text{Na}_2\text{CO}_3 < 0.1\text{M } (\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O} < 0.2\text{M NaOH} < 0.1\text{M AgNO}_3$

Q.17. Why does an azeotropic mixture distils without any change in composition ?

Ans. Azeotropic mixture on boiling forms vapours in the same mole fraction of the two components as present in the liquid mixture.

Q.18. Under what conditions Vant Hoff's factor 'i' is

- (i) equal to unity (ii) less than 1 and (iii) greater than 1 ?

Explain the answer

Ans. (i) When the solute does not undergo any dissociation or association in the solution i.e., for non-electrolyte solutes.

(ii) When the solute undergoes association in the solution.

(iii) When the solute undergoes dissociation in the solution.

Q.19. What would be the value of Vant Hoff's factor for a dilute solution of K_2SO_4 in water ? (A.I.S.B. 2005)

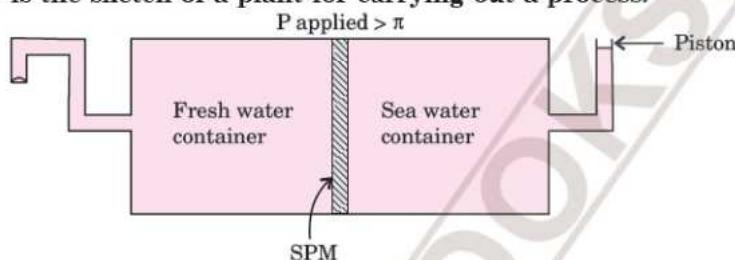
Ans. $i = 3$.

Q.20. State the condition resulting in reverse osmosis.

(A.I.S.B. 2007)

Ans. When pressure larger than osmotic pressure is applied on the solution.

Q.21. Given below is the sketch of a plant for carrying out a process.



(i) Name the process occurring in the above plant.

(ii) To which container does the net flow of solvent take place ?

(iii) Name one SPM which can be used in this plant.

(iv) Give one practical use of the plant.

(C.B.S.E. Sample Paper 2007)

Ans. (i) Reverse osmosis (ii) To fresh water container

(iii) Film of cellulose acetate (iv) This can be used as desalination plants to meet potable water requirements.

Q.22. Which of the following solutions has higher freezing point?

$0.05\text{ M }Al_2(SO_4)_3, 0.1\text{ M }K_3[Fe(CN)_6]$ Justify.

(C.B.S.E. Sample Paper 2017-18)

Ans. $0.05\text{ M }Al_2(SO_4)_3$ has higher freezing point.

$$\Delta T_f \propto i \times \text{concentration}$$

$$\text{For } 0.05\text{ M }Al_2(SO_4)_3, i = 5$$

$$\Delta T_f \propto 5 \times 0.05 = 0.25 \text{ moles of ions}$$

$$\text{For } 0.1\text{ M }K_3[Fe(CN)_6], i = 4$$

$$\Delta T_f \propto 4 \times 0.1 = 0.40 \text{ moles of ions}$$

\therefore Depression in freezing point for $0.05\text{ M }Al_2(SO_4)_3$ will be less and hence freezing point will be higher.



Solution File

Hints & Solutions for Practice Problems

1. Mass of solute (1) = $\frac{300 \times 25}{100} = 75\text{ g}$

$$\text{Mass of solute (2)} = \frac{400 \times 40}{100} = 160\text{ g}$$

$$\text{Total mass of solute} = 75 + 160 = 235\text{ g}$$

$$\text{Total mass of solution} = 300 + 400 = 700\text{ g}$$

$$\% \text{ mass of solute} = \frac{235}{700} \times 100 = 33.57\%$$

$$\% \text{ mass of solvent} = 100 - 33.5 = 66.43\%$$

2. Moles of glucose = $\frac{18}{180} = 0.1\text{ mol}$

$$\text{Molarity} = \frac{0.1}{500} \times 1000 = 0.2\text{ M}$$

Density of solution is needed to calculate the molality of the solution.

3. 10% by weight means that 10 g of glucose is present in 100 g of solution.

$$\text{Mass of solvent} = 100 - 10 = 90\text{ g}$$

$$\text{Moles of glucose} = \frac{10}{180} = 0.0556$$

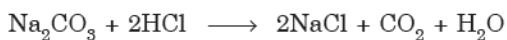
$$\text{Molality} = \frac{0.0556}{90} \times 1000 = 0.618\text{ m.}$$

4. 10% Na_2CO_3 (w/v) means 10 g of Na_2CO_3 are present in 100 mL of solution.

$$\text{Molarity of } Na_2CO_3 \text{ solution} = \frac{10 / 106}{100} \times 1000 = 0.94\text{ M}$$

Solution File

$$\text{Molarity of HCl solution} = \frac{3.65 / 36.5}{100} \times 1000 = 1 \text{ M}$$



$$\left(\frac{M_1 V_1}{1} \right)_{\text{Na}_2\text{CO}_3} = \left(\frac{M_2 V_2}{2} \right)_{\text{HCl}}$$

$$\frac{0.94 \times V_1}{1} = \frac{1 \times 100}{2}$$

$$\therefore V_1 = \frac{1 \times 100}{2 \times 0.94} = 53.19 \text{ mL}$$

5. 95% H_2SO_4 means that 95 g of H_2SO_4 is present in 100 g of solution.

$$\text{Vol. of solution} = \frac{100}{1.85} = 54.05$$

$$\text{Molarity} = \frac{95 \times 1000}{98 \times 54.05} = 17.93 \text{ M}$$

Similarly, 15% H_2SO_4 means 15 g of H_2SO_4 is present in 100 g of solution.

$$\text{Vol. of solution} = \frac{100}{1.10} = 90.91$$

$$\text{Molarity} = \frac{15 \times 1000}{98 \times 90.91} = 1.68 \text{ M}$$

Applying molarity equation,

$$M_1 V_1 = M_2 V_2$$

$$(95\% \text{H}_2\text{SO}_4) \quad (15\% \text{H}_2\text{SO}_4)$$

$$17.93 \times V_1 = 1.68 \times 100$$

$$\therefore V_1 = \frac{1.68 \times 100}{17.93} = 9.37 \text{ cm}^3 = 9.4 \text{ cm}^3$$

∴ Volume of 95% H_2SO_4 required = 9.4 cm³
Mass of 100 cm³ of 15% H_2SO_4 to be prepared
= $100 \times 1.10 = 110 \text{ g}$

Mass of 9.4 cm³ of 95% H_2SO_4 = $9.4 \times 1.85 = 17.4 \text{ g}$

∴ Mass of water to be taken = $110 - 17.4 = 92.6 \text{ g}$.

6. If 100 g is the total mass,

$$\text{Mass of ethanol} = 95 \text{ g}$$

$$\text{Moles of ethanol} = \frac{95}{46} = 2.065$$

$$\text{Moles of water} = \frac{5}{18} = 0.278$$

$$\text{Mole fraction of ethanol} = \frac{2.065}{2.065 + 0.278} = 0.88$$

$$\text{Mole fraction of water} = \frac{0.278}{2.065 + 0.278} = 0.12.$$

7. Moles of water = $\frac{2}{18} = 0.67$

$$\text{Moles of acetic acid} = \frac{108}{60} = 1.8$$

$$\text{Moles of ethanol} = \frac{92}{46} = 2.0$$

$$\text{Mole fraction of water} = \frac{0.67}{0.67 + 1.8 + 2.0} = 0.15.$$

8. 1L of N/2 HCl solution contains
= $36.5/2 = 18.25 \text{ g of HCl}$

Wt. of HCl lost on heating = 3.25 g

Wt. of HCl left after heating = $18.25 - 3.25 = 15.0 \text{ g}$

$$\text{Normality} = \frac{15.0 \times 1000}{36.5 \times 600} = 0.685 \text{ N.}$$

9. 99% H_2SO_4 means that 99 g of H_2SO_4 is present in 100 g of solution.

$$\text{Moles of } \text{H}_2\text{SO}_4 = \frac{99}{98} = 1.01 \text{ mol}$$

$$\text{Vol. of solution} = \frac{100}{1.9} = 52.63 \text{ mL}$$

$$\text{Molarity} = \frac{1.01}{52.63} \times 1000 = 19.19 \text{ M.}$$

10. Moles of urea = $\frac{3}{60} = 0.05$

$$\text{Molality} = \frac{0.05}{250} \times 1000 = 0.2 \text{ m}$$

$$\text{Moles of water} = \frac{250}{18} = 13.89$$

$$\text{Moles fraction of solute} = \frac{0.05}{13.89 + 0.05} = 0.0036.$$

11. 1 kg of water contains ethyl alcohol = 1.55 mol
2 kg of water contain ethyl alcohol = $155 \times 2 = 3.10 \text{ mol}$

$$\text{Mass of ethyl alcohol} = 3.10 \times 46 = 142.6 \text{ g}$$

12. Moles of HCl = $\frac{38}{36.5}$

$$\text{Volume of solution} = \frac{100}{1.19} = 84.03 \text{ mL}$$

$$\text{Molarity} = \frac{38/36.5}{84.03} \times 1000 = 12.39 \text{ M}$$

13. Formality = $\frac{1.24 / 248}{100} \times 1000 = 0.05 \text{ F}$

14. Moles of NaOH = $\frac{4.0}{40} = 0.1$

Volume of solution = 100 mL

Mass of solution = $100 \times 1.038 = 103.8 \text{ g}$

Mass of water = $103.8 - 4.0 = 99.8 \text{ g}$

$$\text{Moles of water} = \frac{99.8}{18} = 5.54$$

(i) Mole fraction of NaOH = $\frac{0.1}{0.1 + 5.54} = 0.018$

(ii) Molarity = $\frac{0.1}{100} \times 1000 = 1 \text{ M}$

$$\text{Molality} = \frac{0.1}{99.8} \times 1000 = 1.002 \text{ m.}$$

15. Suppose 100 mL of each solution is mixed.

Total volume of the solution = 200 mL

$$\text{Wt. of } \text{H}_2\text{SO}_4 \text{ in 30% } \text{H}_2\text{SO}_4 = \frac{100 \times 1.218 \times 30}{100} = 36.54 \text{ g}$$

Solution File

$$\text{Wt. of H}_2\text{SO}_4 \text{ in 70% H}_2\text{SO}_4 = \frac{100 \times 1.610 \times 70}{100} \\ = 112.7 \text{ g}$$

$$\text{Total wt. of H}_2\text{SO}_4 = 36.54 + 112.7 = \mathbf{149.24 \text{ g}}$$

$$\text{Wt. of water} = (100 \times 1.218 + 100 \times 1.610) - 149.24 \\ = \mathbf{133.56 \text{ g}}$$

$$\text{Molarity} = \frac{149.24 / 98}{200} \times 1000 = \mathbf{7.61 \text{ M}}$$

$$\text{Molality} = \frac{149.24 / 98}{133.56} \times 1000 = \mathbf{11.4 \text{ m.}}$$

□ 16. 18 M H₂SO₄ means 18 mole of H₂SO₄ are present in 1000 mL of solution.

$$\text{Mass of solution} = 1000 \times 1.84 = \mathbf{1840 \text{ g}}$$

$$\text{Mass of H}_2\text{SO}_4 = 18 \times 98 = 1764 \text{ g}$$

$$\text{Mass of water} = 1840 - 1764 = 76 \text{ g}$$

$$\text{Moles of water} = \frac{76}{18} = \mathbf{4.22}$$

$$\text{Mole fraction of H}_2\text{SO}_4 = \frac{18}{18 + 4.22} = \mathbf{0.81}$$

$$\text{Mass \% H}_2\text{SO}_4 = \frac{1764}{1840} \times 100 = \mathbf{95.87\%}.$$

□ 17. Gram equivalents of oxalic acid = $\frac{0.2 \times 100}{1000} = 0.02$

$$\text{Mass of oxalic acid} = 0.02 \times 63 = 1.26 \text{ g}$$

$$126 \text{ g of oxalic acid contain} = 6.02 \times 10^{23} \text{ molecules}$$

$$1.26 \text{ g of oxalic acid contain} = \frac{6.02 \times 10^{23} \times 1.26}{126} \\ = \mathbf{6.02 \times 10^{21} \text{ molecules}}$$

□ 18. Mole fraction of benzene = 0.45

$$\text{Mole fraction of chloroform} = 1 - 0.45 = 0.55$$

$$\text{Wt \% benzene} = \frac{0.45 \times 78}{0.45 \times 78 + 0.55 \times 119.5} \times 100 \\ = \mathbf{34.8}$$

□ 19. Mol. mass of Glauber's salt (Na₂SO₄.10H₂O) = 322

$$\text{Mol. mass of Na}_2\text{SO}_4 = 142$$

$$\text{Wt. of Na}_2\text{SO}_4 = \frac{142 \times 8.0575 \times 10^{-2} \times 10^3}{322} \\ = \mathbf{35.533 \text{ g}}$$

$$\text{Moles of Na}_2\text{SO}_4 = \frac{35.533}{142} = 0.25 \text{ M}$$

$$(i) \quad \text{Molarity} = \frac{0.25}{1} = 0.25 \text{ M}$$

$$(ii) \quad \text{Density} = \frac{1077.2 \text{ kg}}{m^3} = \frac{1077.2 \times 10^3 \text{ g}}{10^6 \text{ cm}^3} = 1.0772 \text{ g cm}^{-3}$$

$$\text{Mass of 1 dm}^3 \text{ of solution} = 1000 \times 1.0772 = 1077.2 \text{ g}$$

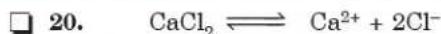
$$\text{Mass of Na}_2\text{SO}_4 = 0.25 \times 142 = 35.5$$

$$\text{Mass of water} = 1077.2 - 35.5 = 1041.7 \text{ g}$$

$$\text{Molality} = \frac{0.25}{1041.7} \times 1000 = \mathbf{0.24 \text{ m}}$$

$$(iii) \quad \text{Moles of water} = \frac{1041.7}{18} = 57.87$$

$$\text{Mole fraction of Na}_2\text{SO}_4 = \frac{0.25}{0.25 + 57.87} = \mathbf{4.3 \times 10^{-3}}$$



2 × 6.02 × 10²³ Cl⁻ ions are obtained from 1 mol of CaCl₂. 1.505 × 10²³ Cl⁻ ions are obtained from CaCl₂.

$$= \frac{1}{2 \times 6.02 \times 10^{23}} \times 1.505 \times 10^{23} = 0.125 \text{ mol}$$

$$\text{Molarity} = \frac{0.125 \times 1000}{500} = \mathbf{0.25 \text{ M.}}$$

$$\boxed{21.} \quad \text{Molarity} = \frac{\text{Mass/Molar mass}}{\text{Vol. of solution}} \times 1000$$

$$\frac{1}{5} = \frac{\text{Mass of NaOH}/40}{200} \times 1000$$

$$\text{Mass of NaOH} = \frac{1}{5} \times \frac{200 \times 40}{1000} = 1.6 \text{ g}$$

Amount of NaOH in 100 mL of solution = 5 g

Total mass of NaOH = 1.6 + 5 = 6.6 g

Total volume = 100 + 200 = 300 mL

$$\text{Molarity} = \frac{6.6/40}{300} \times 1000 = \mathbf{0.55 \text{ M.}}$$

□ 22. 2.05 M acetic acid solution means 2.05 moles of acetic acid are present in 100 mL of solution.

$$\text{Mass of solution} = 1000 \times 1.02 = 1020 \text{ g}$$

$$\text{Mass of 2.05 moles of CH}_3\text{COOH}$$

$$= 60 \times 2.05 = 123 \text{ g}$$

$$\text{Mass of water} = 1020 - 123 = 897 \text{ g}$$

$$\text{Molality} = \frac{2.05}{897} \times 1000 = \mathbf{2.29 \text{ m}}$$

□ 23. 69% HNO₃ means 69 g of HNO₃ is present in 100 g of solution.

$$\text{Vol. of solution} = \frac{100}{1.41} = 70.92 \text{ mL}$$

$$69 \text{ g of HNO}_3 \text{ is present in solution} = 70.92 \text{ mL}$$

$$23 \text{ g of HNO}_3 \text{ is present in solution} = \frac{70.92}{69} \times 23 = \mathbf{23.64 \text{ mL}}$$

□ 24. 4.27 M H₂SO₄ (aq) solution means that 4.27 mol of H₂SO₄ is present in 1000 cm³ of solution.

$$\text{Mass of solution} = 1000 \times 1.25 = 1250 \text{ g}$$

$$\text{Mass of 4.27 mol of H}_2\text{SO}_4 = 4.27 \times 98 = 418.46 \text{ g}$$

$$\text{Mass of water present} = 1250 - 418.46 = 831.54 \text{ g}$$

$$\text{Molality} = \frac{4.27 \times 1000}{831.54} = \mathbf{5.135 \text{ m}}$$

$$\boxed{25.} \quad \text{Moles of Al(NO}_3)_3 = \frac{100}{213} = 0.469 \text{ mol.}$$

$$\text{Mass of water} = 1000 \times 0.9982 = 998.2 \text{ g}$$

$$\text{Molality} = \frac{0.469}{998.2} \times 1000 = \mathbf{0.470 \text{ m}}$$

$$\text{Mass of solution} = 998.2 \text{ g H}_2\text{O} + 100 \text{ g Al(NO}_3)_3 \\ = 1098.2 \text{ g}$$

$$\text{Volume of solution} = \frac{1098.2}{0.9990} = 1099.3 \text{ cm}^3$$

$$\text{Molarity} = \frac{0.469}{1099.3} \times 1000 = \mathbf{0.427 \text{ M.}}$$

Solution File

26. Partial pressure of N₂ in atmosphere \propto mole fraction of N₂ in air

$$\begin{aligned} P_{N_2} &= 0.78 \text{ atm} = 0.78 \times 760 \text{ mm Hg} \\ &= 592.8 \text{ mm Hg} \end{aligned}$$

Now, according to Henry's law, solubility of a gas dissolved is proportional to pressure of gas

$$\begin{aligned} \text{Solubility of N}_2 &= K_H \times P_{N_2} \\ &= 8.42 \times 10^{-7} \text{ M/mm Hg} \times 592.8 \text{ mm Hg} \\ &= 4.99 \times 10^{-4} \text{ M.} \end{aligned}$$

- 27.

$$\begin{aligned} p &= K_H \cdot x \\ x &= \frac{\text{Moles of N}_2}{\text{Moles of N}_2 + \text{Moles of H}_2\text{O}} \\ &= \frac{0.02}{\frac{28}{0.02} + \frac{1000}{28}} = 1.29 \times 10^{-5} \\ p &= 1 \text{ atm} \\ K_H &= \frac{p}{x} \\ &= \frac{1}{1.129 \times 10^{-5}} = 7.75 \times 10^4 \text{ atm.} \end{aligned}$$

- 28.

$$\begin{aligned} x_2 &= \frac{p}{K_H} \\ K_H &= 1.67 \text{ k bar} = 1.67 \times 10^3 \text{ bar} \\ p &= 4 \text{ atm} = 4 \text{ bar} \\ x_2 &= \frac{4 \text{ bar}}{1.76 \times 10^3 \text{ bar}} \\ &= 2.395 \times 10^{-3} \\ x_2 &= \frac{n_2}{n_1 + n_2} = 2.395 \times 10^{-3} \\ \frac{n_2}{1000 + n_2} &= 2.395 \times 10^{-3} \\ n_2 &= 0.133 + 2.395 \times 10^{-3} n_2 \\ 0.998 n_2 &= 0.133 \\ \text{or} \quad n_2 &= 0.133 \text{ mol} \end{aligned}$$

\therefore Amount of CO₂ dissolved = $0.133 \times 44 = 5.85 \text{ g}$

29. Mass of 1L of solution = 1000 g

Mass of water = $1000 - 0.06 = 999.94 \text{ g}$

$$\begin{aligned} \text{Moles of water} &= \frac{999.94}{18} = 55.55 \\ \text{Moles of O}_2 &= \frac{0.06}{32} = 1.875 \times 10^{-3} \end{aligned}$$

$$\begin{aligned} \therefore \text{Mole fraction of O}_2, x_{O_2} &= \frac{1.875 \times 10^{-3}}{55.55 + 1.875 \times 10^{-3}} \\ &\approx \frac{1.875 \times 10^{-3}}{55.55} = 3.37 \times 10^{-5} \end{aligned}$$

$$\begin{aligned} \text{Now, } p_{O_2} &= K_H \times x_{O_2} = (46.82 \times 10^3 \text{ bar}) \times (3.37 \times 10^{-5}) \\ &= 1.58 \text{ bar.} \end{aligned}$$

30. $p_{He} = K_H \times x_{He} = (144.98 \times 10^3 \text{ bar}) \times (1.25 \times 10^{-6})$
 $= 0.181 \text{ bar}$

31. Mole fraction of A in solution = $\frac{0.095}{0.158} = 0.601$

32. Moles of ethyl acetate (CH₃COOC₂H₅) = $\frac{25}{88} = 0.284$

Moles of ethyl propionate (CH₃COOC₃H₇) = $\frac{50}{120} = 0.490$

$$\begin{aligned} \text{Mole fraction of ethyl acetate} &= \frac{0.284}{0.284 + 0.490} \\ &= 0.367 \end{aligned}$$

Mole fraction of ethyl propionate = $1 - 0.367 = 0.633$

$$\begin{aligned} \text{Vap. pressure of ethyl acetate} &= 72.8 \times 0.367 \\ &= 26.72 \text{ torr} \end{aligned}$$

Vap. pressure of ethyl propionate = $27.7 \times 0.633 = 17.53 \text{ torr}$
 Total vap. pressure = $26.72 + 17.53 = 44.25 \text{ torr.}$

33. Moles of liquid A = $\frac{28}{140} = 0.2$

$$\text{Moles of water} = \frac{72}{18} = 4.0$$

$$\text{Mole fraction of liquid A, } x_l = \frac{0.2}{0.2 + 4.0} = 0.048$$

$$\text{Mole fraction of water, } x_w = 1.0 - 0.048 = 0.952$$

$$0.210 = p_l^o x_l + p_w^o x_w$$

$$0.210 = p_l^o \times 0.048 + 0.198 \times 0.952$$

$$p_l^o = \frac{0.210 - 0.198 \times 0.952}{0.048} = 0.448 \text{ bar.}$$

34. Let the weight of benzene and toluene in the solution = w gram.

$$\text{Moles of benzene} = \frac{w}{78} \quad (\text{Molar mass} = 78)$$

$$\text{Moles of toluene} = \frac{w}{92} \quad (\text{Molar mass} = 92)$$

$$\text{Mole fraction of benzene, } x_b = \frac{\frac{w}{78}}{\frac{w}{78} + \frac{w}{92}} = 0.541$$

$$\text{Mole fraction of toluene, } x_t = 1 - 0.541 = 0.459$$

Partial vapour pressure of benzene,

$$p_b = p_b^o \times x_b = 150 \times 0.541 = 81.15 \text{ torr}$$

$$\begin{aligned} \text{Partial vapour pressure of toluene, } p_t &= p_t^o \times x_t = 50 \times 0.459 \\ &= 22.95 \text{ torr} \end{aligned}$$

$$\begin{aligned} \text{Total vapour pressure of solution} &= 81.15 + 22.95 \\ &= 104.1 \text{ torr.} \end{aligned}$$

35. Moles of ethanol = $\frac{60}{46} = 1.304$

$$\text{Moles of methanol} = \frac{40}{32} = 1.250$$

$$\text{Mole fraction of ethanol} = \frac{1.304}{1.304 + 1.250} = 0.51$$

$$\text{Mole fraction of methanol} = 1 - 0.51 = 0.49$$

$$p(\text{ethanol}) = 44.5 \times 0.51 = 22.69 \text{ mm Hg}$$

$$p(\text{methanol}) = 88.7 \times 0.49 = 43.46 \text{ mm Hg}$$

Solution File

$$\begin{aligned}\text{Total vapour pressure} &= 22.69 + 43.46 \\ &= \mathbf{66.15 \text{ mm Hg}}\end{aligned}$$

Mole fraction methanol in vapour phase

$$\begin{aligned}&= \frac{p(\text{methanol})}{\text{Total vapour pressure}} \\ &= \frac{43.46}{66.15} = \mathbf{0.657}.\end{aligned}$$

36. Moles of methanol = $\frac{32}{32} = 1$

$$\text{Moles of ethanol} = \frac{23}{46} = 0.5$$

$$\text{Mole fraction of methanol} = \frac{1}{1+0.5} = 0.67$$

$$\text{Mole fraction of ethanol} = \frac{0.5}{1+0.5} = 0.33$$

$$\begin{aligned}\text{Partial vapour pressure of methanol} &= 90 \times 0.67 \\ &= 60.3 \text{ mm Hg}\end{aligned}$$

$$\begin{aligned}\text{Partial vapour pressure of ethanol} &= 51 \times 0.33 \\ &= 16.8 \text{ mm Hg}\end{aligned}$$

$$p(\text{total}) = 60.3 + 16.8 = \mathbf{77.1 \text{ mm Hg}.}$$

37. Let x_A and x_B are the mole fractions of liquids A and B in the solution, then

$$p_A = p_A^\circ x_A = 22 x_A$$

$$p_B = p_B^\circ x_B = p_B^\circ (1 - x_A) = 75 (1 - x_A)$$

$$p_A + p_B = 22x_A + 75(1 - x_A) = 48.5$$

$$\therefore x_A = 0.5$$

Thus, the solution contains **equal moles of both liquids A and B.**

38. Let the mole fraction of A = x

$$\text{Mole fraction of B} = 1 - x$$

$$0.658 x = 0.264 (1 - x)$$

$$\text{or } x = \mathbf{0.286}$$

39. Since solution is equimolar,

Mole fraction of X = 0.5, Mole fraction of Y = 0.5

$$\begin{aligned}p_{\text{total}} &= p_x + p_y = 200 \times 0.5 + 100 \times 0.5 \\ &= 150\end{aligned}$$

$$\text{Mole fraction of X in vapour phase} = \frac{100}{150} = \mathbf{0.67}$$

40. For CH_3OH , $x = 1$

$$\therefore P = 119 + 135 = \mathbf{254 \text{ mm Hg}}$$

For $\text{C}_2\text{H}_5\text{OH}$, $x = 0$

$$\therefore P = 119 \times 0 + 135 = \mathbf{135 \text{ mm Hg}.}$$

41. $\frac{p_A^\circ - p_A}{p_A^\circ} = \frac{w_B \times M_A}{M_B \times w_A}$

$$p_A^\circ = 23.8 \text{ mm}, w_B = 30 \text{ g}, w_A = 846 \text{ g}$$

$$M_B = 60 \text{ g mol}^{-1}, M_A = 18 \text{ g mol}^{-1}$$

$$\frac{23.8 - p_A}{23.8} = \frac{30 \times 18}{60 \times 846}$$

$$23.8 - p_A = \frac{30 \times 18 \times 23.8}{60 \times 846} = 0.2532$$

$$p_A = 23.8 - 0.2532 = \mathbf{23.55 \text{ mm Hg}}$$

42. Mole fraction of solute = $\frac{1}{1+1000/18} = \mathbf{0.0177}$

$$\frac{12.3 - p_A}{12.3} = 0.0177 \therefore p_A = \mathbf{12.08 \text{ kPa}}$$

43. Moles of sucrose = $\frac{68.4}{342} = 0.2$

$$\text{Moles of water} = \frac{1000}{18} = 55.56$$

$$\text{Mole fraction of sucrose} = \frac{0.2}{0.2 + 55.56} = 0.0036$$

(i) Relative lowering of vapour press. = Mole fraction of solute = **0.0036**

(ii) $\frac{p_A^\circ - p_A}{p_A^\circ} = 0.0036 \text{ or } \frac{17.5 - p_A}{17.5} = 0.0036$

$$\therefore p_A = 17.437 \text{ mm Hg}$$

44. $\frac{262 - 256}{262} = \frac{2}{M_B} \times \frac{78}{100}$

(Mol. wt. of benzene = 78)

$$M_B = \frac{2 \times 78 \times 262}{100 \times 6} = \mathbf{68.12 \text{ g mol}^{-1}.}$$

45. Let mole fraction of liquid A in solution = x_A

Mole fraction of liquid B in solution, $x_B = 1 - x_A$

$$p = p_A^\circ x_A + p_B^\circ x_B \text{ or } = p_A^\circ x_A + p_B^\circ (1 - x_A)$$

$$p = 600 \text{ mm Hg}$$

$$600 = 450 x_A + 700 (1 - x_A)$$

$$\text{Solving } x_A = \frac{100}{250} = 0.4$$

$$\text{Mole fraction of liquid A} = 0.4$$

$$\text{Mole fraction of liquid B} = 1 - 0.4 = 0.6$$

Calculation of composition of vapour phase

$$p_A = p_A^\circ x_A = 450 \text{ mm} \times 0.4 = 180 \text{ mm}$$

$$p_B = p_B^\circ x_B = 700 \times 0.6 = 420 \text{ mm}$$

$$p_{\text{total}} = p_A + p_B = 180 + 420 = 600 \text{ mm}$$

$$y_A = \frac{p_A}{p_{\text{total}}} = \frac{180}{600} = 0.3$$

$$y_B = \frac{p_B}{p_{\text{total}}} = \frac{420}{600} = 0.7.$$

46. $\frac{p_A^\circ - p_A}{p_A^\circ} = \frac{w_B \times M_A}{w_A \times M_B}$

$$w_B = 5.0 \text{ g}, w_A = 100 - 5.0 = 95 \text{ g}$$

$$p_A^\circ = 760 \text{ mm}, p_A = 745 \text{ mm}$$

$$\frac{760 - 745}{760} = \frac{5.0 \times 18}{95 \times M_B}$$

$$\text{Solving } M_B = \mathbf{48 \text{ g mol}^{-1}.}$$

Solution File

47. $\frac{23.76 - 22.98}{23.56} = x_B$

or $x_B = 0.038$

Now for the dilute solution,

$$x_B = \frac{n_B}{n_A} \quad \dots(i)$$

$$\text{Molality, } m = \frac{n_B}{w_A} \times 1000 \quad \dots(ii)$$

Dividing eq. (ii) by eq. (i),

$$\begin{aligned} \frac{m}{x_B} &= \frac{1000}{w_A} \times n_A = \frac{1000}{w_A} \times \frac{w_A}{18} \\ m &= x_B \times \frac{1000}{18} = \frac{0.038 \times 1000}{18} \\ &= 1.83 \text{ m.} \end{aligned}$$

48. Let the initial pressure of solvent, $p_A^\circ = p$

$$\text{Pressure of solution} = p - \frac{25}{100} p = \frac{3}{4} p$$

$$\frac{p - 3/4 p}{p} = \frac{\frac{w_B}{60}}{\frac{w_B + 100}{60 + 18}}$$

or $w_B = 111 \text{ g}$

$$\text{Now, molality, } m = \frac{111/60 \times 1000}{100} = 18.5 \text{ m.}$$

49. $w_A = 90 \text{ g. } w_B = 10 \text{ g}$

$$\frac{p_A^\circ - p_A}{p_A^\circ} = \frac{w_B \times M_A}{w_A \times M_B}$$

$$\frac{55.3 - p_A}{55.3} = \frac{10 \times 18}{90 \times 60} = 0.0333$$

$$55.3 - p_A = 1.84$$

$$\therefore p_A = 53.46 \text{ mm Hg.}$$

50. Lowering in vapour pressure,

$$\begin{aligned} p_A^\circ - p_A &= 0.0231 - 0.0228 \\ &= 0.0003 \text{ bar} \end{aligned}$$

$$\frac{p_A^\circ - p_A}{p_A^\circ} = \frac{w_B M_A}{w_A M_B} \text{ (For dilute solutions)}$$

$$\frac{0.0003}{0.0231} = \frac{108.24 \times 18}{1000 \times M_B}$$

or $M_B = \frac{108.24 \times 0.0231 \times 18}{0.0003 \times 1000} = 150.0.$

51. $\Delta T_b = 36.86 - 35.60 = 1.26^\circ\text{C}, K_b = 2.02 \text{ K m}^{-1}$

$$M_B = \frac{2.02 \times 8 \times 1000}{1.26 \times 100} = 128.25.$$

52. $M_B = \frac{K_b \times w_B \times 1000}{\Delta T_b \times w_A}$

$$= \frac{2.62 \times 1.5 \times 1000}{0.268 \times 100} = 146.6.$$

53. $\Delta T_b = \frac{K_b \times w_B \times 1000}{M_B \times w_A}$

$$= \frac{0.52 \times 18 \times 1000}{180 \times 1000} = 0.052.$$

Boiling point of solution

$$= 373.15 + 0.052 = 373.202 \text{ K}$$

54. $\Delta T_b = 100.52 - 100 = 0.52, w_A = 20 \text{ ml} = 20 \text{ g}$

(assuming density = 1 g ml⁻¹)

$$M_B = \frac{0.52 \times 3 \times 1000}{0.52 \times 20} = 150.$$

55. Calculation of K_b :

$$\begin{aligned} K_b &= \frac{\Delta T_b \times w_A \times M_B}{1000 \times w_B} \\ &= \frac{0.402 \times 50 \times 128}{1000 \times 0.513} = 5.02 \text{ K m}^{-1} \\ M_B &= \frac{5.02 \times 0.625 \times 1000}{0.650 \times 50} = 96.54 \end{aligned}$$

56. $M_B = \frac{2.53 \times 10 \times 1000}{1 \times 1000} = 253$

57. $\Delta T_b = \frac{K_b \times w_B \times 1000}{M_B \times w_A}$

$$= \frac{1.15 \times 5 \times 1000}{60 \times 75} = 1.28^\circ$$

58. $M_B = \frac{0.52 \times 12.5 \times 1000}{0.70 \times 175} = 53.06$

59. For sucrose solution,

$$K_f = \frac{\Delta T_f \times w_A \times M_B}{w_B \times 1000}$$

$$\Delta T_f = 273.15 - 269.15 = 4.0, w_B = 10, w_A = 100 - 10 = 90$$

$$K_f = \frac{4.0 \times 90 \times 342}{10 \times 100} = 12.31 \text{ Km}^{-1}$$

For glucose solution,

$$w_B = 10, w_A = 100 - 10 = 90 \text{ g}$$

$$M_B = 180$$

$$\Delta T_f = \frac{12.31 \times 10 \times 1000}{90 \times 180}$$

$$= 7.6 \text{ K}$$

$$\text{Freezing point of glucose solution} = 273.15 - 7.6 = 265.55 \text{ K}$$

60. $\Delta T_f = \frac{K_f \times 1000 \times w_B}{w_A \times M_B}$

$$0.48 = \frac{5.12 \times 1000 \times w_B}{75 \times 256}$$

$$w_B = \frac{0.48 \times 75 \times 256}{5.12 \times 1000} = 1.8 \text{ g}$$

61. $M_B = \frac{K_f \times 1000 \times w_B}{\Delta T_f \times w_A}$

$$K_f = 1.86 \text{ K kg mol}^{-1}, w_B = 18 \text{ g}, w_A = 200 \text{ g},$$

$$\Delta T_f = 273.15 - 272.07 = 1.08^\circ$$

$$M_B = \frac{1.86 \times 1000 \times 18}{1.08 \times 200} = 155 \text{ g mol}^{-1}$$

Solution File

62.
$$M_B = \frac{K_f \times w_B \times 1000}{\Delta T_f \times w_A}$$

$$= \frac{5.12 \times 1.0 \times 1000}{0.40 \times 50} = 256 \text{ g mol}^{-1}$$

63.
$$M_B = \frac{3.83 \times 2.56 \times 1000}{1000 \times 0.383} = 256$$

If formula of sulphur is S_x

$$32 \times x = 256 \quad \therefore x = 8$$

Molecular formula = S_8 .

64.
$$w_B = \frac{\Delta T_f \times w_A \times M_B}{K_f \times 1000}$$

$$= \frac{10 \times 5500 \times 62}{1.86 \times 1000} = 1833.3 \text{ g}$$

or

$$= 1.833 \text{ kg.}$$

65. For urea, $M_B = \frac{K_f \times 7.5 \times 1000}{\Delta T_f \times 100} = 60$

For X, $M'_B = \frac{K_f \times 42.75 \times 1000}{\Delta T_f \times 100}$

Dividing, $\frac{60}{M'_B} = \frac{7.5}{42.75}$ or $M'_B = 342$.

66. $M_B = \frac{K_f \times w_B \times 1000}{w_A \times \Delta T_f} = \frac{1.86 \times 30.0 \times 1000}{800 \times 1.16}$
 $M_B = 60.1$

$$n = \frac{\text{Mol. formula mass}}{\text{Empirical formula mass}} = \frac{60}{30} = 2$$

Molecular formula = $(CH_2O)_2 = C_2H_4O_2$

67. $w_B = 30 \text{ g}$, $w_A = 70 \text{ g}$, $K_f = 1.86 \text{ Km}^{-1}$, $M_B = 62$
 $\Delta T_f = \frac{1.86 \times 30 \times 1000}{62 \times 70} = 12.86$.

The solution will freeze at -12.86°C and therefore, it will be suitable.

68. $\Delta T_f = 273 - 272.07 = 0.93^\circ$

$$m = \frac{\Delta T_f}{K_f} = \frac{0.93}{1.86} = 0.5 \text{ m}$$

$$\Delta T_b = K_b \times m = 0.512 \times 0.5 = 0.256$$

Boiling point of solution = $373 + 0.256 = 373.256 \text{ K}$.

69. $\Delta T_b = 101.128 - 100 = 1.128^\circ$

$$m = \frac{\Delta T_b}{K_b} = \frac{1.128}{0.512} = 2.203 \text{ m}$$

$$\Delta T_f = K_f \times m = 1.86 \times 2.203 = 4.1$$

Freezing point of solution = $0 - 4.1 = -4.1^\circ \text{C}$.

70. $w_B = \frac{\Delta T_f \times w_A \times M_B}{K_f \times 1000}$

$$\Delta T_f = 0 - (-10) = 10^\circ$$

$$\therefore w_B = \frac{10 \times 1 \times 10^3 \times 62}{1.86 \times 1000} = 333.3 \text{ g.}$$

71. $\pi = \frac{68.4 \times 0.082 \times 300}{342 \times 1} = 4.92 \text{ atm.}$

72. $M_B = \frac{w_B RT}{\pi V} = \frac{3.5 \times 0.0821 \times 310}{25/760 \times 50/1000} = 54159.7$

73. Solution constant, $R = \frac{M_B \pi V}{w_B \times T} = 0.082 \text{ L atm mol}^{-1} \text{ K}^{-1}$.

74. Total volume after mixing = $100 + 100 = 200 \text{ cm}^3 = 0.2 \text{ L}$

$$\pi (\text{urea}) = \frac{1.5 \times 0.082 \times 293}{60 \times 0.2} = 3.0 \text{ atm}$$

$$\pi (\text{sugar}) = \frac{3.42 \times 0.082 \times 293}{342 \times 0.2} = 1.20 \text{ atm.}$$

$$\pi (\text{solution}) = 3.0 + 1.2 = 4.2 \text{ atm.}$$

75. $M_B = \frac{w_B RT}{\pi \times V} = \frac{3.0 \times 0.083 \times 300}{2 \times 1} = 37.35$

76. Total moles = $\frac{10}{180} + \frac{10}{342} = 0.085$
 $\pi = \frac{0.085 \times 0.083 \times 298}{1} = 2.10 \text{ bar.}$

77. $\pi = \frac{nRT}{V}$

$$\pi (\text{glycerine}) = \frac{10.2}{M} \times \frac{RT}{1}$$

$$\pi (\text{glucose}) = \frac{2}{180} \times \frac{RT}{0.1}$$

$$\frac{10.2 \times RT}{M \times 1} = \frac{2}{180} \times \frac{RT}{0.1}$$

$$M = \frac{10.2 \times 180 \times 0.1}{2} = 91.8 \text{ g mol}^{-1}$$

78. $\frac{5 \times RT}{342 \times 0.1} = \frac{0.877 \times RT}{M \times 0.1}$

$$M = 59.99 \text{ g mol}^{-1}$$

79. Let wt. of sugar = w g per litre

$$\frac{w \times R}{342 \times 1} = \frac{6}{60} \times \frac{RT}{1}$$

$$w = 34.2 \text{ g/litre.}$$

80. $M_B = \frac{w_B RT}{\pi \times V} = \frac{7 \times 0.083 \times 310}{3.3 \times 10^{-2} \times 0.1} = 54579.$

81. $M_B = \frac{0.52 \times 68.4 \times 1000}{0.104 \times 1000} = 342$

$$\pi = \frac{68.4 \times 0.082 \times 293}{342 \times 1} (V = 1000 \text{ g} = 1 \text{ L}) = 4.80 \text{ atm.}$$

Solution File

82. $\Delta T_b = 100.104 - 100 = 0.104^\circ$

$$M_B = \frac{0.52 \times 34.2 \times 1000}{0.104 \times 500} = 342.$$

$$\Delta T_f = \frac{1.87 \times 34.2 \times 1000}{342 \times 500} = 0.374$$

∴ Freezing point = -0.374°C .

83. $c = \frac{\pi}{RT} = \frac{7.7}{0.0821 \times 313} = 0.30 \text{ mol L}^{-1}$

Assuming molar concentration as equal to molality

$$m = 0.30, K_f = 1.86 \text{ }^\circ\text{C m}^{-1}$$

$$\Delta T_f = K_f \times m = 1.86 \times 0.30 = 0.558^\circ$$

$$\begin{aligned} \text{Freezing point of blood} &= 0 - 0.558 \\ &= -0.558 \text{ }^\circ\text{C}. \end{aligned}$$

84. $\pi(\text{blood}) = \pi(\text{glucose solution}) = 8.21 \text{ atm.}$

Now, $\pi V = nRT$ or $n = \frac{\pi V}{RT}$

$$n = \frac{8.21 \times 1.0}{0.0821 \times 310} = \frac{10}{31}$$

$$\text{Weight of glucose} = \frac{10}{31} \times 180 = 58.06 \text{ g.}$$

85. $\pi = cRT = \frac{w_2}{M_2 V} RT$ or $M_2 = \frac{w_2 RT}{\pi V}$

$$w_2 = 2.5 \text{ g}, R = 0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1}$$

$$T = 273 + 27 = 300 \text{ K}$$

$$\pi = \frac{25}{760} \text{ atm}, V = \frac{600}{1000} \text{ L}$$

$$M_2 = \frac{(2.5 \text{ g} \times 0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1}) \times (300 \text{ K})}{\left(\frac{25}{760} \text{ atm}\right) \times \left(\frac{600}{1000} \text{ L}\right)}$$

$$= 3119.8 \text{ g mol}^{-1}.$$

86. $\pi = 0.1 \times 0.082 \times 300 = 2.46$

$$i = \frac{4.6}{2.46} = 1.87$$

$$1.87 = \frac{1+\alpha}{1} \text{ or } \alpha = 87\%.$$

87. 1 molar solution means that 1 mole of KCl is dissolved in 1000 mL of solution.

$$\text{Mass of solution} = 1000 \times 1.04 = 1040 \text{ g}$$

$$\text{Mass of KCl} = 74.5 \text{ g}$$

$$\text{Mass of water} = 1040 - 74.5 = 965.5 \text{ g}$$

$$\text{Molality of solution} = \frac{1}{965.5} \times 1000 = 1.0357 \text{ m}$$

Since KCl is strong electrolyte, $i = 2$

$$\begin{aligned} \Delta T_f &= i K_f \times m \\ &= 2 \times 1.86 \times 1.0357 = 3.852^\circ \end{aligned}$$

Freezing point of solution = $0 - 3.852 = -3.852^\circ\text{C}$.

88. Molar mass of KBr = $39 + 80 = 119$

$$\text{Amount of KBr} = 119 \text{ g}$$

$$\text{Mass of solution} = 1000 \times 1.06 = 1060 \text{ g}$$

$$\text{Mass of water} = 1060 - 119 = 941 \text{ g}$$

$$\text{Molality of solution} = \frac{1}{941} \times 1000 = 1.063^\circ$$

Since KBr is a strong electrolyte, $i = 2$

$$\begin{aligned} \Delta T_b &= i \times K_b \times m \\ &= 2 \times 0.52 \times 1.063 = 1.106^\circ \end{aligned}$$

Boiling point of solution = $100 + 1.106 = 101.106^\circ\text{C}$.

89. Since NaCl undergoes complete dissociation as:



One mole of NaCl will give 2 mole particles and the value of i will be equal to 2.

$$\Delta T_f = i K_f m$$

$$K_f = 1.86 \text{ Km}^{-1}, \Delta T_f = 3 \text{ K}, i = 2$$

$$\therefore 3 = 2 \times 1.86 \times m$$

$$\text{or } m = \frac{3}{2 \times 1.86} = 0.806 \text{ mol/kg}$$

Grams of NaCl = $0.806 \times 58.5 = 47.151 \text{ g per kg}$

90. $M_B(\text{observed}) = \frac{5.12 \times 1000 \times 5}{250 \times 0.70} = 146.3$

Molar mass of phenol (C_6H_5OH) = 94

$$i = \frac{94}{146.3} = 0.64$$



Initial	1	0
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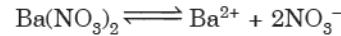
After association	$1 - \alpha$	$\alpha/2$
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$$i = \frac{1 - \alpha + \alpha/2}{1} = \frac{1 - \alpha/2}{1} = 0.64$$

$$\alpha = 72\%$$

91. $M_B(\text{observed}) = \frac{1.86 \times 1000 \times 1.5}{0.280 \times 100} = 99.64$

$$i = \frac{261}{99.64} = 2.62$$



Initial	1	0	0
After dissociation	$1 - \alpha$	α	2α
	$i = \frac{1 - \alpha + \alpha + 2\alpha}{1} = 2.62$		

$$\alpha = 81\%$$

92. $\Delta T_b(\text{glucose}) = 0.52 \times 0.5 = 0.26$

$$T_b = 100.26$$

$$\Delta T_b(Na_2SO_4) = 3 \times 0.52 \times 0.2 = 0.312$$

$$T_b = 100.312$$

Difference in boiling point = $100.312 - 100.26 = 0.052^\circ$.

93. $M_B(\text{observed}) = \frac{5.12 \times 0.2 \times 1000}{20 \times 0.45} = 113.78$

$$i = \frac{60}{113.78} = 0.527$$



Initial	1	0
After dissociation	$1 - \alpha$	$\alpha/2$

$$i = \frac{1 - \alpha + \alpha/2}{1} = \frac{1 - \alpha/2}{1} = 0.527$$

$$\alpha = 94.6\%$$

Solution File

94. Moles of NaCl = $3.8/58.5 = 0.065$
 Moles of MgCl₂ = $0.12/95 = 0.00126$
 $\text{NaCl} \longrightarrow \text{Na}^+ + \text{Cl}^-$ (2 particles)
 $\text{MgCl}_2 \longrightarrow \text{Mg}^{2+} + 2\text{Cl}^-$ (3 particles)
 Total moles of all species = $2 \times 0.065 + 3 \times 0.00126$
 $= 0.1338 \text{ mol}$
 Mass of water in 100 g of sea water = $100 - (3.8 + 0.12)$
 $= 96.08 \text{ g}$
 Molality = $\frac{0.1338}{96.08} \times 1000 = 1.39 \text{ m}$
 $\Delta T_f = 1.86 \times 1.39 = 2.59$
 Freezing point = -2.59°C
95. $\text{NaCl} \longrightarrow \text{Na}^+ + \text{Cl}^-$ ($i = 2$)
 $\text{Na}_2\text{CO}_3 \longrightarrow 2\text{Na}^{2+} + \text{CO}_3^{2-}$ ($i = 3$)
 $\Delta T_b(\text{NaCl}) = \Delta T_b(\text{Na}_2\text{CO}_3)$
 $i \times K_b \times m = i \times K_f \times m$
 $2 \times 0.52 \times m = 3 \times 1.86 \times 0.25$
 $m = 1.34 \text{ m.}$
96. $(\Delta T_f)_{\text{cal}} = 1.86 \times 0.01 = 0.0186$
 $i = \frac{0.062}{0.0186} = 3.33$
 $\text{K}_3[\text{Fe}(\text{CN})_6] \rightleftharpoons 3\text{K}^+ + [\text{Fe}(\text{CN})_6]^{3-}$

Initial	1	0	0
After dissociation	$1 - \alpha$	3α	$\alpha/2$

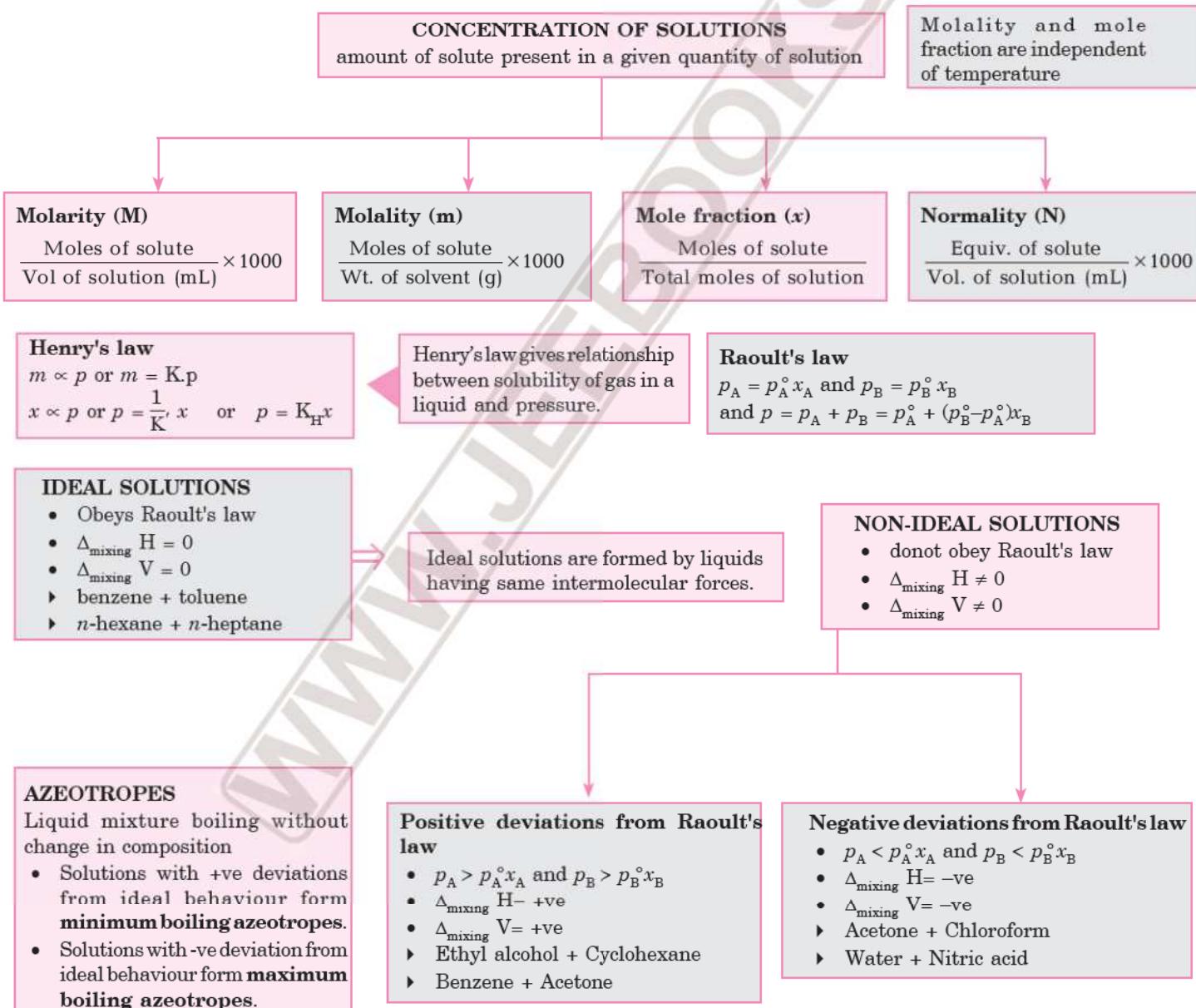
 $i = \frac{1 + 3\alpha}{1} = 3.33$
 $\therefore \alpha = 77.7\%$
97. Since KCl undergoes complete dissociation as:
 $\text{KCl} \longrightarrow \text{K}^+ + \text{Cl}^-$
 One mole of KCl will give 2 mole particles and the value of ' i ' will be equal to 2.
- $\Delta T = i K_f m$
 $K_f = 1.86 \text{ K kg mol}^{-1}, \Delta T_f = 2\text{K}, i = 2$
 $\therefore 2 = 2 \times 1.86 \times m$
 or $m = \frac{2}{2 \times 1.86} = 0.5376 \text{ mol/kg}$
 Grams of KCl = $0.5376 \times 74.5 = 40.05 \text{ g per kg}$
98. $M_B = \frac{w_B RT}{\pi \times V}$
 $= \frac{4.9 \times 0.082 \times 300}{2.1 \times 0.5} = 114.8$
- Since, observed molar mass is more than the theoretical molar mass, the solute is associated in nature.
99. i for KCl = 2, i for BaCl₂ = 3
 $\Delta T_f(\text{KCl}) = 2 \times K_f \times 0.01$
 $\Delta T_f(\text{BaCl}_2) = 3 \times K_f \times 0.01$
 $\frac{\Delta T_f(\text{KCl})}{\Delta T_f(\text{BaCl}_2)} = \frac{2}{3}$
 $\therefore \Delta T_f(\text{BaCl}_2) = \frac{3}{2} \times \Delta T_f(\text{KCl}) = \frac{3}{2} \times 2 = 3^\circ$
 \therefore Freezing point of BaCl₂ = -3°C.
100. For MgBr₂,
 $\text{MgBr}_2 \longrightarrow \text{Mg}^{2+} + 2\text{Br}^-$
 $i = 3$
 $\Delta T_f = \frac{i \times K_f \times w_B \times 1000}{w_A \times M_B}$
 $= \frac{3 \times 1.86 \times 10.50 \times 1000}{200 \times 184}$
 $= 1.59$
 Freezing point = $0 - 1.59^\circ \text{C}$
 $= -1.59^\circ \text{C.}$

Key Terms & Laws

- **Vapour pressure.** It is the pressure exerted by the vapours above the liquid surface in equilibrium with the liquid at a given temperature.
- **Henry's law.** The mass of a gas dissolved in a given volume of the liquid at a given temperature is directly proportional to the pressure of the gas in equilibrium with the solution.
- **Raoult's law.** At a given temperature, for a solution of volatile liquids, the partial vapour pressure of each component in solution is equal to the product of the vapour pressure of the pure component and its mole fraction.
- **Ideal solution.** The solution which obeys Raoult's law exactly over the entire range of concentration.
- **Non-ideal solution.** The solution which does not obey Raoult's law.
- **Azeotropes.** The solutions (liquid mixtures) which boil at constant temperature and can distil unchanged in composition are called azeotropes.

- Colligative properties.** These are the properties of the solutions which depend only on the number of solute particles but not on the nature of the solute.
- Osmosis.** It is the phenomenon of the flow of solvent through a semipermeable membrane from pure solvent to the solution.
- Osmotic pressure.** It is the excess pressure which must be applied to a solution to prevent the passage of solvent into it through a semipermeable membrane.
- Isotonic solutions.** The solutions having the same osmotic pressure at the same temperature are isotonic solutions.
- Van't Hoff factor.** It is the ratio of the normal molar mass to the observed molar mass of solute or it is the ratio of the observed colligative property to the normal colligative property.

QUICK CHAPTER ROUND UP



COLLIGATIVE PROPERTIES
depend only on the number of solute particles

Relative lowering in vapour pressure : $\frac{p_A^\circ - p_A}{p_A^\circ} = x_B$ and $M_B = \frac{w_B \times M_A}{w_A \left(\frac{p_A^\circ - p_A}{p_A^\circ} \right)}$

Elevation in boiling point : $\Delta T_b = K_b \times m$, $M_B = \frac{K_b \times w_B \times 1000}{\Delta T_b \times w_A}$
and $K_b = \frac{MRT_b^2}{\Delta H_{vap} \times 1000}$

Depression in freezing point : $\Delta T_f = K_f \times m$, $M_B = \frac{K_f \times w_B \times 1000}{\Delta T_f \times w_A}$
and $K_f = \frac{MRT_f^2}{\Delta H_{fusion} \times 1000}$

Osmotic pressure : $\pi = cRT = \frac{n}{V}RT$ and $M_B = \frac{w_B RT}{\pi V}$.
 $i = \frac{\text{Observed colligative property}}{\text{Normal colligative property}}$

- In osmosis, there is net flow of solvent from solvent to the solution or from less concentrated solution to more concentrated solution through the semi-permeable membrane.
- The common semi-permeable membrane used in the laboratory is copper ferrocyanide, $Cu_2[Fe(CN)_6]$.

- The solutions having same osmotic pressure are called **isotonic solutions**.
- If a solution has more osmotic pressure than some other solution, it is called **hypertonic**.
- A solution having less osmotic pressure than the other is called **hypotonic solution**.

- The reverse osmosis process can be used for **desalination** of sea water.

Van't Hoff factor

$$i = \frac{\text{Normal molar mass}}{\text{Observed molar mass}} = \frac{\text{Observed colligative property}}{\text{Normal colligative property}}$$

- If observed colligative property < normal colligative property
or observed molar mass > normal molar mass.
 \Rightarrow *the solute is associated.*
- If observed colligative property > normal colligative property
or observed molar mass < normal molar mass
 \Rightarrow *the solute is dissociated.*

- For solutes which do not undergo association or dissociation,
 $i = 1$
- For solutes undergoing **association**,
 $i < 1$
- For solutes undergoing **dissociation**,
 $i > 1$

Colligative Properties for solutes undergoing association or dissociation

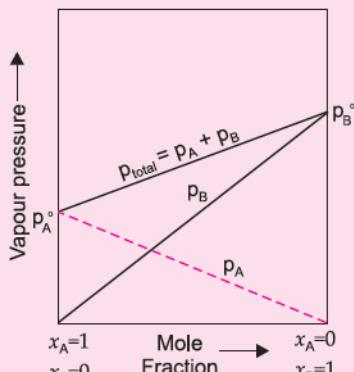
$$\frac{p_A^\circ - p_A}{p_A^\circ} = i x_B$$

$$\Delta T_f = i K_f m$$

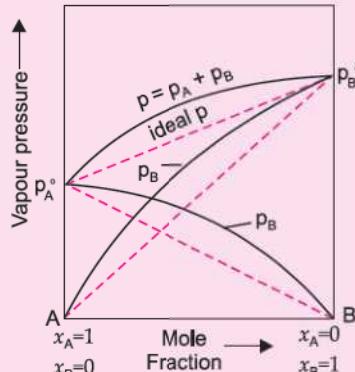
$$\Delta T_b = i K_b m$$

$$\pi = i cRT$$

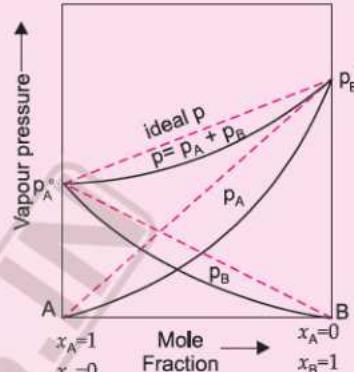
Important Graphs



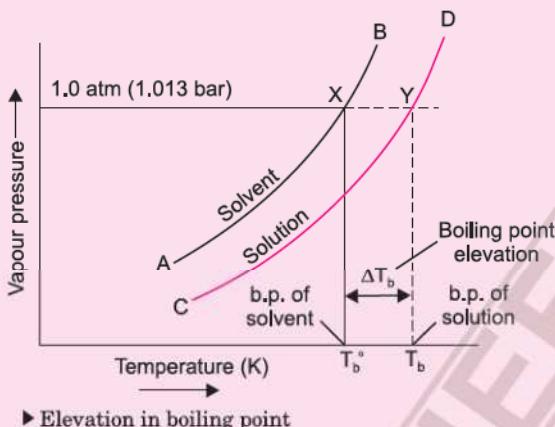
► Ideal behaviour



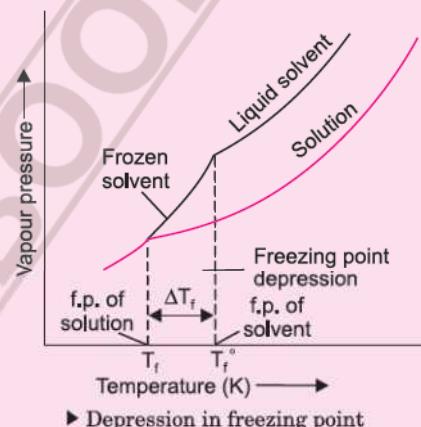
► Positive deviation from ideal behaviour



► Negative deviation from ideal behaviour



► Elevation in boiling point



► Depression in freezing point



NCERT

NCERT FILE

Solved

In-text Questions

Q.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. Total mass of solution = $22 + 122 = 144$ g

$$\text{Mass \% benzene} = \frac{22}{144} \times 100 = 15.28\%$$

$$\text{Mass \% } CCl_4 = \frac{122}{144} \times 100 = 84.72\%$$

Ans. Mass of benzene = 30 g

$$\text{Moles of benzene} = \frac{30}{78} = 0.385$$

(Mol. mass of C_6H_6 = 78)

$$\text{Mass of } CCl_4 = 70 \text{ g}$$

$$\text{Moles of } CCl_4 = \frac{70}{154} = 0.454$$

(Mol. mass of CCl_4 = 154)

$$x_{C_6H_6} = \frac{0.385}{0.385 + 0.454} = 0.459$$

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

Q.3. Calculate the molarity of each of the following solutions :

(a) 30 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 4.3 L of solution.

(b) 30 mL of 0.5 M H_2SO_4 diluted to 500 mL.

Ans. (a) Molar mass of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$

$$\begin{aligned} &= 58.93 + 2 \times 14 + 6 \times 16 + 6 \times 18 \\ &= 290.93 \end{aligned}$$

$$\text{Moles of } \text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} = \frac{30}{290.93} = 0.103$$

$$\text{Molarity} = \frac{0.103}{4.3} = 0.024 \text{ M}$$

$$(b) \quad M_1 V_1 = M_2 V_2$$

$$0.5 \times 30 \text{ mL} = M_2 \times 500 \text{ mL}$$

$$\therefore M_2 = \frac{0.5 \times 30}{500} = 0.03 \text{ M}$$

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

Ans. 0.25 molal solution means 0.25 moles of urea in 1000 g of water

$$\text{Mass of urea} = 0.25 \times 60 = 15 \text{ g}$$

$$\text{Total mass of solution} = 1000 + 15 = 1015 \text{ g}$$

$$\text{or} \quad = 1.015 \text{ kg}$$

$$1.015 \text{ kg of solution contain urea} = 15 \text{ g}$$

$$2.5 \text{ kg of solution will require urea} = \frac{15}{1.015} \times 2.5$$

$$= 36.94 \text{ g}$$

Q.5. Calculate (a) molality (b) molarity and (c) mole fraction of KI if density of 20% (mass/mass) aqueous solution of KI is 1.202 g mL^{-1} . (Hr. S.B. 2013)

Ans. 20% solution of KI means 20 g of KI are present in 100 g of solution or 80 g of water.

$$\text{Mass of KI} = 20 \text{ g}$$

$$\text{Molar mass of KI} = 39 + 127 = 166$$

$$\text{Moles of KI} = \frac{20}{166} = 0.120$$

$$(a) \quad \text{Molality} = \frac{0.120}{80} \times 1000 = 1.5 \text{ m.}$$

$$(b) \quad \text{Volume of solution} = \frac{100}{1.202} = 83.19 \text{ mL}$$

$$\text{Molarity} = \frac{0.120}{83.19} \times 1000 = 1.44 \text{ M}$$

$$(c) \quad \text{Moles of KI} = 0.120$$

$$\text{Moles of H}_2\text{O} = \frac{80}{18} = 4.44$$

$$x_{\text{KI}} = \frac{0.120}{4.44 + 0.120} = 0.0263.$$

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

Ans. 0.195 m solution means that 0.195 moles of H_2S is dissolved in 1 kg of water.

$$\text{Moles of H}_2\text{S} = 0.195$$

$$\text{Moles of water} = \frac{1000}{18} = 55.55$$

$$\text{Mole fraction of H}_2\text{S} = \frac{0.195}{55.55 + 0.195} = 0.0035$$

$$\text{Now, } p = K_H x_2 \quad \text{Pressure} = 0.987 \text{ bar}$$

$$\text{or } K_H = \frac{p}{x_2} = \frac{0.987 \text{ bar}}{0.0035} = 282 \text{ bar.}$$

Q.7. Henry's law constant for CO_2 in water is $1.67 \times 10^8 \text{ Pa}$ 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. $K_H = 1.67 \times 10^8 \text{ Pa}$
 $p = 2.5 \text{ atm} = 2.5 \times 101.325 \times 10^3 \text{ Pa}$
 $= 2.533 \times 10^5 \text{ Pa}$

$$\text{Now, } p = K_H x_2$$

$$\text{or, } x_2 = \frac{p}{K_H} = \frac{2.533 \times 10^5 \text{ Pa}}{1.67 \times 10^8 \text{ Pa}} = 1.517 \times 10^{-3}$$

$$\text{Moles of water} = \frac{500}{18} = 27.78$$

$$x_2 = \frac{n_2}{n_1 + n_2} = \frac{n_2}{27.78 + n_2} = 1.517 \times 10^{-3}$$

$$\text{or } n_2 = 0.0419 + 0.0015 n_2$$

$$0.9985 n_2 = 0.0419$$

$$n_2 = 0.0420$$

$$\text{Amount of CO}_2 \text{ dissolved} = 0.0420 \times 44 = 1.85 \text{ g.}$$

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

Ans. Let mole fraction of liquid A in solution = x_A

$$\text{Mole fraction of liquid B is solution} = x_B = (1 - x_A)$$

$$p = p_A + p_B = x_A p_A^\circ + x_B p_B^\circ$$

$$x_A p_A^\circ + (1 - x_A) p_B^\circ = x_A p_A^\circ + p_B^\circ - x_A p_B^\circ$$

$$\therefore 600 = x_A \times 450 + 700 - x_A \times 700$$

$$250 x_A = 100$$

$$\therefore x_A = \frac{100}{250} = 0.4$$

$$x_B = 1 - 0.4 = 0.6$$

Composition in vapour phase

$$p_A = x_A p_A^\circ = 0.4 \times 450 = 180 \text{ mm}$$

$$p_B = x_B p_B^\circ = 0.6 \times 700 = 420 \text{ mm}$$

$$\text{Total pressure} = 180 + 420 = 600 \text{ mm}$$

$$\text{Mole fraction of A in vapour phase, } y_A = \frac{180}{600} = 0.3$$

$$\text{Mole fraction of B in vapour phase, } y_B = \frac{420}{600} = 0.7$$

Q.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.

$$\text{Ans. Moles of urea} = \frac{50}{60} = 0.833$$

$$\text{Moles of water} = \frac{850}{18} = 47.222$$

$$\text{Mole fraction of urea} = \frac{0.833}{0.833 + 47.222} = 0.0173$$

$$\frac{p_A^o - p_A}{p_A^o} = x_B = 0.0173$$

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

$$23.8 - p_A = 0.412$$

$$p_A = 23.39$$

$$\text{Relative lowering of vapour pressure} = 0.0173.$$

Q.10. Boiling point of water at 750 mm Hg is 99.63°C . How much sugar is to be added to 500 g of water such that it boils at 100°C .

$$\text{Ans. } \Delta T_b = 100 - 99.63 = 0.37^\circ$$

$$M_B = \frac{K_b \times 100 \times w_B}{w_A \times \Delta T_b}$$

$$342 = \frac{0.522 \times 1000 \times w_B}{500 \times 0.37}$$

$$w_B = \frac{342 \times 500 \times 0.37}{0.522 \times 1000} = 121.7 \text{ g.}$$

Q.11. Calculate the mass of ascorbic acid (Vitamin C, $\text{C}_6\text{H}_8\text{O}_6$) to be dissolved in 75 g of acetic acid to lower its melting point by 1.5°C . $K_f = 3.9 \text{ K kg mol}^{-1}$.

Ans.

$$\Delta T_f = 1.5^\circ$$

$$M = 6 \times 12 + 1 \times 8 + 6 \times 16 = 176$$

$$M = \frac{K_f \times 1000 \times w_B}{w_A \times \Delta T_f}$$

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

$$w_B = \frac{176 \times 75 \times 1.5}{3.9 \times 1000} = 5.08 \text{ g.}$$

Q.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.

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

$$n = \frac{1.0}{185000}$$

$$V = 450 \text{ mL}$$

$$T = 273 + 37 = 310 \text{ K}$$

$$R = 8.314 \times 10^3 \text{ Pa L mol}^{-1} \text{ K}^{-1}$$

$$\pi = \frac{1.0 \times 8.314 \times 10^3 \times 310}{185,000 \times 450/1000}$$

$$= 30.96 \text{ Pa.}$$



NCERT

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

Ans. A solution is a homogeneous mixture of two or more substances whose composition can be varied. There are nine types of solutions.

For details refer Text Page 1 – 2.

Q.2. Suppose a solid solution is formed between two substances, one whose particles are very large and the other whose particles are very small. What kind of solid solution is this likely to be?

Ans. Interstitial solid solution.

Q.3. Define the following terms : (i) Mole fraction, (ii) Molality, (iii) Molarity, (iv) Mass percentage.

Ans. Refer Text Page 2 – 5.

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

Ans. 68% HNO_3 means that 68 g HNO_3 is present in 100 g of solution.

$$\text{Moles of } \text{HNO}_3 = \frac{68}{63} = 1.08$$

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

Textbook Exercises

$$\text{Volume of solution} = \frac{1000}{1.504} = 66.49$$

$$\text{Molarity} = \frac{1.08}{66.49} \times 1000 = 16.24 \text{ M}$$

Q.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 g mL^{-1} , then what shall be the molarity of the solution?

Ans. Refer Solved Example 12 (Page 9).

Q.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 two?

Ans. Refer Solved Example 21 (Page 12).

Q.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.

$$\text{Ans. } 300 \text{ g of 25% solution contains solute} = \frac{300 \times 25}{100} = 75 \text{ g}$$

$$400 \text{ g of 40% solution contains solute} = \frac{400 \times 40}{100} = 160 \text{ g}$$

$$\text{Total solute} = 75 + 160 = 235 \text{ g}$$

$$\text{Total solution} = 300 + 400 = 700 \text{ g}$$

$$\% \text{ of solute in the final solution} = \frac{235}{700} \times 100 = 33.5\%$$

$$\% \text{ of water in the final solution} = 100 - 33.5 = 65.5\%$$

Q.8. An antifreeze solution is prepared from 222.6 g of ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$) 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. Refer Solved Example 15 (Page 10).

Q.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. Refer Solved Example 19 (Page 10).

Q.10. What role does the molecular interactions play in solution of alcohol and water?

Ans. There are strong hydrogen bonding in alcohol molecules as well as water molecules. On mixing alcohol and water, the molecular interactions become weak. Therefore, they show positive deviation from ideal behaviour. As a result, the solution will have higher vapour pressure and lower boiling point than that of alcohol and water.

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

Ans. The dissolution of a gas in a liquid is exothermic process. Therefore, in accordance with Le-Chatelier's principle, with increase in temperature, the equilibrium shifts in the backward direction.



Therefore, the solubility of gas in solution decreases with rise in temperature.

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

Ans. Refer Text Page 17 – 19.

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

Ans. According to Henry's law

$$m = k \times p$$

$$6.56 \times 10^{-3} \text{ g} = k \times 1 \text{ bar}$$

or

$$k = 6.56 \times 10^{-3} \text{ g bar}^{-1}$$

Now, when

$$m = 5.00 \times 10^{-2} \text{ g}, p = ?$$

Applying

$$m' = k \times p'$$

$$5.00 \times 10^{-2} \text{ g} = 6.56 \times 10^{-3} \text{ g bar}^{-1} \times p$$

∴

$$p = \frac{5.00 \times 10^{-2}}{6.56 \times 10^{-3}} = 7.62 \text{ bar}$$

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

Ans. Refer text ; Page 28.

For positive deviation $\Delta_{\text{mix}}^{\text{H}} = +ve$

For negative deviation $\Delta_{\text{mix}}^{\text{H}} = -ve$

Q.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. Vapour pressure of pure water at the boiling point = 1 atm = 1.013 bar
Vapour pressure of solution = 1.004 bar

$$\text{Mass of solute} = 2 \text{ g}$$

$$\text{Mass of solution} = 100 \text{ g}$$

$$\text{Mass of solvent} = 100 - 2 = 98 \text{ g}$$

Applying Raoult's law

$$\frac{p^{\circ} - p_s}{p^{\circ}} = x_2 = \frac{W_2 \times M_1}{M_2 \times M_1}$$

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

$$\text{or} \quad M_2 = \frac{2 \times 18 \times 1.013}{0.009 \times 98} = 41.35 \text{ g mol}^{-1}$$

Q16. Heptane and octane form 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?

$$\text{Ans. Moles of heptane} = \frac{26.0}{100} = 0.26$$

$$\text{Moles of octane} = \frac{35.0}{114} = 0.31$$

$$x(\text{heptane}) = \frac{0.26}{0.26 + 0.31} = 0.456$$

$$x(\text{octane}) = \frac{0.31}{0.26 + 0.31} = 0.544$$

$$\begin{aligned} \text{Total pressure} &= 105.2 \times 0.456 + 46.8 \times 0.544 \\ &= 47.97 + 25.46 \\ &= 73.43 \text{ kPa}. \end{aligned}$$

Q.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.

$$\text{Ans. Mole fraction of solute} = \frac{1}{1 + 1000/18} = 0.0177$$

$$\frac{p^{\circ} - p_A}{p^{\circ}} = 0.0177$$

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

$$p_A = 12.08 \text{ kPa}.$$

Q.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. Refer Solved Example 33 (Page 37).

Q.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, 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. Refer Solved Example 35 (Page 37).

Q.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. For cane sugar, $\Delta T_f = 273.15 - 271.0 = 2.15^\circ$

$$K_f = \frac{2.15 \times 100 \times 342}{1000 \times 5} \\ = 14.706 \text{ K m}^{-1}$$

For glucose solution,

$$\Delta T_f = \frac{14.706 \times 1000 \times 5}{100 \times 180} = 4.085 \text{ K}$$

∴ Freezing point = $273.15 - 4.085 = 269.07 \text{ K}$.

Q.21. Two elements A and B form compounds having formula AB_2 and AB_4 . When dissolved in 20 g of benzene (C_6H_6), 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 $5.1 \text{ K kg mol}^{-1}$. Calculate atomic masses of A and B.

Ans. Refer Solved Example 49 (Page 45).

Q.22. At 300K, 36 g of glucose present per litre in its solution has an 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. Refer Solved Example 53 (Page 52).

Q.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 ($\text{C}_3\text{H}_6\text{O}$).

Ans. (i) van der Waals interactions, (ii) van der Waals interactions (iii) ion-dipole (iv) hydrogen bonding (v) dipole-dipole interactions.

Q.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. $\text{KCl} < \text{CH}_3\text{OH} < \text{CH}_3\text{CN} <$ cyclohexane.

Q.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) partially soluble (ii) insoluble (iii) soluble (iv) soluble (v) insoluble (vi) partially soluble.

Q.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. Mass of Na^+ ions = 92 g

$$\text{Moles of } \text{Na}^+ \text{ ions} = \frac{92}{23} = 4$$

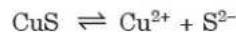
Mass of water = 1 kg

$$\text{Molality} = \frac{\text{Moles of solute}}{\text{Mass of solvent in kg}} \\ = \frac{4}{1} = 4 \text{ m.}$$

Q.27. If the solubility product of CuS is 6×10^{-16} . Calculate the maximum molarity of CuS in aqueous solution.

Ans. K_{sp} of $\text{CuS} = 6 \times 10^{-16}$

If s is the solubility, then



$$[\text{Cu}^{2+}] = s, [\text{S}^{2-}] = s$$

$$K_{sp} = [\text{Cu}^{2+}][\text{S}^{2-}] \\ = s \times s = s^2$$

$$\therefore \text{Solubility, } s = \sqrt{K_{sp}} = \sqrt{6 \times 10^{-16}}$$

$$= 2.45 \times 10^{-8} \text{ M}$$

$$\therefore \text{Highest molarity} = 2.45 \times 10^{-8} \text{ M}$$

Q.28. Calculate the mass percentage of aspirin ($\text{C}_9\text{H}_8\text{O}_4$) in acetonitrile (CH_3CN) when 6.5 g of $\text{C}_9\text{H}_8\text{O}_4$ is dissolved in 450 g of CH_3CN .

Ans. Refer Solved Example 11 (Page 9).

Q.29. Nalorphene ($\text{C}_{19}\text{H}_{21}\text{NO}_3$), 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 $1.5 \times 10^{-3} \text{ M}$ aqueous solution required for the above dose.

$$\text{Ans. Molality} = \frac{\text{Moles of solute}}{\text{Mass of solvent (in g)}} \times 1000$$

Molecular mass of nalorphene

$$= 19 \times 12 + 21 \times 1 + 1 \times 14 + 3 \times 16 \\ = 311$$

$$\text{Moles of nalorphene} = \frac{1.5 \times 10^{-3}}{311} = 4.82 \times 10^{-6} \text{ mol}$$

$$1.5 \times 10^{-3} = \frac{4.82 \times 10^{-6}}{\text{Mass of water}} \times 1000$$

$$\therefore \text{Mass of water} = \frac{4.82 \times 10^{-6} \times 1000}{1.5 \times 10^{-3}}$$

$$= 3.21 \text{ g.}$$

Q.30. Calculate the amount of benzoic acid ($\text{C}_6\text{H}_5\text{COOH}$) required for preparing 250 mL of 0.15 M solution in methanol.

$$\text{Ans. Molarity} = \frac{\text{Moles of solute}}{\text{Vol. of solution (in mL)}}$$

$$0.15 = \frac{\text{Moles of benzoic acid}}{250} \times 1000$$

$$\therefore \text{Moles of benzoic acid} = \frac{0.15 \times 250}{1000} = 0.0375$$

Molecular mass of benzoic acid ($\text{C}_6\text{H}_5\text{COOH}$)

$$= 7 \times 12 + 6 \times 1 + 2 \times 16 \\ = 122$$

$$\text{Amount of benzoic acid} = 0.0375 \times 122 = 4.575 \text{ g.}$$

Q.31. The depression in the 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. The acids can be arranged in the following order of depression in freezing point :

acetic acid < trichloroacetic acid < trifluoroacetic acid

This can be explained on the basis of degree of ionization which depends upon the strength of the acid.

Trifluoroacetic acid is more acidic than trichloroacetic acid which is more acidic than acetic acid. Therefore, degree of ionization of these will decrease as :



Greater the degree of ionization, greater will be γ and hence depression of freezing point.

- Q.32.** Calculate the depression in the freezing point of water when 10 g of $\text{CH}_3\text{CH}_2\text{CHClCOOH}$ is added to 250 g of water. $K_a = 1.4 \times 10^{-3}$, $K_f = 1.86 \text{ K kg mol}^{-1}$.

Ans. Molar mass of $\text{CH}_3\text{CH}_2\text{CHClCOOH}$

$$= 4 \times 12 + 7 \times 1 + 35.5 + 2 \times 16 = 122.5 \text{ g mol}^{-1}$$

$$\text{Moles of } \text{CH}_3\text{CH}_2\text{CHClCOOH} = \frac{10}{122.5} = 8.16 \times 10^{-2} \text{ mol}$$

$$\text{Molality of solution} = \frac{8.16 \times 10^{-2} \times 1000}{250} \\ = 0.3265 \text{ m}$$

If α is the degree of dissociation of $\text{CH}_3\text{CH}_2\text{CHClCOOH}$,



$$\begin{array}{ccc} \text{Initial conc. } c & 0 & 0 \end{array}$$

Conc. after dissociation

$$c(1-\alpha) \quad c\alpha \quad c\alpha$$

$$K_a = \frac{c\alpha \cdot c\alpha}{c(1-\alpha)} = c\alpha^2$$

$$\text{or } \alpha = \sqrt{K_a/c} = \sqrt{\frac{1.4 \times 10^{-3}}{0.3265}} = 0.065$$

To calculate Van't Hoff factor,



$$\begin{array}{ccc} \text{At equi. } & 1-\alpha & \alpha & \alpha \end{array}$$

$$i = \frac{1-\alpha+\alpha+\alpha}{1} = \frac{1+\alpha}{1} = 1 + 0.065 = 1.065$$

$$\Delta T_f = iK_f m = 1.065 \times 1.86 \times 0.3265 \\ = 0.647^\circ$$

- Q.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.

(C.B.S.E. Sample Paper 2010)

Ans. Molecular mass of CH_2FCOOH

$$= 2 \times 12 + 3 \times 1 + 1 \times 19 + 2 \times 16 = 78$$

$$\text{Moles of } \text{CH}_2\text{FCOOH} = \frac{19.5}{78} = 0.25$$

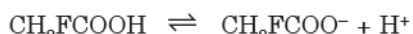
$$\text{Molality} = \frac{0.25 \times 1000}{500} = 0.50 \text{ m}$$

$$\Delta T_f = K_f \times m \\ = 1.86 \times 0.50 = 0.93 \text{ K}$$

Van't Hoff factor

$$= \frac{\text{Observed freezing point depression}}{\text{Calculated freezing point depression}} \\ = \frac{1.0}{0.93} = 1.0753$$

CH_2FCOOH dissociates as :



$$\begin{array}{ccc} \text{Initial conc. } m & 0 & 0 \end{array}$$

$$\begin{array}{ccc} \text{After dissociation } m(1-\alpha) & m\alpha & m\alpha \end{array}$$

(α is degree of dissociation)

Total number of moles = $m(1-\alpha) + m\alpha + m\alpha = m(1 + \alpha)$

$$i = \frac{m(1+\alpha)}{m} = 1 + \alpha = 1.0753$$

$$\therefore \alpha = 1.0753 - 1 = 0.0753$$

$$[\text{CH}_2\text{FCOO}^-] = m\alpha = 0.50 \times 0.0753 = 0.03765$$

$$[\text{H}^+] = m\alpha = 0.50 \times 0.0753 = 0.03765$$

$$[\text{CH}_3\text{COOH}] = m(1-\alpha)$$

$$= 0.50(1 - 0.0753) = 0.462$$

$$K_a = \frac{[\text{CH}_2\text{FCOO}^-][\text{H}^+]}{[\text{CH}_2\text{FCOOH}]} \\ = \frac{(0.03765)(0.03765)}{0.462}$$

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

- Q.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.

$$\frac{p^\circ - p}{p^\circ} = x_2 \approx \frac{W_B}{M_B} \frac{M_A}{W_A}$$

$$\frac{17.535 - p}{17.535} = \frac{25 \times 18}{180 \times 450}$$

$$\frac{17.535 - p}{17.535} = 5.56 \times 10^{-3}$$

$$17.535 - p = 0.0975$$

$$p = 17.438 \text{ mm Hg.}$$

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

Ans.

$$p = k \times C$$

$$760 \text{ mm} = 4.25 \times 10^5 \text{ mm} \times C$$

$$\therefore C = \frac{760}{4.25 \times 10^5} = 178 \times 10^{-5}$$

$$= 1.78 \times 10^{-3}$$

- Q.36.** 100 g of liquid A (molar mass 140 g mol⁻¹) was dissolved in 1000 g of liquid B (molar mass 180 g 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.

$$\text{Moles of A} = \frac{100}{140} = 0.714$$

$$\text{Moles of B} = \frac{1000}{180} = 5.556$$

$$\text{Mole fraction of A} = \frac{0.714}{0.714 + 5.556} = 0.114$$

$$\text{Mole fraction of B} = 1 - 0.114 = 0.886$$

$$P_{\text{total}} = P_A + P_B = P_A^\circ x_A + P_B^\circ x_B$$

$$475 = P_A^\circ \times 0.114 + 500 \times 0.886$$

$$475 = 0.114 P_A^\circ + 443$$

$$0.114 P_A^\circ = 32$$

$$P_A^\circ = 280.7 \text{ torr}$$

∴ Vap. press. of pure A = 280.7 torr

Vap. pressure of A in solution = $280.7 \times 0.114 = 32 \text{ torr}$

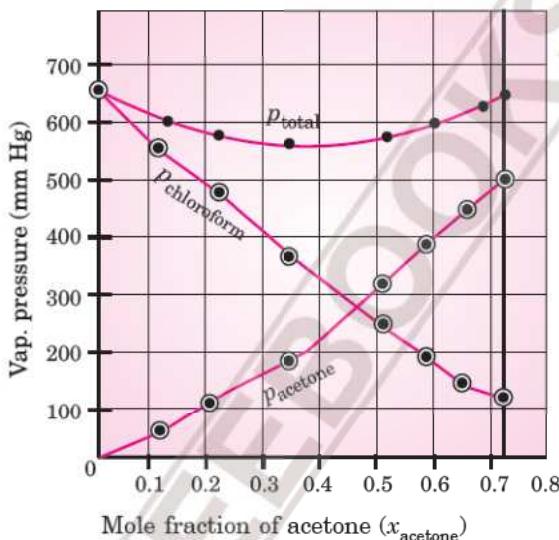
- Q.37.** Vapour pressure of pure acetone and chloroform at 328 K are 632.8 mm Hg and 741.8 mm Hg respectively. Assuming that they form ideal solution over the entire range of composition, plot p_{total} , $p_{\text{chloroform}}$ and p_{acetone} as a function of x_{acetone} . The experimental data observed for different compositions of mixture is :

$100 \times x_{\text{acetone}}$	0	11.8	23.4	36.0	50.8	58.2	64.5	72.1
$p_{\text{acetone}}/\text{mm Hg}$	0	54.9	110.1	202.4	322.7	405.9	454.1	521.1
$p_{\text{chloroform}}/\text{mm Hg}$	632.8	548.1	469.4	359.7	257.7	193.6	161.2	120.7

Plot this data also on the same graph paper. Indicate whether it has positive deviation or negative deviation from the ideal solution.

Ans.

x_{acetone}	0.00	0.118	0.234	0.360	0.508	0.582	0.645	0.721
$p_{\text{acetone}}/\text{mm Hg}$	0	54.9	110.1	202.4	322.7	405.9	454.1	521.1
$p_{\text{chloroform}}/\text{mm Hg}$	632.8	548.1	469.4	359.7	257.7	193.6	161.2	120.7
$p(\text{total})$	632.8	603.0	579.5	562.1	580.4	599.5	615.3	641.8



The plot of $p(\text{total})$ dips downwards and therefore, the solution shows negative deviation from ideal behaviour.

- Q.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. Moles of benzene = $\frac{80}{78} = 1.026$
(Molecular mass of $C_6H_6 = 78$)

Moles of toluene = $\frac{100}{92} = 1.087$
(Molecular mass of $C_7H_8 = 92$)

Mole fraction of benzene,

$$x_b = \frac{1.026}{1.026 + 1.087} = 0.486$$

Mole fraction of toluene,

$$x_t = 1 - 0.486 = 0.514$$

$$\begin{aligned} p_b &= p_b^{\circ} \times x_b \\ &= 50.71 \times 0.486 = 24.65 \text{ mm Hg} \\ p_t &= p_t^{\circ} \times x_t \\ &= 32.06 \times 0.514 = 16.48 \end{aligned}$$

Total vapour pressure

$$\begin{aligned} &= 24.65 + 16.48 \\ &= 41.13 \text{ mm Hg} \end{aligned}$$

Mole fraction of benzene in vapour phase

$$y_b = \frac{24.65}{41.13} = 0.60$$

- Q.39.** The air is a mixture of 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. Henry's law constants for oxygen and nitrogen at 298 K are 3.30×10^7 mm and 6.51×10^7 mm respectively. Calculate the composition of these gases in water.

- Ans.** The vapour pressure of air over water = 10 atm. The partial pressures of N_2 and O_2 are :

$$\begin{aligned} p_{N_2} &= \frac{79 \times 10}{100} = 7.9 \text{ atm} \\ &= 7.9 \times 760 \text{ mm} = 6004 \text{ mm Hg} \\ p_{O_2} &= \frac{20 \times 10}{100} = 2.0 \text{ atm.} \end{aligned}$$

$$= 2.0 \times 760 \text{ mm Hg} = 1520 \text{ mm Hg}$$

Applying Henry's law

$$P_{N_2} = K_H(N_2) \times x_{N_2}$$

or

$$x_{O_2} = \frac{P_{N_2}}{K_H(N_2)} = \frac{6004}{6.51 \times 10^7} \\ = 9.22 \times 10^{-5}$$

Similarly,

$$x_{O_2} = \frac{P_{O_2}}{K_H(O_2)} = \frac{1520}{3.30 \times 10^7} \\ = 4.6 \times 10^{-5}$$

- Q.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. For CaCl_2 ,

$$i = 2.47$$

$$\pi = i cRT$$

$$= i \frac{n_B}{V} \times RT$$

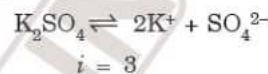
$$0.75 = \frac{2.47 \times n_B \times 0.082 \times 300}{2.5}$$

$$n_B = \frac{0.75 \times 2.5}{2.47 \times 0.082 \times 300} \\ = 0.0308 \text{ mol.}$$

Amount of CaCl_2 dissolved = $0.0308 \times 111 = 3.42 \text{ g}$

- Q.41.** Determine the osmotic pressure of a solution prepared by dissolving 25 mg of K_2SO_4 in 2 litre of water at 25°C , assuming that it is completely dissociated.

Ans. If K_2SO_4 is completely dissociated,



$$\text{Mol. mass of } \text{K}_2\text{SO}_4 = 2 \times 39 + 32 + 4 \times 16 = 174$$

$$\pi = i cRT$$

$$= i \frac{W_B \times RT}{M_B \times V}$$

$$= \frac{3 \times 25 \times 10^{-3} \times 0.082 \times 298}{174 \times 2.0}$$

$$= 5.27 \times 10^{-3} \text{ atm.}$$



NCERT

Note: Objective Questions from Exemplar Problems are given in Competition File, page 113.

Short Answer Type Questions

- Q.1.** Components of a binary mixture of two liquids A and B were being separated by distillation. After some time separation of components stopped and composition of vapour phase became same as that of liquid phase. Both the components started coming in the distillate. Explain why this happened.

Ans. Since both the components are coming in the distillate and composition of liquid and vapour phase become same, this shows that liquids have formed azeotropic mixture. Therefore, these components cannot be separated at this stage by distillation.

- Q.2.** Explain why on addition of 1 mol of NaCl to 1 litre of water, the boiling point of water increases, while addition of 1 mol of methyl alcohol to one litre of water decreases its boiling point.

Ans. NaCl is a non volatile solute, therefore, addition of NaCl to water lowers the vapour pressure of water. As a result, boiling point of water increases. On the other hand, methyl alcohol is more volatile than water, therefore its addition increases the total vapour pressure over the solution. As a result, boiling point of water decreases.

- Q.3.** Explain the solubility rule "like dissolves like" in terms of intermolecular forces that exist in solutions.

Ans. A substance dissolves in a solvent if the intermolecular interactions are similar in both the components. For

Exemplar Problems

Subjective Questions

example, polar solutes dissolve in polar solvents and non polar solutes in non polar solvents. Thus, we can say "like dissolves like".

- Q.4.** Concentration terms such as mass percentage, ppm, mole fraction and molality are independent of temperature, however molarity is a function of temperature. Explain.

Ans. Molarity of a solution is defined as the number of moles of solute dissolved per litre of solution. Since volume depends on temperature and changes with change in temperature, therefore, the molarity will also change with change in temperature. On the other hand, mass does not change with change in temperature, and therefore, concentration terms such as mass percentage, mole fraction and molality which do not involve volume are independent of temperature.

- Q.5.** What is the significance of Henry's Law constant K_H ?

Ans. Higher the value of Henry's law constant K_H , the lower is the solubility of the gas in the liquid.

- Q.6.** Why are aquatic species more comfortable in cold water in comparison to warm water?

(A.I.S.B. 2018)

Ans. At a given pressure, the solubility of oxygen in water increases with decrease in temperature. Therefore, the concentration of oxygen in sea is more in cold water and thus presence of more oxygen at lower temperature makes the aquatic species more comfortable in cold water.

Q.7. (a) Explain the following phenomena with the help of Henry's law.

- Painful condition known as bends.
- Feeling of weakness and discomfort in breathing at high altitude.

(b) Why soda water bottle kept at room temperature fizzes on opening ?

Ans. (a) (i) Deep sea divers depends upon compressed air for breathing at high pressure under water. The compressed air contains N_2 in addition to O_2 , which are not very soluble in blood at normal pressure. However, at great depths when the diver breathes in compressed air from the supply tank, more N_2 dissolves in the blood and other body fluids because the pressure at that depth is far greater than the surface atmospheric pressure. When the diver comes towards the surface, the pressure decreases, N_2 comes out of the body quickly forming bubbles in the blood stream. These bubbles restrict blood flow, affect the transmission of nerve impulses. The bubbles can even burst the capillaries or block them and starve the tissues of O_2 . This condition is called "the bends," which are painful and dangerous to life.

(ii) At high altitudes the partial pressure of O_2 is less than that at the ground level. This results in low concentration of oxygen in the blood and tissues of the people living at high altitudes or climbers. The low blood oxygen causes climbers to become weak and unable to think clearly known as **anoxia**.

(b) To increase the solubility of CO_2 in soft drinks, the soda water bottles are sealed under high pressure.



QUICK

MEMORY TEST

When the bottle is opened at room temperature under normal atmosphere conditions, the pressure inside the bottle decreases to atmospheric pressure and excess CO_2 fizzes out.

Q.8. Why is the vapour pressure of an aqueous solution of glucose lower than that of water?

Ans. In pure liquid water, the entire surface of liquid is occupied by the molecules of water. When a non volatile solute, such as glucose is dissolved in water some of the surface is covered by non volatile glucose molecules. Therefore, the fraction of surface covered by the solvent molecules decreases. As a result number of solvent molecules escaping from the surface also gets reduced and consequently the vapour pressure of aqueous solution of glucose is reduced.

Q.9. How does sprinkling of salt help in clearing the snow covered roads in hilly areas? Explain the phenomenon involved in the process.

Ans. When salt is spread over snow covered roads, it lowers the freezing point of water to such an extent that water does not freeze to form ice. As a result, the snow starts melting from the surface and therefore, it helps in clearing the roads. Hence, common salt acts as de-icing agent.

Q.10. What is "semi permeable membrane"?

Ans. The continuous sheets or films (natural or synthetic) which contain a network of submicroscopic pores or holes through which small solvent molecules like water can pass; but the bigger molecules of solute cannot pass are known as semi permeable membrane.

Q.11. Give an example of a material used for making semipermeable membrane for carrying out reverse osmosis.

Ans. Cellulose acetate.

A. Say True or False

- Both molality and mole fraction are independent of temperature.
- The solubilities of all ionic substances increase with increase of temperature.
- The depression in freezing point for 1 m solution of a solute in water and benzene is same.
- If observed value of the colligative property is more than the normal value of same property then Van't Hoff factor is more than one.
- Van't Hoff factor, $i < 1$ if there is association of the solute in the solution.
- The freezing point of 0.1 m solution of acetic acid in benzene is more than freezing point of 0.01 m solution.
- Lowering in vapour pressure is a colligative property.

- Two liquids A and B boil at $125^\circ C$ and $146^\circ C$ respectively. Liquid A will have higher vapour pressure.
- Elevation in boiling point of 0.1 m NaCl solution will be nearly twice that of 0.1 m glucose solution.
- Solution of ethanol and cyclohexane shows positive deviation from Raoult's law.
- Colligative properties depend only upon the moles of solute and are independent of the nature of solute and solvent.
- The more concentrated solution is said to be hypertonic with respect to less concentrated solution.
- Minimum boiling azeotropes are obtained in liquid solution showing negative deviation from Raoult's law.
- For solution showing positive deviation from Raoult's law $\Delta V_{\text{mixing}} = -\text{ve}$ and $\Delta H_{\text{mixing}} = +\text{ve}$.
- Molality of 1 M aqueous solution is less than 1 m.

B. Complete the missing links

- At the same temperature, nitrogen gas is soluble in water than oxygen.
- For a non-ideal solution showing positive deviation from Raoult's law, ΔH_{mixing} is and ΔV_{mixing} is
- The solubility of a solute decreases with increase in temperature if dissolution process is and increases with increase in temperature if dissolution is
- For 100% dissociation of $K_4[Fe(CN)_6]$, Van't Hoff factor $i =$
- If observed molar mass of a solute is more than calculated molar mass, then the solute undergoes in the solvent.
- The sum of mole fractions of all the components in a three component system is equal to
- If 0.1 m solution of NaCl freezes at -4.2°C , then 0.1 m solution of glucose will freeze at in the same solvent.
- The molarity of pure water is
- The freezing point of 0.1 M NaCl solution is than that of 0.1 M $MgCl_2$ solution.
- A solution which has lower osmotic pressure compared to that of other solution is called
- ΔH_{mixing} for solution having positive deviations from Raoult's law is
- A solution of some organic substance in benzene boils at 0.126°C higher than benzene. The molality of the solution ($K_b = 2.52 \text{ Km}^{-1}$) is
- The most suitable colligative property to measure molecular mass of polymers is
- Desalination of sea water is based on the phenomenon of

- The variation of solubility of $Na_2SO_4 \cdot 10H_2O$ is a discontinuous curve. With increase in temperature, it first and then
- Because of low concentration of oxygen in the blood and tissues, people living at high altitude suffer from a disease called
- People taking a lot of salt develop swelling or puffiness of their tissues. This disease is called
- The solution having same osmotic pressure are called and they have same

C. Choose the correct alternative

- The concentration term independent of temperature is *molarity/molality*.
- For acetone + ethyl alcohol non-ideal solution, ΔV_{mixing} is *+ve/-ve*.
- Chloroform + Benzene form non-ideal solution showing *positive/negative* deviations.
- A pure NaCl solution with concentration more than 0.91% is called *hypertonic/hypotonic*.
- A 0.01 m solution of cane sugar has *less/more* osmotic pressure than 0.001 m solution.
- A non-ideal solution showing positive deviation forms an azeotrope with *lowest/highest* boiling point.
- The freezing of aqueous 0.1 M Na_2CO_3 solution is *less/more* than 0.2 M NaOH solution.
- When the solute undergoes association in solution, the value of Van't Hoff factor is *less/more* than 1.
- In the reverse osmosis pressure *larger/smaller* than osmotic pressure is applied on the solution.
- Normality of 1.5 M CH_3COOH solution is $1.5N/3.0N$.
- Solubility of most of the gases in A liquid increases with *decrease/increase* in temperature.
- Elevation in boiling point of 0.1 m $CaCl_2$ solution *less/more* than 0.1 m NaCl solution.

Answers

QUICK

MEMORY TEST



A. Say True or False

- True
- False.** Solubility increases or decreases with temperature depending upon whether solubility process is endothermic or exothermic.
- False.** It depends upon nature of solvent.
- True
- True
- False.** The depression in 0.1 m solution of acetic acid is more than 0.01 m solution of benzene so that f.p. of first solution is less.
- False.** Relative lowering in vapour pressure is colligative property and not lowering in vapour pressure.
- True
- True
- True
- False.** Colligative properties depend upon the nature of solvent.
- True
- False
- False.** $\Delta H_{\text{mixing}} = +ve$, $\Delta V_{\text{mixing}} = +ve$
- False.

B. Complete the missing links

- less
- +ve, -ve
- exothermic, endothermic
- 5
- association
- 1
- -2.1°C
- 55.6 M
- more
- hypotonic
- +ve
- 0.05 m
- osmotic pressure
- reverse osmosis
- increases, decreases
- anoxia
- edema
- isotonic, molar concentration.

C. Choose the correct alternative

- molality
- +ve
- negative
- hypertonic
- more
- lowest
- more
- less
- larger
- 1.5 N
- decrease
- more

HOTS

Higher Order Thinking Skills & Advanced Level

QUESTIONS WITH ANSWERS

HOTS

1. Why is a person suffering from high blood pressure is advised to take minimum quantity of common salt ?

Ans. Osmotic pressure is directly proportional to the concentration of the solutes. Our body fluids contain a number of solutes. If a person takes more salt, the concentration of Na^+ and Cl^- ions entering into the body fluid, raises the concentration of the solutes. As a result, osmotic pressure increases which may rupture the blood cells.

2. Why water cannot be separated completely from ethanol by fractional distillation ?

Ans. Ethanol and water (95.4% ethanol and 4.6% H_2O) form a constant boiling mixture (azeotrope) boiling at 351.5 K. Hence, further water cannot be removed by fractional distillation.

3. Why is melting point of a substance used as a criterion for testing the purity of a substance ?

Ans. A pure compound has a sharp melting point. Impurities present, if any, lowers the melting point of the compound (similar to depression in freezing point).

4. If glycerine, $\text{C}_3\text{H}_5(\text{OH})_3$ and methyl alcohol, CH_3OH are sold at the same price per kg, which would be cheaper for preparing an anti-freeze solution for the radiator of a car ?

Ans. Methyl alcohol, CH_3OH is cheaper because it has lower molecular mass and a given mass of CH_3OH contains more moles than the same mass of glycerine. More moles of solute means higher molality and therefore, it causes lower freezing point (because ΔT_f will be more). In other words, it would take less methyl alcohol to protect a radiator to a given freezing point.

5. If K_f for water is $1.86^\circ \text{C}/\text{m}$, explain why 1 m NaCl in water does not have a freezing point equal to

(i) -1.86°C and (ii) -3.72°C .

Ans. (i) There are two moles of ions per mol of NaCl . Therefore, ΔT_f cannot be equal to 1.86 and freezing point cannot be equal to $0 - 1.86 = -1.86^\circ \text{C}$.

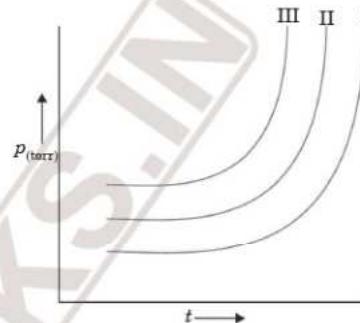
(ii) ΔT_f cannot be equal to $2 \times 1.86 = 3.72$ and freezing point = -3.72 because there are strong interionic attractions for 1m solution so that the degree of ionization is not 100% at the freezing point. The value of i is some what less than 2.

6. Why is camphor preferred as a solvent in finding the molecular mass of naphthalene by Rast method ?

Ans. Camphor has a large value of K_b ($39.7^\circ \text{C m}^{-1}$) so the depression in freezing point is large for solution of naphthalene in camphor. This can be measured by even ordinary thermometer.

7. The following figure shows vapour pressure curves of two pure liquids and solution of the two. Which curves

I, II, or III represent pure liquids and which represents the solution ?



Ans. The vapour pressure of a mixture of two volatile liquids is always intermediate between the vapour pressures of the two liquids. Thus, the curves I and III represent pure liquids and the middle curve II represents the solution.

8. If vapour pressure of liquid A is greater than the vapour pressure of liquid B, then boiling point of A is lower than that of liquid B. Do you agree with the statement? Explain.

Ans. This statement is true. If vapour pressure of a liquid is high, lesser heating is needed to make its vapour pressure equal to the external pressure (atmospheric pressure). Therefore, its boiling point is lower.

9. Pure benzene has vapour pressure three times that of pure toluene. They form nearly ideal solution. What would be the ratio of their mole fractions in the vapour phase of a solution having equal mole fractions of benzene and toluene.

Ans. Since benzene and toluene have equal mole fractions in the solution,

$$\frac{p_b}{p_t} = \frac{p_b^o}{p_t^o} = 3 \quad (\because x_b = x_t)$$

Since the vapour pressures in the vapour phase are in the ratio of their mole fractions, then

$$\frac{x_y}{x_y} = 3$$

Advanced Level Problems

10. 0.052 g of glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) has been dissolved in 80.2 g of water. Calculate (i) the boiling point and (ii) freezing point of the solution ($K_b = 1.86 \text{ K m}^{-1}$, $K_b = 5.2 \text{ K m}^{-1}$).

Ans. Elevation in boiling point may be calculated from the relation,

$$\Delta T_b = \frac{K_b \times w_B \times 1000}{M_B \times w_A}$$

$$w_B = 0.052 \text{ g}, w_A = 80.2 \text{ g}, K_b = 5.2 \text{ K m}^{-1}, M_B = 180$$

$$\therefore \Delta T_b = \frac{5.2 \times 0.052 \times 1000}{180 \times 80.2} = 0.0187$$

Boiling point of water = 373 K

$$\begin{aligned}\text{Boiling point of solution} &= 373 + 0.0187 = 373.0187 \\ &= 373.02 \text{ K}\end{aligned}$$

Now, depression in freezing point,

$$\Delta T_f = \frac{K_f \times w_B \times 1000}{M_B \times w_A}$$

$$w_B = 0.052 \text{ g}, w_A = 80.2 \text{ g}, K_f = 1.86 \text{ K m}^{-1}, M_B = 180$$

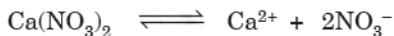
$$\therefore \Delta T_f = \frac{1.86 \times 0.052 \times 1000}{180 \times 80.2} = 0.067$$

Freezing point of water = 273 K

Freezing point of solution = 273 - 0.067 = 272.933 K.

11. The degree of dissociation of Ca (NO₃)₂ in dilute aqueous solution containing 7.0 g of the salt per 100 g of water at 100°C is 70 percent. If the vapour pressure of water at 100°C is 760 mm, calculate the vapour pressure of the solution.

Ans. Calcium nitrate dissociates as :



Initial moles	1	0	0
After dissociation	1 - x	x	2x
Total no. of moles after dissociation	= 1 - x + x + 2x		= 1 + 2x

$$\text{Here } x = 70\% = 0.7$$

$$\text{No. of moles after dissociation} = 1 + 2 \times 0.7 = 2.4$$

$$i = \frac{\text{Moles of solute after dissociation}}{\text{Normal moles of solute}} = \frac{2.4}{1} = 2.4$$

$$\text{Now, } \frac{P_A^\circ - p_A}{P_A^\circ} = i x_B$$

$$x_B = \frac{n_B}{n_A + n_B} \approx \frac{n_B}{n_A} = \frac{w_B \times M_A}{M_B \times w_A} \quad (\text{For dilute solution})$$

$$w_B = 7.0 \text{ g}, w_A = 100 \text{ g}, M_B = 164, M_A = 18$$

$$\therefore w_B = \frac{7.0 \times 18}{164 \times 100} = 0.00768$$

$$\frac{P_A^\circ - p_A}{P_A^\circ} = 2.4 \times 0.00768$$

$$\begin{aligned}P_A^\circ - p_A &= 2.4 \times 0.00768 \times 760 = 14.0 \text{ mm Hg} \\ \therefore P_A &= 760 - 14.0 = 746 \text{ mm Hg.}\end{aligned}$$

12. A motor vehicle radiator was filled with 8 L of water to which 2 L of methyl alcohol (density 0.8 g/mL) were added. What is the lowest temperature at which the vehicle can be parked outdoors without a danger that water in the radiator will freeze ? K_f of water = 1.86 K m⁻¹)

Ans. Let us calculate the depression caused by the addition of methyl alcohol.

$$\Delta T_f = \frac{K_f \times 1000 \times w_B}{w_A \times M_B}$$

$$w_A = 8000 \times 1.0 = 8000 \text{ g} \quad (\text{Density of water} = 1 \text{ g/mL})$$

$$w_B = 2000 \times 0.8 = 1600 \text{ g}$$

$$M_B = 32$$

$$\Delta T_f = \frac{1.86 \times 1000 \times 1600}{8000 \times 32}$$

$$= 11.625$$

$$\text{Freezing point} = 0 - 11.625$$

$$= -11.625^\circ\text{C}$$

∴ Vehicle may be parked outdoor not below -11.625°C temperature.

13. The mole fraction of toluene in a solution in benzene is 0.50. Calculate the weight percent of toluene in solution.

Ans. Let the weight percent of toluene in solution is x. This means x g of toluene are present in 100 g of solution.

$$\text{Wt. of toluene} = x \text{ g}$$

$$\text{Wt. of benzene} = (100 - x) \text{ g}$$

$$\text{Mol. wt. of benzene (C}_6\text{H}_6\text{)} = 78$$

$$\text{Mol. wt. of toluene (C}_6\text{H}_5\text{CH}_3\text{)} = 92$$

Now,

$$\frac{n_t}{n_t + n_b} = 0.5$$

$$\frac{\frac{x}{92}}{\frac{x}{92} + \frac{(100-x)}{78}} = 0.5$$

$$\frac{\frac{x}{92}}{\frac{78x + 92(100-x)}{92 \times 78}} = 0.5$$

$$\frac{x}{92 \times 78} \times \frac{92 \times 78}{78x + 92(100-x)} = 0.5$$

$$78x = 39x + 4600 - 46x$$

$$85x = 4600$$

$$x = 54.1$$

$$\text{Wt\% of toluene} = 54.1.$$

14. The freezing point of a solution containing 50 cm³ of ethylene glycol in 50 g of water is found to be -34°C. Assuming ideal behaviour, calculate the density of ethylene glycol.

Ans. Depression in freezing point,

$$\Delta T_f = \frac{K_f \times w_B \times 1000}{M_B \times w_A}$$

$$K_f = 1.86 \text{ K m}^{-1}, \Delta T_f = 0 - (-34) = 34$$

$$w_B = ?, w_A = 50 \text{ g}, M_B = 62$$

$$34 = \frac{1.86 \times w_B \times 1000}{62 \times 50}$$

$$\therefore w_B = \frac{34 \times 62 \times 50}{1.86 \times 1000} = 56.67$$

$$\text{Now, } w_B = V \times d$$

$$56.67 = 50 \times d$$

$$\text{or } d = \frac{56.67}{50} = 1.13 \text{ g cm}^{-3}.$$



Revision Exercises

Very Short Answer Questions Carrying 1 mark

- Give one example of each of solid in gas and liquid in gas solution.
- Why does the molality of a solution remain unchanged with temperature? *(Assam S.B. 2013)*
- What will be mole fraction of water in methanol solution containing equal number of moles of water and methanol?
- Define molal depression constant. How is it related to enthalpy of fusion?
- The boiling point increases and freezing point decreases when sodium chloride is added to water. Explain. *(H.P.S.B. 2002)*
- Sodium chloride is used to clear snow from roads. Explain. *(H.P.S.B. 2002)*
- What is the general effect of temperature on the solubility of a gas in a liquid?
- When is the value of Vant Hoff's factor more than one?
- Why does water from the soil rise to the top of a tall tree?
- What is the effect of temperature on molality of solution? *(Hr. S.B. 2005, H.P.S.B. 2005)*
- Calculate the normality of 1.5 M H_2SO_4 . *(Hr. S.B. 2006)*
- How is ΔT_f and ΔT_b related to molecular mass of a solute? *(Pb. S.B. 2006)*
- What is the normality of 0.5 M aqueous solution of tribasic acid? *(Pb. S.B. 2006)*
- Two liquids A and B boil at 145°C and 190°C respectively. Which of them has a higher vapour pressure at 80°C? *(D. S.B. 2006)*
- Under what condition Van't Hoff factor ' i ' is less than one? *(Pb. S.B. 2007)*
- Under what condition Van't Hoff factor ' i ' is equal to unity? *(Pb. S.B. 2007)*
- Define Raoult's law. *(H.P.S.B. 2012)*
- Why does rubbing of isopropyl alcohol give a cooling sensation to the skin?
- Define azeotropic mixture. *(H.P.S.B. 2013, 2015)*
- Why is molality preferred for expressing concentration than molarity? *(J.K.S.B. 2013, H.P.S.B. 2013)*
- Mention the enthalpy of mixing ($\Delta_{\text{mix}}H$) value to form an ideal solution. *(Karnataka S.B. 2014)*
- Define Henry's law. *(H.P.S.B. 2012, Karnataka S.B. 2018, Manipur S.B. 2018)*

CBSE QUESTIONS

- What is the sum of the mole fractions of all the components in a three component system? *(A.I.S.B. 2004)*
- How is the molality of a solution different from its molarity? *(A.I.S.B. 2004)*
- What would be the value of van't Hoff factor for a dilute solution of K_2SO_4 in water? *(A.I.S.B. 2005, Uttarakhand S.B. 2012)*

- State the condition resulting in Reverse Osmosis. *(A.I.S.B. 2007)*
- Define osmotic pressure. *(A.I.S.B. 2007)*
- What is meant by reverse osmosis? *(A.I.S.B. 2011)*

MCQs from State Boards' Examinations

- Which of the following solution shows maximum depression in freezing point?

<i>(a) 0.5 M Li_2SO_4</i>	<i>(b) 1 M NaCl</i>
<i>(c) 0.5 M $\text{Al}_2(\text{SO}_4)_3$</i>	<i>(d) 0.5 M BaCl_2</i>

(Maharashtra S.B. 2013)
- The molality of pure water is

<i>(a) 55.5</i>	<i>(b) 50.5</i>
<i>(c) 18</i>	<i>(d) 60.5</i>

(Hr. S.B. 2013, 2015, 2018)
- Constant boiling mixtures are called

<i>(a) ideal solutions</i>	<i>(b) azeotropes</i>
<i>(c) isotonic</i>	<i>(d) None of these</i>

(Hr. S.B. 2013)
- The colligative properties of a dilute solution depend on

<i>(a) the nature of the solute</i>	<i>(b) the nature of the solvent</i>
<i>(c) the number of particles of solute</i>	<i>(d) the molecular mass of solute.</i> <i>(Mizoram S.B. 2014)</i>
- The concentration term independent of temperature is :

<i>(a) Normality</i>	<i>(b) Mass-volume per cent</i>
<i>(c) Molality</i>	<i>(d) Molarity</i>

(Manipur S.B. 2014, Hr. S.B. 2015, Meghalaya S.B. 2015, Mizoram S.B. 2018)
- The number of moles of NaCl in 3 litres of 3 M solution is:

<i>(a) 1</i>	<i>(b) 3</i>
<i>(c) 9</i>	<i>(d) 27.</i> <i>(Mizoram S.B. 2014)</i>
- In countries nearer to polar region, the roads are sprinkled with CaCl_2 . This is

<i>(a) to minimise the effect of snow on roads</i>	<i>(b) to minimise pollution</i>
<i>(c) to minimise the accumulation of dust on the road</i>	<i>(d) to minimise the wear and tear of the roads</i>

(H.P. S.B. 2015)
- For solutes which do not undergo any association or dissociation in a solute, van't Hoff factor (i) will be

<i>(a) less than 1</i>	<i>(b) more than 1</i>
<i>(c) equal to 1</i>	<i>(d) zero</i> <i>(Mizoram S.B. 2015)</i>
- Which of the following 0.1 M aqueous solution is likely to have the highest boiling point?

<i>(a) Na_2SO_4</i>	<i>(b) KCl</i>
<i>(c) Glucose</i>	<i>(d) Urea</i> <i>(Tripura S.B. 2016)</i>
- Which of the following solutions will have the minimum freezing point?

<i>(a) 0.1M FeCl_3</i>	<i>(b) 0.1M BaCl_2</i>
<i>(c) 0.1M NaCl</i>	<i>(d) 0.1M Urea</i>

(Mizoram S.B. 2016)

39. Isotonic solutions have

- (a) same boiling point
 - (b) same vapour pressure
 - (c) same melting point
 - (d) same osmotic pressure
- (Meghalaya S.B. 2016)

40. The value of Henry's constant K_H

- (a) increases with increase in temperature
- (b) decreases with increase in temperature
- (c) remains constant
- (d) first increases, then decreases (Meghalaya S.B. 2016)

41. Mole fraction of a solute in 2.5 molal aqueous solution is

- (a) 0.43
- (b) 0.043
- (c) 4.3
- (d) 43 (Hr. S.B. 2017)

42. Which of the following concentration of solution depends on temperature ?

- (a) molality
 - (b) molarity
 - (c) mass %
 - (d) mole fraction
- (Assam S.B. 2017)

43. Two solutions A and B are separated by a semipermeable membrane. If the solvent flows from A to B, then

- (a) A is more concentrated than B
- (b) A is less concentrated than B
- (c) both A and B are of same concentration
- (d) both A and B get diluted (Meghalaya S.B. 2017)

44. The van't Hoff factor i for a compound which undergoes dissociation in one solvent and association in another solvent is respectively

- (a) less than one and greater than one
 - (b) less than one and less than one
 - (c) greater than one and less than one
 - (d) greater than one and greater than one
- (Meghalaya. S.B. 2017)

45. At higher altitudes, the boiling point of water decreases because

- (a) the atmospheric pressure is low
- (b) the atmospheric pressure is high
- (c) the temperature is low
- (d) the temperature is high (Mizoram S.B. 2017)

46. Maximum amount of a solid solute that can be dissolved in a given amount of a liquid solvent does not depend upon

- (a) pressure
 - (b) temperature
 - (c) nature of solute
 - (d) nature of solvent
- (Hr. S.B. 2017)

47. Low concentration of O_2 in the blood of people living at high altitude is due to

- (a) low temperature
- (b) low atmospheric pressure
- (c) high atmospheric pressure
- (d) none of the above (Hr. S.B. 2017)

48. The units of ebullioscopic constant is

- (a) $K \text{ kg mol}^{-1}$
 - (b) mol kg^{-1}
 - (c) $K \text{ mol kg}^{-1}$
 - (d) none of these
- (Hr. S.B. 2017)

49. Molar solution means 1 mole of solute present in

- (a) 1000 g of solvent
- (b) 1000 g of solution
- (c) 1 litre of solvent
- (d) 1 litre of solution (Mizoram S.B. 2018)

50. An ether is more volatile than an alcohol having the same molecular formula due to

- (a) dipolar character of ether
- (b) alcohols having resonance structure

(c) intermolecular hydrogen bonding in ether

(d) intermolecular hydrogen bonding in alcohol

(Nagaland S.B. 2018)

Short Answer Questions Carrying 2 or 3 marks

1. Define the following terms:

- (a) Molality
- (b) Osmotic pressure
- (c) Van't Hoff factor
- (d) Molarity (Hr. S.B. 2018)

2. (a) Establish a relationship between mole fraction of solute and molality of a binary dilute solution.

(Manipur S.B. 2014)

(b) Molality is preferred over molarity. Why?

(c) Which has higher boiling point 0.1M NaCl or 0.1M glucose? (H.P.S.B. 2018)

3. (a) Define Raoult's law and derive it. (Uttarakhand S.B. 2014)

(b) Why is osmotic pressure considered to be a colligative property? (Maghalaya S.B. 2013)

4. (a) How is the colligative property changed when the solute undergoes association in solution?

(b) Describe a method to determine the osmotic pressure of a solution. How does it help in calculating the molar mass of the solute?

5. Why do we get abnormal molecular masses from colligative properties? What is Van't Hoff factor? How will you explain cases of association and dissociation of solute in such cases? (Hr. S.B. 2013)

6. (a) 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?

(b) Mixing acetone and chloroform occurs with reduction in volume and is endothermic process. What type of deviation from Raoult's law is shown in this case and why?

7. Explain :

(i) A person suffering from high blood pressure is advised to take minimum quantity of common salt. Explain.

(ii) A peeled egg when dipped in water swells while in saturated brine solution it shrinks.

(iii) The bottle of liquid ammonia is cooled before opening the seal.

(iv) Semipermeable membrane of $Cu_2[Fe(CN)_6]$ is not used for studying osmosis in non-aqueous solutions.

8. (a) What is osmotic pressure and how is it related to the molecular mass of the non-volatile substance?

(b) What advantage the osmotic pressure has over the elevation in boiling point method for determining the molecular masses?

9. Define azeotropes and explain briefly minimum boiling azeotropes by taking suitable example.

(CBSE Sample Paper 2011)

10. State Raoult's law for a solution containing volatile liquids. Explain with suitable example the concept of maximum boiling azeotropes? (CBSE Sample Paper 2011)

11. (a) When dehydrated fruits and vegetables are placed in water, they slowly swell and return to original form. Why? What is the effect of temperature on the process? Explain.

(Pb. S.B. 2016)

- (b) Prove that relative lowering in vapour pressure of a liquid on addition of non volatile solute is a colligative property. (H.P.S.B. 2012)
- 12.** (a) Sodium chloride solution freezes at lower temperature than water but boils at higher temperature than water. Explain.
 (b) What are hypertonic solutions? Explain with the help of example. (H.P.S.B. 2012)
- 13.** (a) Define osmotic pressure. How can molar mass of a substance be determined from the measurement of osmotic pressure of a solution? (Assam S.B. 2013)
 (b) What is osmotic pressure ? Show that it is a colligative property. (Hr. S.B. 2017)
 (c) What will happen if a patient is given hypertonic solution of glucose ? (Meghalaya S.B. 2018)
- 14.** (a) Prove that relative lowering in the vapour pressure is a colligative property.
 (b) Differentiate between ideal and non-ideal solutions.
 (c) Define colligative properties and give its types. (H.P.S.B. 2018)
- 15.** (a) Define the following :
 (i) Henry's law
 (ii) Raoult's law (Hr. S.B. 2018)
 (b) Give two applications of Henry's law. (Hr. S.B. 2018)
- 16.** (a) When HgI_2 is added to aqueous solution of KI, why is there an increase in osmotic pressure of solution?
 (b) Out of 1M urea solution and 1M KCl solution, which one has higher freezing point? (Pb. S.B 2018, H.P.S.B. 2018)
 (c) Commercially available HCl contains 38% HCl by mass. Calculate molality of the solution. (Pb. S.B. 2018)
- 17.** Define freezing point. Explain why the freezing point of a solvent is lowered on dissolving a non-volatile solute into it.
Or
 What do you mean by abnormal molecular mass? Show that relative lowering of vapour pressure is a colligative property. (Jammu S.Z. 2018)
- 18.** (a) Define :
 (i) Molality of a solution
 (ii) Isotonic solutions. (Karnataka S.B. 2018)
 (b) Van't Hoff's factor for a solution is less than 1, what is the conclusion drawn from it? (Karnataka S.B. 2018)
 (c) Why do some non-ideal solutions show positive deviation from ideal behaviour? Give suitable diagram. (Nagaland S.B. 2018)
- 19.** What are the colligative properties ? Name the colligative property which is widely used to determine the molecular mass of macromolecules. (Meghalaya S.B. 2017)
- 20.** (a) Define an ideal solution and write one of its characteristics.
 (b) Some liquids on mixing form 'azeotropes'. What are 'azeotropes'? (D.S.B. 2014)
- 21.** (a) State Henry's law. What is the effect of temperature on the solubility of a gas in a liquid ?
 (b) State Raoult's law for the solution containing volatile components. What is the similarity between Raoult's law and Henry's law ? (D.S.B. 2014)
- 22.** (a) $CaCl_2$ is used to clear snow in cold countries. Explain. (Hr. S.B. 2015)
 (b) Define the following and write their units:
 (a) Molarity (b) Molality (c) Normality
Or
 What are colligative properties? Show that relative lowering in vapour pressure is a colligative property. (Hr. S.B. 2015)
- 23.** Define the following:
 (i) Boiling point
 (ii) Molal depression constant (Hr. S.B. 2015)
- 24.** (a) Why is boiling point of water increased on addition of a non-volatile solute in it?
 (b) Why does NaCl solution freeze at lower temperature than water but boils at higher temperature than water? (Pb. S.B. 2015)
- 25.** (a) Define hypertonic solution.
 (b) Explain that the depression in freezing point is a colligative property. Calculate the molar mass of a solute with it. (H.P.S.B 2017)
- 26.** State Henry's law.
 At the same temperature, CO_2 gas is more soluble in water than O_2 gas. Which one of them will have higher value of K_H ? (Assam S.B. 2017)
- 27.** (a) State Henry's law and mention its important applications.
 (b) What would be the value of van't Hoff factor for a dilute solution of K_2SO_4 ? (Uttarakhand S.B. 2015)
- 28.** (a) What are the characteristics of ideal solution?
 (b) Why does vapour pressure of a liquid decrease when a non-volatile solute is added into it? (Manipur S.B. 2017)
- 29.** (a) Define molarity and mole fraction giving examples.
 (b) How is the molecular mass of a solute related to the depression in freezing point of the solution? (Manipur S.B. 2017)
- (c) What is reverse osmosis? Mention one of its application. (Meghalaya S.B. 2018)
- 30.** What is meant by positive deviations from Raoult's law? Give an example. What is the sign of $\Delta_{mix}H$ for positive deviation?
Or
 Define azeotropes. What type of azeotrope is formed by positive deviation from Raoult's law? Give an example. (D.S.B. 2015)
- 31.** (i) Two solutions are isotonic. What is meant by the statement.
 (ii) When a little amount of common salt is added in water, the boiling point increases. Explain why? (Kolkata S.B. 2016)
- 32.** What are colligative properties? Prove that relative lowering in vapour pressure is a colligative property. (H.P. S.B. 2016)
- 33.** State Raoult's law for an ideal solution containing non-volatile solute. Why do non-ideal solutions show positive deviation from Raoult's law? (H.P.S.B. 2016, Tripura S.B. 2016)
- 34.** Define boiling point. What is elevation in boiling point? How will you find the molecular mass of a solute by using this property? (H.P.S.B. 2016)
- 35.** (a) What is osmotic pressure? How is it related to the concentration of a solute in a solution?

Or

- (b) State and explain Raoult's law for a solution containing non-volatile solute. (Meghalaya S.B. 2016)

36. Define the following terms:

- (i) Ideal solution
(ii) Molarity (M) (D.S.B. 2017)

37. Define the following terms:

- (i) Abnormal molar mass
(ii) Van't Hoff factor (D.S.B. 2017)

CBSE QUESTIONS

38. State Raoult's law for solutions of volatile liquids. Taking suitable examples explain the meaning of positive and negative deviations from Raoult's law. (A.I.S.B. 2008; D.S.B. 2008)

39. Define the terms, 'osmosis' and 'osmotic pressure'. What is the advantage of using osmotic pressure as compared to other colligative properties for the determination of molar masses of solutes in solutions? (A.I.S.B. 2010)

40. State the following:

- (i) Raoult's law in its general form in reference to solutions.
(ii) Henry's law about partial pressure of a gas in a mixture. (A.I.S.B. 2011)

41. State Henry's law. Why do gases always tend to be less soluble in liquids as the temperature is raised?

Or

State Raoult's law for the solution containing volatile components. Write two differences between an ideal solution and a non-ideal solution. (A.I.S.B. 2015)

42. (i) Write the colligative property which is used to find the molecular mass of macromolecules.

- (ii) In non-ideal solution, what type of deviation shows the formation of minimum boiling azeotropes? (A.I.S.B. 2016)

43. Give reasons for the following:

- (a) Measurement of osmotic pressure method is preferred for the determination of molar masses of macromolecules such as proteins and polymers.
(b) Aquatic animals are more comfortable in cold water than in warm water.
(c) Elevation of boiling point of 1 M KCl solution is nearly double than that of 1 M sugar solution. (A.I.S.B. 2018)

Long Answer Questions

Carrying 5 marks

- What are ideal and non-ideal solutions? What type of non-idealities are exhibited by cyclohexane ethanol and acetone chloroform mixtures. Give reasons for your answer.
- What is Van't Hoff's factor? What possible values can it have if the solute molecules undergo (i) association (ii) dissociation in solution. Prove that osmotic pressure is a colligative property.
- (a) What is elevation in boiling point? How can you calculate molecular mass of a solute using it? Show that it is a colligative property.
(b) Calculate molality and molarity of KI if density of 20% (mass/mass) aqueous KI is 1.202 g/mL. (Hr. S.B. 2013)
- Osmotic pressure is a colligative property and it is proportional to the molarity of solution.
 - What is osmotic pressure?
 - Molecular mass of NaCl determined by osmotic pressure measurement is found to be half of the actual value. Account for it.
 - Calculate the osmotic pressure exerted by a solution prepared by dissolving 1.5 g of a polymer of molar

mass 185000 in 500 ml of water at 37°C. [$R = 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}$]. (Kerala S.B. 2014)

5. Either

- (a) A solution of NaOH is made by dissolving 0.8 g of it in 100 ml of its solution. Calculate the molarity of the solution.
(b) What is the effect of addition of non-volatile solute to the vapour pressure of a pure liquid? Give reasons for your answer.
(c) Calculate the molar mass of a substance 1.3 g of which when dissolved in 169 g of water gave the solution which will boil at 100.025 °C at 1 atm. ($K_b = 0.52 \text{ K m}^{-1}$). *Or*

- (d) Calculate the molarity and molality of a 15% solution (by weight) of H_2SO_4 of density 1.020 g. cm^{-3} .
(e) State Henry's law of solubility of gases in liquid. Why do we see effervescence when a cold drink bottle is opened?
(f) Molar mass of CH_3COOH in aqueous solution as determined by the use of colligative properties is approximately double of the expected value. Why? (Meghalaya S.B. 2014)

6. (a) Among the following, which is not a colligative property?

- (i) Osmotic pressure
(ii) Elevation of boiling point
(iii) Vapour pressure
(iv) Depression of freezing point

- (b) 200 cm^3 of an aqueous solution of a protein contains 1.26 g of protein. The osmotic pressure of solution at 300 K is found to be 8.3×10^{-2} bar. Calculate the molar mass of protein ($R = 0.083 \text{ L bar K}^{-1} \text{ mol}^{-1}$).

- (c) What is the significance of van't Hoff factor? (Kerala S.B. 2015)

7. (a) Mention a method used for desalination of sea water.
(b) Define the term 'osmotic pressure'. How does osmotic pressure of a solution vary with temperature?

- (c) Calculate molarity of a solution containing 11.7 g NaCl in 2.0 L solution. ($M_{\text{NaCl}} = 58.5 \text{ g mol}^{-1}$) (Assam S.B. 2016)

8. (a) Number of moles of the solute per kilogram of the solvent is

- | | |
|-------------------|-----------------|
| (i) Mole fraction | (ii) Molality |
| (iii) Molarity | (iv) Molar mass |

- (b) The extent to which a solute is dissociated or associated can be expressed by Van't Hoff factor. Substantiate the statement.

- (c) The vapour pressure of pure benzene at a certain temperature is 0.850 bar. A non-volatile, non-electrolyte solid weighing 0.5 g when added to 39 g of benzene (molar mass 78 g mol⁻¹), vapour pressure becomes 0.845 bar. What is the molar mass of the solid substance? (Kerala S.B. 2016)

9. (i) Prove that elevation in boiling point is a colligative property.
(ii) The boiling point of benzene is 353.23 K. When 1.80 g of a non-volatile solute was dissolved in 90 g of benzene, the boiling point is raised to 354.11 K. Calculate the molar mass of solute. (K_b for benzene = 2.53 K kg mol⁻¹) (Pb. S.B. 2017)

10. (i) Prove that depression in freezing point is a colligative property.
(ii) 45 g of ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$) is mixed with 600 g of water. Calculate the freezing point depression. (K_f for water = 1.86 K kg mol⁻¹) (Pb. S.B. 2017)

11. (i) Prove that osmotic pressure is a colligative property.
(ii) Calculate the molar concentration of urea solution if it exerts an osmotic pressure of 2.45 atmosphere at 300 K. ($R = 0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1}$) (Pb. S.B. 2017)

12. (a) Give the definition of solubility of a substance.
 (b) Show that total vapour pressure over the solution of two liquids 1 and 2 at a particular temperature varies linearly with the mole fraction of a component.

(Assam S.B. 2018)

13. (a) A solution containing 15 g urea (molar mass = 60 g mol⁻¹) per litre of solution in water has the same osmotic pressure as a solution of glucose (molar mass = 180 g mol⁻¹) in water. Calculate the mass of glucose present in one litre of its solution.
 (b) Define minimum boiling azeotropes with example.

(Kerala S.B. 2018)

CBSE QUESTIONS

14. (a) Why is meant by
 (i) colligative properties
 (ii) molality of a solution ?
 (b) What concentration of nitrogen should be present in a glass of water at room temperature ? Assume a temperature of 25°C, a total pressure of 1 atmosphere and mole fraction of nitrogen in air is 0.78 [K_H for nitrogen = 8.42 × 10⁻⁷ M/min Hg].

(A.I.S.B. 2010)

15. (a) State the following :
 (i) Henry's law about partial pressure of a gas in a mixture.
 (ii) Raoult's law in its general form in reference to solutions.
 (b) A solution prepared by dissolving 8.95 mg of a gene fragment in 35.0 mL of water has an osmotic pressure of 0.335 torr at 25°C. Assuming the gene fragment is a non-electrolyte, determine its molar mass.

Or

- (a) Differentiate between molarity and molality in a solution. What is the effect of temperature change on molarity and molality in a solution ?
 (b) What would be the molar mass of a compound if 6.21 g of it dissolved in 24.0 g of chloroform form a solution that has a boiling point of 68.04°C. The boiling point of pure chloroform is 61.7°C and the boiling point elevation constant, K_b for chloroform is 3.63°C/m.

(A.I.S.B. 2011)

16. (a) Define the following terms :
 (i) Mole fraction
 (ii) Ideal solution
 (b) 15.0 g of an unknown molecular material is dissolved in 450 g of water. The resulting solution freezes at -0.34°C. What is the molar mass of the material ? (K_f for water = 1.83 K kg mol⁻¹).

Or

- (a) Explain the following :
 (i) Henry's law about dissolution of a gas in a liquid
 (ii) Boiling point elevation constant for a solvent.
 (b) A solution of glycerol (C₃H₈O₃) in water was prepared by dissolving some glycerol in 500 g of water. This solution has a boiling point of 100.42°C. What mass of glycerol was dissolved to make this solution ? (K_b for water = 0.512 K kg mol⁻¹).

(A.I.S.B. 2012)

17. (a) State Raoult's law for a solution containing volatile components. How does Raoult's law become a special case of Henry's law ?
 (b) 1.00 g of non-electrolyte solute dissolved in 50 g of benzene lowered the freezing point of benzene by 0.40 K. Find the molar mass of the solute. (K_f for benzene = 5.12 K kg mol⁻¹).

Or

- (a) Define the following terms :
 (i) Ideal solution (ii) Azeotrope (iii) Osmotic pressure
 (b) A solution of glucose (C₆H₁₂O₆) in water is labelled as 10% by weight. What would be molality of the solution? (Molar mass of glucose = 180 g mol⁻¹). (A.I.S.B. 2013)

18. (a) Define the following terms:
 (i) Molarity
 (ii) Molal elevation constant (K_b).
 (b) A solution containing 15 g urea (molar mass = 60 g mol⁻¹) per litre of solution in water has the same osmotic pressure (isotonic) as a solution of glucose (molar mass = 180 g mol⁻¹) in water. Calculate the mass of glucose present in one litre of its solution.

Or

- (a) What type of deviation is shown by a mixture of ethanol and acetone ? Give reason.
 (b) A solution of glucose (molar mass = 180 g mol⁻¹) in water is labelled as 10% (by mass). What would be the molality and molarity of the solution ? (Density of solution = 1.2 g mL⁻¹).

19. (a) A 10% solution (by mass) of sucrose in water has a freezing point of 269.15 K. Calculate the freezing point of 10% glucose in water if the freezing point of pure water is 273.15 K.

Given : (Molar mass of sucrose = 342 g mol⁻¹)
 (Molar mass of glucose = 180 g mol⁻¹)

- (b) Define the following terms:

- (i) Molality (m)
 (ii) Abnormal molar mass

Or

- (a) 30 g of urea (M = 60 g mol⁻¹) is dissolved in 846 g of water. Calculate the vapour pressure of water for this solution if vapour pressure of pure water at 298 K is 23.8 mm Hg.

- (b) Write two differences between ideal solutions and non-ideal solutions.

(A.I.S.B. 2017)

NUMERICAL PROBLEMS

1. The density of a 3 M sodium thiosulphate (Na₂S₂O₃) solution is 1.25 g mL⁻¹. Calculate

- (i) the % by weight of sodium thiosulphate.
 (ii) the mole fraction of sodium thiosulphate.
 (iii) the molalities of Na⁺ and S₂O₃²⁻ ions.

[Ans. (i) 37.92% (ii) 0.065 (iii) 7.730 m, 3.865 m]

2. Calculate the freezing point of an aqueous solution of a non-electrolyte having an osmotic pressure of 2 atm at 300 K (K_f = 1.86 K m⁻¹, R = 0.082 L atm K⁻¹ mol⁻¹)

[Ans. - 0.151]

3. 0.01 m aqueous solution of sodium sulphate depresses the freezing point of water by 0.0284°C. Calculate the degree of dissociation of the salt. (K_f for water = 1.86 K m⁻¹).

[Ans. 26.5%]

4. Ice begins to separate at -0.744°C from a solution containing 2.4 g of a non-electrolyte solute in 100 g of water. Calculate the molecular weight of non-electrolyte and osmotic pressure which the solution would exert at 20°C.

[Ans. 60, 9.622 atm.]

5. A solution of glycerol (C₃H₈O₃; molar mass = 92 g mol⁻¹) in water was prepared by dissolving some glycerol in 500 g of water. This solution has a boiling point of 100.42°C. What mass of glycerol was dissolved to make this solution? (K_b for water = 0.512 K kg mol⁻¹).

(D.S.B. 2010)

[Ans. 37.73 g]

6. 0.52 g of glucose ($C_6H_{12}O_6$) is dissolved in 80.2 g of water. Calculate the boiling point of the solution. (K_b for water is 0.52 K kg mol $^{-1}$). (Assam S.B. 2013) [Ans. 100.019°C]
7. 9 g of a non-volatile solute when dissolved in 100 g of water causes lowering of freezing point by 0.93 K. Calculate the molecular weight of the solute when K_f for water is 1.86 K/m. (Mizoram S.B. 2017)
8. (a) 7.45 g KCl is dissolved in 100 g of water. What will be the mole fraction of KCl in solution. [Ans. 0.0177] (b) On dissolving 9.0 g of glucose in 100 g of water, its freezing point is lowered by 0.93 °C. Calculate the molal depression constant of water. (Uttarakhand S.B. 2013) [Ans. 3.53 K m $^{-1}$]
9. Calculate the boiling point of one molar aqueous solution (density 1.03 g mL $^{-1}$) of NaCl. K_b for water = 0.52 Km $^{-1}$. (Nagaland S.B. 2016)
10. Calculate the osmotic pressure at 273 K of a 5% solution of compound A. (molecular mass = 60) (Given that $R = 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}$) (Mizoram S.B. 2016)
11. Calculate the molar mass of a substance 1.3 g of which when dissolved in 169 g of H_2O gave the solution which will boil at 100.025 °C at 1 atm. ($K_b = 0.52 \text{ K m}^{-1}$) (Meghalaya S.B. 2017)
12. A solution containing 4.2 g of an organic compound in 50 g of acetone shows an elevation of boiling point by 1.8 K. Determine the molar mass of the organic compound. K_b of acetone = 1.71 K kg mol $^{-1}$. (Nagaland S.B. 2017)
13. The boiling point of water is 100°C. Calculate the boiling point of an aqueous solution containing 0.6 g of urea (molar mass = 60) in 100 g of water. (K_b for water = 0.52 Km $^{-1}$) (Mizoram S.B. 2018)
14. The vapour pressure of a compound A of molar mass 80 g mol $^{-1}$ at 20°C is 2.0 bar. When 4g of a non-volatile solid is added to 40 g of compound A in a beaker, the resulting vapour pressure is 1.5 bar. Calculate molar mass of the non-volatile solid. (Mizoram S.B. 2018)
15. 1.8 g of glucose ($C_6H_{12}O_6$) is dissolved in 100 g of water in a beaker. At what temperature will water in the solution boil at 1.013 bar? Given boiling point of pure water at 1.013 bar is 373.15 K and K_b for water is 0.052 K kg mol $^{-1}$. (Assam S.B. 2018)
16. The freezing point of 0.1 molal solution of CH_3COOH in benzene is 0.256 K ($K_f = 5.12 \text{ K m}^{-1}$). What conclusion will you draw about molecular state of CH_3COOH in C_6H_6 ? (Meghalaya S.B. 2018)

CBSE QUESTIONS

17. A 0.1539 molal aqueous solution of cane sugar (molar mass = 342 g mol $^{-1}$) has a freezing point of 271 K while the freezing point of pure water is 273.15 K. What will be the freezing point of an aqueous solution containing 5 g of glucose (mol. mass = 180 g mol $^{-1}$) per 100 g of solution. (A.I.S.B. 2007) [Ans. 269.07 K]
18. Calculate the temperature at which a solution containing 54 g of glucose ($C_6H_{12}O_6$) in 250 g of water will freeze. (K_f for water = 1.86 K kg mol $^{-1}$). (A.I.S.B. 2008, D.S.B. 2008) [Ans. -2.23°C]
19. A solution containing 8 g of a substance in 100 g of diethyl ether boils at 36.86°C, whereas pure ether boils at 35.60°C. Determine the molecular mass of the solute (For ether $K_b = 2.02 \text{ K kg mol}^{-1}$) (A.I.S.B. 2008) [Ans. 128.25]
20. 100 mg of a protein is dissolved in just enough water to make 10.0 mL of solution. If this solution has an osmotic pressure of 13.3 mm Hg at 25°C, what is the molar mass of the protein? ($R = 0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1}$ and 760 mm Hg = 1 atm) (A.I.S.B. 2009, D.S.B. 2009) [Ans. 13980.4]
21. What mass of ethylene glycol (molar mass = 62.0 g mol $^{-1}$) must be added to 5.50 kg of water to lower the freezing point of water from 0 to -10.0°C (K_f for water = 1.86 K kg mol $^{-1}$). (A.I.S.B. 2010) [Ans. 1.83 kg]
22. 15 g of unknown molecular substance was dissolved in 450 g of water. The resulting solution freezes at -0.34°C. What is the molar mass of the substance (K_f for water = 1.86 K kg mol $^{-1}$)? (A.I.S.B. 2010) [Ans. 182.35]
23. What mass of NaCl must be dissolved in 65.0 g of water to lower the freezing point of water by 7.50°C? The freezing point depression constant (K_f) for water is 1.86°C/m. Assume Van't Hoff factor for NaCl is 1.87. (Molar mass of NaCl = 58.5 g). (A.I.S.B. 2011) [Ans. 8.20 g]
24. The freezing point of benzene decreases by 2.12 K when 2.5 g of benzoic acid (C_6H_5COOH) is dissolved in 25 g of benzene. If benzoic acid forms a dimer in benzene, calculate the van't Hoff factor and the percentage association of benzoic acid. (K_f for benzene = 5.12 K kg mol $^{-1}$) (CBSE Sample Paper 2017-18) [Ans. $i = 0.505$, $\alpha = 99.0\%$]

Hints & Answers

for Revision Exercises

Very Short Answer Questions

1. Dust, water vapour in air (humidity)
2. This is because molality involves masses which do not change with temperature.
3. 0.5
4. Molal depression constant K_f is related to the enthalpy of fusion, ΔH_f as :

$$K_f = \frac{RT_f^2 M}{\Delta H_f \times 1000}$$

where M is the molar mass and T_f is the freezing point.

5. When sodium chloride is added to water, there is elevation in boiling point and depression in freezing point.
6. Because it depresses the freezing point to such an extent that it cannot freeze to form ice.
7. Solubility decreases

SOLUTIONS

8. $i > 1$ when the solute undergoes dissociation in the solution.
9. Due to osmosis.
10. Remains unchanged.
11. 3.0 N
12. ΔT_f and ΔT_b are inversely proportional to molecular mass of solute.
13. 1.5 N
14. A
15. When solute undergoes association.
16. Solute behaves as non-electrolyte and does not undergo association or dissociation.
18. Being volatile in nature, isopropyl alcohol absorbs certain energy from the skin which becomes cold.
20. Because molality does not change with temperature.
21. Zero
23. One
24. Molarity changes with temperature but molality does not change with temperature.
25. $K_2SO_4 \rightarrow 2K^+ + SO_4^{2-}; i = 3$
26. When pressure higher than osmotic pressure is applied to the solution to get pure solvent.
29. (c) 30. (a) 31. (b) 32. (c) 33. (c)
34. (c) 35. (a) 36. (c) 37. (a) 38. (a)
39. (d) 40. (a) 41. (b) 42. (b) 43. (b)
44. (c) 45. (a) 46. (a) 47. (b) 48. (a)
49. (d) 50. (d)

Short Answer Questions

4. (a) The association causes a decrease in the number of particles and the colligative property also decreases.
7. (i) The osmotic pressure increases with the amount of solute. Since the body fluid contains Na^+ and Cl^- ions and if we take more salt, the concentration of these ions will increase leading to high osmotic pressure. The high osmotic pressure may cause rupture of the cells. Therefore, the patients suffering from high blood pressure are advised to take less of common salt.
- (iii) To lower the vapour pressure of NH_3 otherwise the gas will bump out of the bottle.
- (iv) Because $Cu_2[Fe(CN)_6]$ is soluble in non-aqueous solutions.
42. (i) Osmotic pressure
- (ii) Positive deviation from Raoult's law.

Long Answer Questions

3. (b) 20% (mass/mass) means that 20 g of KI is present in 100g of solution or 80 g of water.

$$\text{Molar mass of KI} = 39 + 127 = 166$$

$$\text{Molality} = \frac{20/166}{80} \times 1000 = 1.51 \text{ m}$$

$$\text{Volume of solution} = \frac{100}{1.202} = 83.19 \text{ mL}$$

$$\text{Molarity} = \frac{20/166}{83.19} \times 1000 = 1.45 \text{ M}$$

$$\begin{aligned} 4. (c) \quad \pi &= \frac{w_B}{M_B} \frac{RT}{V} \\ &= \frac{1.5}{185000} \times \frac{0.0821 \times 310}{500/1000} \\ &= 4.13 \times 10^{-4} \text{ atm} \end{aligned}$$

$$\begin{aligned} 7. (c) \text{ Moles of NaCl} &= \frac{11.7}{58.5} \\ \text{Molarity} &= \frac{11.7}{58.5 \times 2} = 0.1 \text{ M} \end{aligned}$$

8. (c) Refer Solved Example 32 (Page 37)

9. Refer Solved Example 37 (Page 40)

10. Refer Solved Example 44 (Page 44)

$$11. \pi = cRT$$

$$2.45 = c \times 0.0821 \times 300$$

$$c = \frac{2.45}{0.0821 \times 300} = 0.099 \text{ mol L}^{-1}$$

12. (a) Refer Solved Example 56 (Page 52)

14. (b) Refer Solution to Practice Problem 26 (Page 69)

15. (b) Refer Solved Example 55 (Page 52).

Or

Refer Solved Example 40 (Page 41).

16. (b) Refer Solution to Practice Problem 61. (Page 71)

Or

Refer Solved Example 41 (Page 41).

17. Refer Solution to Practice Problem 62 (Page 72)

18. Refer Solution to Practice Problem 57 (Page 71)

Or

Refer Solved Example 12 (Page 9)

19. (a) Refer Solution to Practice Problem 59 (Page 71)

Or

(b) Refer Solution to Practice Problem 41 (Page 70)

Numerical Problems

$$\begin{aligned} \blacklozenge 1. (i) \text{ Wt. of 1000 mL of } Na_2S_2O_3 \text{ solution} &= 1.25 \times 1000 \\ &= 1250 \text{ g} \end{aligned}$$

$$\begin{aligned} \text{Molar mass of } Na_2S_2O_3 &= 23 \times 2 + 32 \times 2 + 16 \times 3 \\ &= 158 \end{aligned}$$

$$\begin{aligned} \text{Wt. of } Na_2S_2O_3 \text{ in 1000 mL of M solution} &= 3 \times 158 = 474 \text{ g} \end{aligned}$$

$$\text{Now, 1250 g of solution contain} = 474 \text{ g } Na_2S_2O_3$$

$$\therefore \% \text{ by weight of sod. thiosulphate} = \frac{474}{1250} \times 1000 \\ = 37.92\%$$

$$\begin{aligned} (ii) \text{ Wt. of } Na_2S_2O_3 \text{ present in 100 g of solution} &= 37.92 \text{ g} \end{aligned}$$

$$\text{Wt. of water present} = 100 - 37.92 = 62.08 \text{ g}$$

$$\text{Moles of } Na_2S_2O_3 = \frac{37.92}{158} = 0.24$$

$$\text{Moles of water} = \frac{62.08}{18} = 3.45$$

$$\therefore \text{Mole fraction of } \text{Na}_2\text{S}_2\text{O}_3 = \frac{0.24}{0.24 + 3.45} = 0.065.$$

(iii) 62.08 g of water contain = 0.24 moles of $\text{Na}_2\text{S}_2\text{O}_3$

$$\text{Molality of solution} = \frac{0.24}{62.08} \times 1000 = 3.865 \text{ m.}$$

Since 1 mole of $\text{Na}_2\text{S}_2\text{O}_3$ contains 2 moles of Na^+ and 1 mole of $\text{S}_2\text{O}_3^{2-}$

$$\therefore \text{Molality of } \text{Na}^+ = 2 \times 3.865 = 7.730$$

Similarly, Molality of $\text{S}_2\text{O}_3^{2-} = 1 \times 3.865 = 3.865$

$$\blacklozenge 2. \text{ Osmotic pressure, } \pi = cRT \text{ or } c = \frac{\pi}{RT}$$

$$c = \frac{2.0}{0.0821 \times 300} = 0.0812 \text{ mol L}^{-1}$$

Since density of water is 1.0 g cm^{-3} , the molarity of aqueous solution may be taken equal to molality.

$$\therefore \text{Molality of solution} = 0.0812 \text{ m}$$

$$\text{Now, } \Delta T_f = K_f \times m \\ = 1.86 \times 0.0812 = 0.151$$

$$\text{Freezing point of solution} \\ = 0 - 0.151 = -0.151.$$

◆ 3. The observed molecular mass can be calculated from the reaction :

$$M_B = \frac{K_f \times 1000 \times w_B}{w_A \times \Delta T_f}$$

0.01 m aqueous solution means 0.01 mole or 0.01×142 (mol. wt. of $\text{Na}_2\text{SO}_4 = 142$) g of sodium sulphate are dissolved in 1000 g of water.

$$w_B = 1.42 \text{ g}, w_A = 1000 \text{ g}, \Delta T_f = 0.0284$$

$$M_B (\text{observed}) = \frac{1.86 \times 1000 \times 1.42}{1000 \times 0.0284} = 93$$

$$\text{Vant' Hoff factor, } i = \frac{\text{Normal mol. mass}}{\text{Observed mol. mass}}$$

$$i = \frac{142}{93} = 1.53$$

Degree of dissociation can be calculated as :



$$\text{Initial moles } 1 \quad 0 \quad 0$$

$$\text{After dissociation } 1 - \alpha \quad 2\alpha \quad \alpha$$

Total number of moles after dissociation

$$= 1 - \alpha + 2\alpha + \alpha = 1 + 2\alpha$$

$$i = \frac{\text{Moles after dissociation}}{\text{Normal moles}}$$

$$i = \frac{1 + 2\alpha}{1} = 1.53$$

$$\therefore \frac{1 + 2\alpha}{1} = 1.53$$

$$\text{or} \quad 2\alpha = 1.53 - 1 = 0.53 \\ \alpha = 0.53/2 = 0.256$$

\therefore Degree of dissociation = 26.5%.

$$\blacklozenge 4. \quad M_B = \frac{K_f \times w_B \times 1000}{w_A \times \Delta T_f}$$

$$K_f = 1.86, w_B = 2.4 \text{ g}, w_A = 100 \text{ g}$$

$$\Delta T_f = 0 - (-0.744) = 0.744$$

$$M_B = \frac{1.80 \times 2.4 \times 1000}{100 \times 0.744} = 60$$

Now, osmotic pressure

$$\pi = \frac{w_B \pi RT}{M_B V}$$

$$\pi = \frac{2.4 \times 82.1 \times 293}{60 \times 1000} = 9.622 \text{ atm.}$$

$$\blacklozenge 5. \quad \Delta T_b = \frac{K_b \times 1000 \times w_B}{w_A \times M_B}$$

$$\Delta T_b = 100.42 - 100 = 0.42, w_A = 500 \text{ g,}$$

$$K_b = 0.512 \text{ K kg mol}^{-1}, M_B = 92, w_B = ?$$

$$0.42 = \frac{0.512 \times 1000 \times w_B}{500 \times 92}$$

$$w_B = \frac{0.42 \times 500 \times 92}{0.512 \times 1000} = 37.73 \text{ g.}$$

$$\blacklozenge 6. \quad \Delta T_b = \frac{K_b \times w_B \times 1000}{w_A \times M_B} = \frac{0.52 \times 0.52 \times 1000}{80.2 \times 180} \\ = 0.019.$$

$$\text{Boiling point of solution} = 100 + 0.019 = 100.019 \text{ }^\circ\text{C.}$$

$$\blacklozenge 7. \quad M_B = \frac{K_f \times 1000 \times w_B}{w_A \times \Delta T_f}$$

$$K_f = 1.86 \text{ Km}^{-1}, w_B = 9 \text{ g, } w_A = 100 \text{ g}$$

$$\Delta T_f = 0.93 \text{ K}$$

$$\therefore M_B = \frac{1.86 \times 1000 \times 9}{100 \times 0.93} \\ = 180 \text{ g mol}^{-1}$$

$$\blacklozenge 8. (a) \text{ Moles of KCl} = \frac{7.45}{74.5} = 0.1$$

$$(\text{Molar mass of KCl} = 39 + 35.5 = 74.5)$$

$$\text{Moles of water} = \frac{100}{18} = 5.56$$

$$\text{Mole fraction of KCl} = \frac{0.1}{0.1 + 5.56} = 0.0177.$$

$$(b) w_B = 9.0 \text{ g, } w_A = 100 \text{ g, } \Delta T_f = 0.93 \text{ }^\circ\text{C, } M_B = 342$$

$$\Delta T_f = \frac{K_f \times 1000 \times w_B}{w_A \times M_B}$$

$$\text{or } K_f = \frac{\Delta T_f \times w_A \times M_B}{1000 \times w_B} = \frac{0.93 \times 100 \times 342}{1000 \times 9.0} \\ = 3.53 \text{ Km}^{-1}.$$

$$\blacklozenge 9. \quad \text{NaCl} \longrightarrow \text{Na}^+ + \text{Cl}^-$$

$$i = 2$$

$$\Delta T_b = i \times K_b \times m \\ = 2 \times (0.52 \text{ Km}^{-1}) \times (1 \text{ m}) \\ = 1.04 \text{ K}$$

$$\text{Boiling point of solution} = 373 + 1.04 = 374.04 \text{ K}$$

◆ 10. Concentration of solution = $\frac{5 \text{ g}}{100 \text{ mL}}$

$$\pi = \frac{w_B RT}{M_B V_B}$$

$$= \frac{5 \times 0.0821 \times 273}{60 \times 100 / 1000}$$

$$= 18.68 \text{ atm}$$

◆ 11. $M_B = \frac{K_b \times 1000 \times w_B}{w_A \times \Delta T_b}$

$$K_b = 0.52 \text{ Km}^{-1}, w_B = 1.3 \text{ g}, w_A = 169 \text{ g}$$

$$\Delta T_b = 100.025 - 100 = 0.025 \text{ K}$$

$$M_B = \frac{0.52 \times 1000 \times 1.3}{169 \times 0.025}$$

$$= 160 \text{ g mol}^{-1}$$

◆ 12. $M_B = \frac{K_b \times 1000 \times w_B}{w_A \times \Delta T_b}$

$$w_B = 4.2 \text{ g}, w_A = 50 \text{ g}, \Delta T_b = 1.8 \text{ K}$$

$$K_f = 1.71 \text{ Km}^{-1}$$

$$M_B = \frac{1.71 \times 1000 \times 4.2}{50 \times 1.8}$$

$$= 79.8 \text{ g mol}^{-1}$$

◆ 13. $\Delta T_b = \frac{K_b \times w_b \times 1000}{M_B \times w_A}$

$$= \frac{0.52 \times 0.6 \times 1000}{60 \times 100}$$

$$= 0.052^\circ$$

Boiling point of solution = $100 + 0.052 = 100.052^\circ\text{C}$
or $273.15 + 100.052 = 373.202 \text{ K}$

◆ 14. $\frac{p_A^o - p_A}{p_A^o} = x_B = \frac{w_B \times M_A}{M_B \times w_A}$

$$\frac{2.0 - 1.5}{2.0} = \frac{4 \times 80}{M_B \times 40}$$

$$\frac{0.5}{2.0} = \frac{4 \times 80}{M_B \times 40}$$

$$M_B = \frac{4 \times 80 \times 2.0}{0.5 \times 40} = 32 \text{ g mol}^{-1}$$

◆ 15. $\Delta T_b = \frac{K_b \times w_B \times 1000}{M_B \times w_A}$

$$= \frac{0.52 \times 1.8 \times 1000}{180 \times 100}$$

$$= 0.052^\circ$$

Boiling point of solution = $373.15 + 0.052 = 373.202 \text{ K}$

◆ 16. $\Delta T_f = K_f \times m$
 $= 5.12 \times 0.1 = 0.512 \text{ K}$

Observed $\Delta T_f = 0.256 \text{ K}$

Van't Hoff factor, $i = \frac{\text{Observed freezing point depression}}{\text{Calculated freezing point depression}}$

$$= \frac{0.256}{0.512} = 0.5$$

Since 'i' is less than one, this means that CH_3COOH undergoes association in benzene. The value 0.5 indicates that the number of particles become half and therefore, CH_3COOH dimerises in benzene.

◆ 17. Refer Solved Example 47 (page 44)

◆ 18. $\Delta T_f = \frac{K_f \times 1000 \times w_B}{w_A \times M_B}$

$$\frac{1.86 \times 1000 \times 54}{250 \times 180} = 2.23^\circ$$

Freezing point of solution = $0 - 2.23$
 $= -2.23^\circ\text{C}$

◆ 19. $M_B = \frac{K_b \times 1000 \times w_B}{w_A \times \Delta T_b}$

$$= \frac{2.02 \times 1000 \times 8}{100 \times 1.26} = 128.25 \text{ g mol}^{-1}$$

◆ 20. $\pi = cRT = \frac{w_2}{M_2 V} RT \text{ or } M_2 = \frac{w_2 RT}{\pi V}$

$$w_2 = 100 \times 10^{-3} \text{ g}, R = 0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1}$$

$$T = 298 \text{ K}$$

$$\pi = \frac{13.3}{760} \text{ atm}, V = \frac{10}{1000} \text{ L}$$

$$M_2 = \frac{(100 \times 10^{-3} \text{ g}) \times (0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1}) \times (298 \text{ K})}{\left(\frac{13.3}{760} \text{ atm}\right) \times \left(\frac{10}{1000} \text{ L}\right)}$$

$$= 13980.45 \text{ g mol}^{-1}$$

◆ 21. Refer Solution to Practice Problem 63 (page 72).

◆ 22. Refer Solution to Practice Problem 60 (page 71).

◆ 23. Lowering in freezing point, $\Delta T_f = 7.50^\circ\text{C}$

$$K_f = 1.86^\circ\text{C/m}$$

Mass of water, $w_A = 65.0 \text{ g}$

Molar mass of NaCl, $M_B = 58.5$

Van't Hoff factor, $i = 1.87$, Mass of NaCl, $w_B = ?$

$$\Delta T_f = \frac{i K_f \times 1000 \times w_B}{w_A \times M_B}$$

$$\text{or } w_B = \frac{\Delta T_f \times w_A \times M_B}{i \times K_f \times 1000}$$

$$= \frac{7.50 \times 65.0 \times 58.5}{1.87 \times 1.86 \times 1000} = 8.20 \text{ g.}$$

Competition File

Additional Useful Information and Objective Questions

ADDITIONAL USEFUL INFORMATION

Relation between molarity (M) and molality (m)

Molarity (M) means that M moles of the solute are present in 1000 mL of the solution. If density of the solution is ρ g cm⁻³, then

$$\text{Mass of solution} = 1000 \rho$$

Mass of solute = MM_2 (M_2 is the molar mass of solute)

$$\therefore \text{Mass of solvent} = 1000 \rho - MM_2$$

$$\therefore \text{Molality} = \frac{M}{1000\rho - MM_2} \times 1000 = \frac{1000 M}{1000\rho - MM_2}$$

$$\text{or } m = \frac{M}{\rho - \frac{MM_2}{1000}}$$

$$\text{or } \frac{1}{m} = \frac{\rho - \frac{MM_2}{1000}}{M}$$

$$\frac{1}{m} = \frac{\rho}{M} \frac{MM_2}{1000}$$

$$\frac{\rho}{M} = \frac{1}{m} + \frac{MM_2}{1000}$$

Relation between molality (m) and mole fraction (x_2)

Molality means moles of solute in 1000 g of the solvent.

$$\text{Moles of solvent} = \frac{1000}{M_1} \quad (\text{M}_1 \text{ is molar mass of solvent})$$

$$\text{Moles of solute} = m$$

$$\text{Mole fraction} (x_2) = \frac{m}{m + \frac{1000}{M_1}}$$

$$\therefore x_2 = \frac{mM_1}{mM_1 + 1000}$$

$$\text{or } \frac{1}{x_2} = \frac{mM_1 + 1000}{mM_1} = 1 + \frac{1000}{mM_1}$$

$$\text{or } \frac{1000}{mM_1} = \frac{1}{x_2} - 1 = \frac{1 - x_2}{x_2} = \frac{x_1}{x_2}$$

$$\therefore m = \frac{1000 x_2}{x_1 M_1}$$

Relation between molarity (M) and mole fraction (x_2)

Molarity (M) means that M moles of solute are present in 1000 mL of solution. If ρ is the density of the solution, then mass of solution is 1000ρ . Mass of solute = MM_2 (M_2 is the molar mass of solute).

$$\text{Mass of solvent} = 1000 \rho - MM_2$$

$$\text{Moles of solvent} = \frac{1000 \rho - MM_2}{M_1} \quad (\text{M}_1 \text{ is molar mass of solvent})$$

$$\text{Mole fraction, } x_2 = \frac{M}{1000 \rho - MM_2 + M}$$

$$= \frac{MM_1}{(1000 \rho - MM_2) + MM_1}$$

$$= \frac{MM_1}{M(M_1 - M_2) + 1000 \rho}$$

$$\text{or } x_2 = \frac{MM_1}{M(M_1 - M_2) + 1000 \rho}$$

Rearranging

$$M(M_1 - M_2)x_2 + 1000 \rho x_2 = MM_1$$

$$\text{or } MM_1 - MM_1 x_2 + MM_2 x_2 = 1000 \rho x_2$$

$$MM_1(1 - x_2) + MM_2 x_2 = 1000 \rho x_2$$

$$MM_1 x_1 + MM_2 x_2 = 1000 \rho x_2$$

$$M(M_1 x_1 + M_2 x_2) = 1000 \rho x_2$$

$$\therefore M = \frac{1000 \rho x_2}{x_1 M_1 + x_2 M_2}$$

Note : If molarity (M) is in mol/litre and density, ρ is in kg/L and molality m is in mol/kg of solvent then 1000 will be replaced by 1 in the above relations.

AZEOTROPES - BOILING POINT DIAGRAMS

Some liquids on mixing form azeotropes which are binary mixtures having same composition in liquid and vapour phase and boil at constant temperature. In such cases, it is not possible to separate the components by fractional distillation. There are two types of azeotropes called *minimum boiling azeotropes* and *maximum boiling azeotropes*.

(i) **Minimum boiling azeotropes:** In case of solutions showing very large positive deviations from Raoult's law, there is a maximum in the vapour pressure curve which is above the vapour pressure of either of the pure components. For one of the intermediate compositions, the total vapour pressure of such a solution will be the highest and the boiling point will be the lowest (because higher the vapour pressure, lower is the boiling point). At this point, the composition of liquid and vapour phase is same and the liquid mixture boils at constant temperature and remains unchanged in composition. Therefore, this liquid mixture distils over as if it is a *pure liquid*. The solution acquires the property of boiling at constant temperature and remains unchanged in composition. These types of solutions are called **minimum boiling azeotropes**.

For example, ethanol and water form minimum

boiling azeotrope. In this boiling point diagram (Fig. 1), we indicate the composition of the vapour phase by the upper curve and composition of the liquid phase by the lower curve. As shown in Fig. 1, the boiling point diagram shows an azeotropic composition at $x(\text{H}_2\text{O}) = 0.056$ and $x(\text{C}_2\text{H}_5\text{OH}) = 0.944$ at a temperature of 351 K (or 78°C) which is lower than that of pure ethanol 351.5 K (or 78.5°C) and water 373 K (or 100°C).

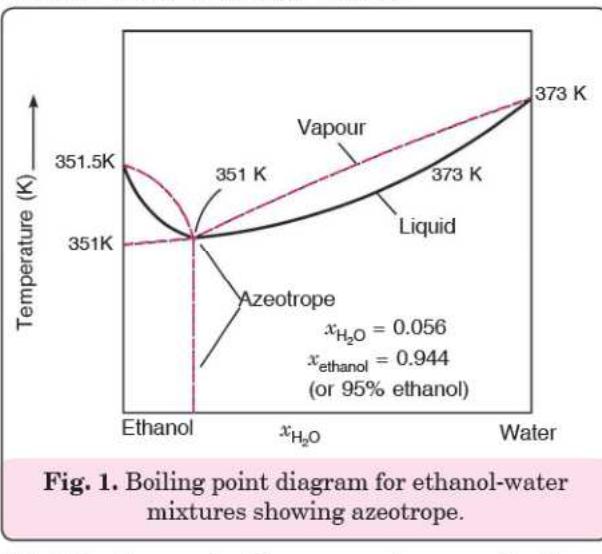


Fig. 1. Boiling point diagram for ethanol-water mixtures showing azeotrope.

(ii) Maximum boiling azeotropes: In the case of solutions showing negative deviations, total vapour pressure becomes less than the corresponding ideal solution of same composition (because lower the vapour pressure, higher is the boiling point). The boiling points of such solutions are increased because lower the vapour pressure, higher is the boiling point). For one of the intermediate composition, the total vapour pressure will be the least and the boiling point will be the highest (Fig. 2). At this composition, the solution also boils at constant temperature without a change in composition. These types of solution are called **maximum boiling azeotropes**.

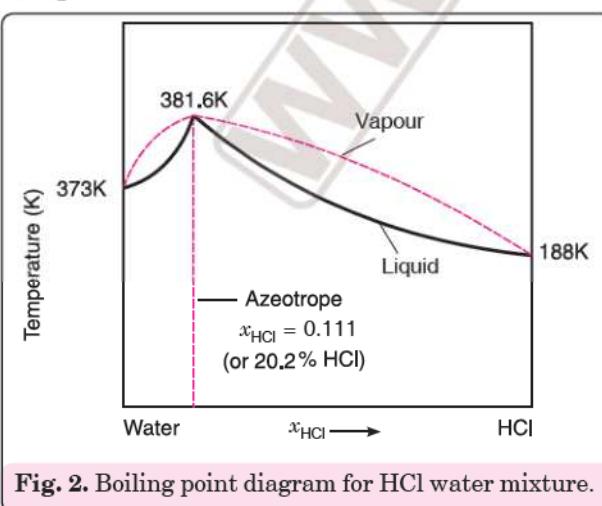


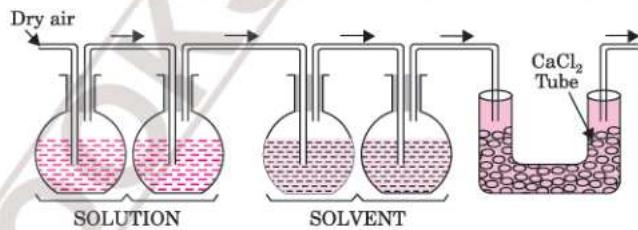
Fig. 2. Boiling point diagram for HCl water mixture.

For example, hydrochloric acid and water form maximum boiling point azeotrope at the composition $x(\text{H}_2\text{O}) = 0.889$ and $x(\text{HCl}) = 0.111$ (or 20.2% HCl) which boils at 381.6 K (or 108.6°C) which has higher value than that of pure water and HCl as shown in Fig. 2.

MEASUREMENT OF RELATIVE LOWERING IN VAPOUR PRESSURE

In this method, a stream of dry and pure air is passed through bulbs containing solution and then through bulbs containing pure solvent and finally through U-tubes containing calcium chloride (if solvent is water).

As the dry air passes through the solution, it becomes saturated upto the vapour pressure of the solution or the solvent. The actual loss of vapours from the bulbs is obtained by weighing them before and after the air has been passed through them.



The loss of water from the solution and the solvent is noted. These are proportional to p_A and $p_A^\circ - p_A$ respectively. i.e., Loss in weight of solution bulb \propto vap. pressure of the solution (p_A).

Loss in weight of solvent bulb \propto vap. pressure of solvent –vap. pressure of solution ($p_A^\circ - p_A$).

From this relative lowering in vapour pressure can be calculated. This method is known as **Ostwald Walker dynamic method**.

Illustration: A current of dry air was passed through a solution of 13.4 g of non-volatile substance 'S' in 100 g of water and then through water alone. The loss in weight of the former was 1.02 g and that of the latter was 0.05 g. Calculate

(i) mole fraction of the solute in the solution

(ii) molecular mass of the solute.

Solution: Loss in weight of solution $\propto p_A = 1.02 \text{ g}$

$$\text{Loss in weight of solvent (water)} \propto p_A^\circ - p_A$$

$$= 0.05 \text{ g}$$

$$p_A^\circ = (p_A^\circ - p_A) + p_A = 0.05 + 1.02 \\ = 1.07 \text{ g}$$

$$\frac{p_A^\circ - p_A}{p_A^\circ} = \frac{0.05}{1.07} = 0.0467$$

$$\therefore x_2 = 0.0467$$

$$\text{Now } \frac{p_A^\circ - p_A}{p_A^\circ} = \frac{n_2}{n_1} = \frac{w_2 / M_2}{w_1 / M_1} \\ = 0.0467$$

$$\text{or } \frac{13.4 / M_2}{100 / 18} = 0.0467$$

$$\text{or } M_2 = \frac{13.4 \times 18}{100 \times 0.0467} \\ = 51.65 \text{ g mol}^{-1}.$$

Competition File

OBJECTIVE TYPE QUESTIONS

Multiple Choice Questions

M. C. Q.

A **Topicwise** MULTIPLE CHOICE QUESTIONS with only one correct answer

Types of Solutions and Expressing their Concentrations

- A1.** An aqueous solution containing 6 g of urea in 500 mL of solution has a density equal to 1.05. If the molar mass of urea is 60, then the molality of solution is :
 (a) 0.20 (b) 0.19 (c) 0.10 (d) 1.2.
- A2.** 2.5 litre of 1 M NaOH solution are mixed with another 3 litre of 0.5 M NaOH solution. Then the molarity of the resulting solution is
 (a) 0.80 M (b) 0.1 M
 (c) 0.73 M (d) 0.50 M
- A3.** The volume of 4N HCl and 10 N HCl required to make 1 litre of 6N HCl are
 (a) 0.75 litre of 4 N HCl and 0.25 litre of 10 N HCl
 (b) 0.25 litre of 4 N HCl and 0.75 litre of 10 N HCl
 (c) 0.67 litre of 4 N HCl and 0.33 litre of 10 N HCl
 (d) 0.50 litre of 4 N HCl and 0.20 litre of 10 N HCl
- A4.** The mole fraction of methanol in its 4.5 molal aqueous solution is
 (a) 0.250 (b) 0.125
 (c) 0.100 (d) 0.075
- A5.** Density of 3M NaCl solution is 1.28 g/cc. The molality of the solution is
 (a) 2.79 molal (b) 0.279 molal
 (c) 1.279 molal (d) 3.85 molal
- A6.** The mole fraction of solute in 2.5 m aqueous solution is
 (a) 0.045 (b) 0.043
 (c) 0.86 (d) 0.25
- A7.** Battery acid is 4.27M H_2SO_4 (*aq*) and has the density of 1.25 g mL^{-1} . The molality of H_2SO_4 in the solution is
 (a) 3.416 m (b) 3.342 m
 (c) 5.135 m (d) 2.135 m
- A8.** A 7M solution of potassium hydroxide (KOH) in water contains 40% by weight of KOH. The density of the solution is
 (a) 1.96 (b) 1.28
 (c) 0.49 (d) 0.98
- A9.** What volume of 12M and 4M HCl must be mixed to prepare 1000 mL of 6M HCl?
 (a) 200, 800 (b) 700, 300

Answers

- | | | | | | | | | | |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|----------------|----------------|----------------|-----------------|
| A1. (b) | A2. (c) | A3. (c) | A4. (d) | A5. (a) | A6. (b) | A7. (c) | A8. (d) | A9. (c) | A10. (d) |
| A11. (c) | A12. (a) | A13. (a) | A14. (d) | A15. (a) | A16. (a) | | | | |

- (c) 250, 750 (d) 400, 600
- A10.** The volume of 80% sulphuric acid (H_2SO_4) by weight (density = 1.80 g mL^{-1}) required to prepare 1L of 0.2 M H_2SO_4 is
 (a) 14.7 mL (b) 29.4 mL
 (c) 6.8 mL (d) 13.60 mL

Solubility, Vapour Pressure of Liquid Solutions, Ideal and Non-ideal Solutions

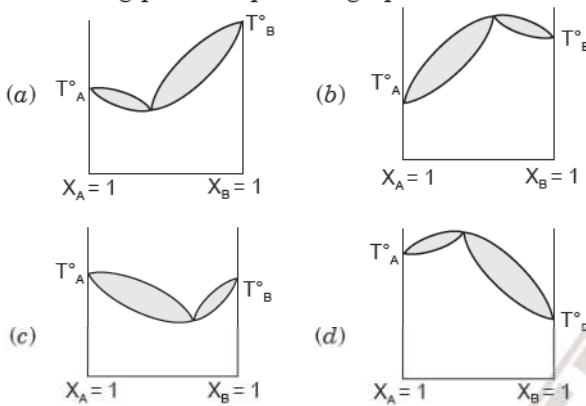
- A11.** The vapour pressure pure liquid 'A' is 70 torr at 27°C. It forms an ideal solution with another liquid B. The mole fraction of B in the solution is 0.2 and total pressure of solution is 84 torr at 27°C. The vapour pressure of pure liquid B at 27°C is :
 (a) 14 torr (b) 56 torr (c) 140 torr (d) 70 torr.
- A12.** Which of the following plots represents the behaviour of an ideal binary liquid solution?
 (a) plot of $1/p_{\text{total}}$ vs y_A is linear (mol fraction of A in vapour phase)
 (b) plot of p_{total} vs y_B is linear
 (c) plot of p_{total} vs y_A is linear
 (d) plot of $1/p_{\text{total}}$ vs y_B is non-linear
- A13.** The vapour pressure of a solution prepared by dissolving 1 mol of liquid A and 2 mol of liquid B has been found to be 38 torr. The vapour pressure of pure A and pure B are 45 and 36 torr respectively. The solution
 (a) shows negative deviation
 (b) is a minimum boiling azeotrope
 (c) is an ideal solution
 (d) has ΔH_{mixing} positive
- A14.** Which pair will not form an ideal solution ?
 (a) $\text{C}_2\text{H}_5\text{Br}$ and $\text{C}_2\text{H}_5\text{I}$ (b) $\text{C}_6\text{H}_5\text{Br}$ and $\text{C}_6\text{H}_5\text{I}$
 (c) C_6H_6 and $\text{C}_6\text{H}_5\text{CH}_3$ (d) $\text{C}_2\text{H}_5\text{I}$ and $\text{C}_2\text{H}_5\text{OH}$
- A15.** When a gas is bubbled through water at 298 K, a very dilute solution of the gas is obtained. Henry's law constant for the gas at 298 K is 100 kbar. If the gas exerts a partial pressure of 1 bar, the number of millimoles of the gas dissolved in one litre of water is
 (a) 0.555 (b) 5.55
 (c) 0.0555 (d) 55.5
- A16.** The partial pressure of oxygen in air is 0.2 atm. What is the concentration of dissolved oxygen in water in equilibrium with air at 25°C? (K_H for oxygen at 25°C is 4.34×10^4 atm)
 (a) 2.56×10^{-4} M (b) 3.68×10^{-6} M
 (c) 4.26×10^{-4} M (d) 2.96×10^{-6} M

Competition File

A17. The vapour pressure of pure components X and Y are 200 torr and 100 torr respectively. Assuming a solution of these components obeys Raoult's law, the mole fraction of component X in the vapour phase in equilibrium with a solution containing equimoles of X and Y is
 (a) 0.22 (b) 0.33
 (c) 0.50 (d) 0.67

A18. If the ratio of vapour pressure of pure liquids A and B is 1 : 2 and their mole fraction in solution is 1:2, then mole fraction of B in vapours is
 (a) 0.25 (b) 0.80
 (c) 0.56 (d) 0.20

A19. Two completely miscible liquids A and B form an azeotropic mixture having maximum vapour pressure. If the liquid A is more volatile, then which of the following respresents the boiling point-composition graph?



A20. Two liquids P and Q have vapour pressures 450 and 200 torr respectively at certain temperature. In an ideal solution of the two, the mole fraction of P at which two liquids have equal partial pressures is
 (a) 0.80 (b) 0.308
 (c) 0.444 (d) 0.154

Colligative Properties

A21. A solution of solute X in benzene boils at 0.126°C higher than benzene. What is the molality of the solution ?
 (K_b for benzene = 2.52 K/m)
 (a) 0.05 (b) 2 (c) 1 (d) 20.

A22. The osmotic pressure of 0.2 molar solution of urea at 27°C ($R = 0.082 \text{ litre atm mol}^{-1} \text{ K}^{-1}$) is :
 (a) 4.92 atm (b) 1 atm (c) 0.2 atm (d) 27 atm.

A23. A 5% solution of glucose (molar mass = 180) is isotonic with a 2.5% solution of a substance X at the same temperature. The molar mass of X is
 (a) 360 (b) 180
 (c) 90 (d) 45

A24. An aqueous solution containing 1 g of urea boils at 100.25°C. The aqueous solution containing 3 g of glucose in the same volume will boil at

- (a) 100.75°C (b) 100.5°C
 (c) 100°C (d) 100.25°C.

A25. An aqueous solution of sucrose boils at 100.01°C. The number of dextrose molecules in 100 g solution are (K_b of water = 0.50 K kg mol⁻¹)
 (a) 1.2×10^{21} (b) 2.0×10^{22}
 (c) 3.0×10^{23} (d) 6.0×10^{11}

A26. The vapour pressure of the solvent decreased by 10 mm of Hg when a non-volatile solute was added to the solvent. The mole fraction of the solute in the solution is 0.2. What should be the mole fraction of the solvent if a decrease in vapour pressure of 20 mm of Hg is desired :
 (a) 0.6 (b) 0.8 (c) 0.4 (d) 0.2

A27. Which of the following colligative property can provide molar mass of proteins (or polymers or colloids) with greater precision ?
 (a) Relative lowering of vapour pressure ?
 (b) Elevation of boiling point
 (c) Depression in freezing point
 (d) Osmotic pressure

A28. An aqueous solution of a substance X boils at 100.512°C. The freezing point of the solution is ($K_f = 1.86 \text{ Km}^{-1}$ and $K_b = 0.512 \text{ Km}^{-1}$)
 (a) 0.93°C (b) -0.93°C
 (c) 1.86°C (d) -1.86°C

A29. When a non-volatile solute (A) is added to solvent (B), its vapour pressure is reduced by 10%. If molar mass of B is 30% of molar mass of A, the mass ratio of B and A is
 (a) 0.33 (b) 6.0
 (c) 3.0 (d) 0.66

A30. When 0.6 g of urea is dissolved in 100 g water, the solution will boil at (K_b for water = 0.52 K m⁻¹ and normal boiling point of water = 100°C):
 (a) 372.48 K (b) 273.52 K
 (c) 373.052 K (d) 273.052 K.

Colligative Properties of Electrolytic Solutions : Abnormal Molar Masses

A31. The osmotic pressure of equimolar solutions of glucose, sodium chloride and barium chloride will be in the order :
 (a) $\text{BaCl}_2 > \text{NaCl} > \text{glucose}$ (b) $\text{BaCl}_2 > \text{glucose} > \text{NaCl}$
 (c) Glucose > $\text{BaCl}_2 > \text{NaCl}$ (d) $\text{NaCl} > \text{BaCl}_2 > \text{glucose}$.

A32. Equal weights of m gram of the following substances were dissolved in equal amount of water. Which of these will have highest boiling points ?
 (a) Urea (NH_2CONH_2)
 (b) Glucose ($\text{C}_6\text{H}_{12}\text{O}_6$)
 (c) Sodium chloride (NaCl)
 (d) Calcium chloride (CaCl_2)

Answers

- A17.** (d) **A18.** (b) **A19.** (a) **A20.** (b) **A21.** (a) **A22.** (a) **A23.** (c) **A24.** (d) **A25.** (a) **A26.** (a)
A27. (d) **A28.** (d) **A29.** (c) **A30.** (c) **A31.** (a) **A32.** (c)

Competition File

A33. Which one of the following pairs of solutions can be expected to be isotonic at the same temperature?

- (a) 0.1 M urea and 0.1 M NaCl
- (b) 0.1 M urea and 0.1 M MgCl₂
- (c) 0.1 M NaCl and 0.1 M Na₂SO₄
- (d) 0.1 M Ca(NO₃)₂ and 0.1 M Na₂SO₄

A34. The Van't Hoff factor for 0.1 M Ba(NO₃)₂ solution is 2.74. The degree of dissociation is

- (a) 91.3% (b) 87% (c) 100% (d) 74%

A35. A 0.2 molal aqueous solution of weak acid (HX) is 20% ionized. The freezing point of this solution is:

- (K_f = 1.86 K kg mol⁻¹ for water)
- (a) -0.45°C (b) -0.90°C
 - (c) -0.31°C (d) -0.53°C

A36. Electrolyte A gives 3 ions and B is a non-electrolyte. If 0.1 molar solution of solute B produces an osmotic pressure p , then 0.05 molar solution of A will produce an osmotic pressure equal to

- (a) p (b) $1.5 p$ (c) $0.5 p$ (d) $0.75 p$

A37. 0.01 M solution each of urea, common salt and sodium sulphate are taken, the ratio of depression in freezing point of these solutions is

- (a) 1 : 1 : 1 (b) 1 : 2 : 1
- (c) 1 : 2 : 3 (d) 2 : 2 : 3

A38. Which of the following 0.10 m aqueous solution will have the lowest freezing point?

- (a) Al₂(SO₄)₃ (b) C₆H₁₂O₆
- (c) C₁₂H₂₂O₁₁ (d) KI

A39. In a 0.2 molal aqueous solution of a weak acid, HX, the degree of dissociation is 0.3. Taking K_f for water as 1.86, the freezing point of the solution will be nearest to

- (a) -0.360°C (b) -0.206°C
- (c) +0.480°C (d) -0.480°C

A40. Which of the following solutions are isotonic with one another?

- | | |
|-----------------------------|------------------------------|
| (1) 0.15 M urea | (2) 0.05 M CaCl ₂ |
| (3) 0.1 M MgSO ₄ | (4) 0.15 M glucose |

Select the correct answer using the codes given below:

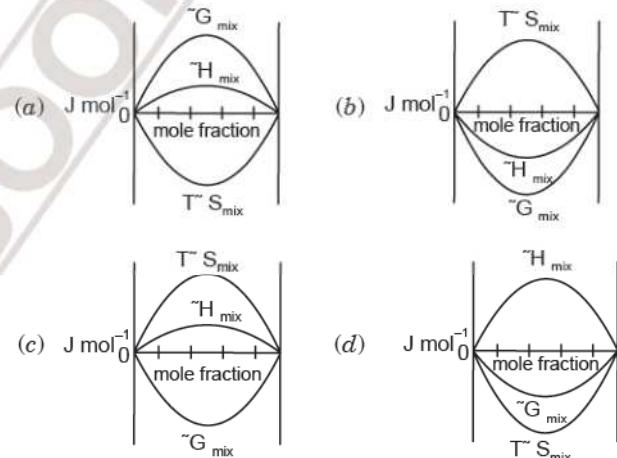
- | | |
|----------------|----------------|
| (a) 1 and 4 | (b) 2 and 3 |
| (c) 1, 2 and 4 | (d) 2, 3 and 4 |

Advanced Level

A41. Two volatile liquids A and B having vapour pressures p_A° and p_B° respectively form an ideal solution. If x_A and x_B are the mole fractions in the solution and y_A and y_B are the mole fractions in vapour phase of A and B respectively, then a plot of $1/y_A$ along y -axis against $1/x_A$ along x -axis gives a straight line. The slope of the straight line is

- (a) p_A°/p_B° (b) p_B°/p_A°
- (c) $p_A^\circ - p_B^\circ$ (d) $p_B^\circ - p_A^\circ$

A42. Which of the following graph represents correctly the variation in thermodynamic functions during the formation of a binary solution showing positive deviations from ideal behaviour?



A43. Dry air was passed successively through a solution of 5 g of a solute in 80 g of water and then through pure water. The loss in weight of the solution was 2.5 g and that of pure water 0.05 g. The molar mass of solute is

- (a) 48 (b) 32
- (c) 40 (d) 35

Answers

- | | | | | | | | | |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| A33. (d) | A34. (b) | A35. (a) | A36. (b) | A37. (c) | A38. (a) | A39. (d) | A40. (c) | A41. (b) |
| A42. (c) | A43. (a) | | | | | | | |

B MULTIPLE CHOICE QUESTIONS from Competitive Examinations AIPMT & Other State Boards' Medical Entrance

B1. Concentrated aqueous sulphuric acid is 98% H₂SO₄ by mass and has a density of 1.80 g mL⁻¹. Volume of acid required to make one litre of 0.1 M H₂SO₄ is

- (a) 5.55 mL (b) 11.10 mL
- (c) 16.65 mL (d) 22.20 mL

(C.B.S.E. PMT. 2007)

B2. 0.5 molal aqueous solution of a weak acid is 20% ionized. If K_f for water is 1.86 K kg mol⁻¹, the lowering in freezing point of the solution is

- (a) -0.56 K (b) -1.12 K
- (c) 0.56 K (d) 1.12 K (C.B.S.E. PMT. 2007)

Answers

- | | |
|----------------|----------------|
| B1. (a) | B2. (d) |
|----------------|----------------|

Competition File

B3. A 0.0020 m aqueous solution of an ionic compound $\text{Co}(\text{NH}_3)_5(\text{NO}_2)_2\text{Cl}$ freezes at -0.00732°C . Number of moles of ions which 1 mol of ionic compound produces on being dissolved in water will be ($K_f = 1.86^\circ\text{C}/\text{m}$)

- (a) 3 (b) 4
 (c) 1 (d) 2 (C.B.S.E. PMT 2009)

B4. 25.3 g of sodium carbonate, Na_2CO_3 is dissolved in enough water to make 250 ml of solution. If sodium carbonate dissociates completely, molar concentration of sodium ion, Na^+ and carbonate ions, CO_3^{2-} are respectively (Molar mass of $\text{Na}_2\text{CO}_3 = 106 \text{ g mol}^{-1}$):

- (a) 1.90 M and 1.910 M (b) 0.477 M and 0.0477 M
 (c) 0.955 M and 1.910 M (d) 1.910 M and 0.955 M (C.B.S.E. Med 2010)

B5. An aqueous solution is 1.00 molal in KI. Which change will cause the vapour pressure of the solution to increase?

- (a) addition of 1.00 molal KI (b) addition of water
 (c) addition of NaCl (d) addition of Na_2SO_4 (C.B.S.E. Med 2010)

B6. A solution of sucrose (molar mass = 342 g mol^{-1}) has been prepared by dissolving 68.5 g of sucrose in 100 g of water. The freezing point of the solution obtained will be (K_f for water = $1.86 \text{ K kg mol}^{-1}$).

- (a) $+ 0.372^\circ\text{C}$ (b) $- 0.570^\circ\text{C}$
 (c) $- 0.372^\circ\text{C}$ (d) $- 0.520^\circ\text{C}$ (C.B.S.E. Med. 2010)

B7. The van't Hoff factor *i* for a compound which undergoes dissociation in one solvent and association in other solvent is respectively

- (a) less than one and greater than one
 (b) less than one and less than one
 (c) greater than one and less than one
 (d) greater than one and greater than one (C.B.S.E. PMT. 2011)

B8. p_A and p_B are the vapour pressure of pure liquid components, A and B, respectively of an ideal binary solution. If x_A represents the mole fraction of component A, the total pressure of the solution will be

- (a) $p_A + x_A(p_B - p_A)$ (b) $p_A + x_A(p_A - p_B)$
 (c) $p_B + x_A(p_B - p_A)$ (d) $p_B + x_A(p_A - p_B)$ (A.I.P.M.T. 2012)

B9. 6.02×10^{20} molecules of urea are present in 100 mL of its solution. The concentration of solution is

- (a) 0.001 M (b) 0.1 M
 (c) 0.02 M (d) 0.01 M (NEET 2013)

B10. How many grams of concentrated nitric acid solution should be used to prepare 250 mL of 2.0 M HNO_3 ? The concentrated acid is 70% HNO_3 .

- (a) 90.0 g conc. HNO_3 (b) 70.0 g conc. HNO_3
 (c) 54.0 g conc. HNO_3 (d) 45.0 g conc. HNO_3 (NEET 2013)

B11. Of the following 0.10 m aqueous solutions, which one will exhibit the largest freezing point depression?

- (a) KCl (b) $\text{C}_6\text{H}_{12}\text{O}_6$
 (c) $\text{Al}_2(\text{SO}_4)_3$ (d) K_2SO_4

(A.I.P.M.T. 2014)

B12. The boiling point of 0.2 mol kg^{-1} solution of X in water is greater than equimolar solution of Y in water. Which one of the following statements is true in this case?

- (a) Molecular mass of X is less than the molecular mass of Y.
 (b) Y is undergoing dissociation in water while X undergoes no change.
 (c) X is undergoing dissociation in water.
 (d) Molecular mass of X is greater than the molecular mass of Y. (A.I.P.M.T. 2015)

B13. Which one of the following electrolytes has the same value of van't Hoff factor (*i*) as that of $\text{Al}_2(\text{SO}_4)_3$ (if all are 100% ionised)?

- (a) $\text{Al}(\text{NO}_3)_3$ (b) $\text{K}_4[\text{Fe}(\text{CN})_6]$
 (c) K_2SO_4 (d) $\text{K}_3[\text{Fe}(\text{CN})_6]$ (A.I.P.M.T. 2015)

B14. What is the mole fraction of the solute in a 1.00 m aqueous solution?

- (a) 0.0354 (b) 0.0177
 (c) 0.177 (d) 1.770 (A.I.P.M.T. 2015)

B15. Which of the following statement about the composition of the vapour over an ideal 1 : 1 molar mixture of benzene and toluene is correct? Assume that the temperature is constant at 25°C . (Given, vapour pressure data at 25°C , benzene = 12.8 kPa, toluene = 3.85 kPa)

- (a) The vapour will contain equal amounts of benzene and toluene.
 (b) Not enough information is given to make a prediction.
 (c) The vapour will contain a higher percentage of benzene.
 (d) The vapour will contain a higher percentage of toluene. (NEET 2016)

B16. At 100°C the vapour pressure of a solution of 6.5 g of a solute in 100 g water is 732 mm. If $K_b = 0.52 \text{ Km}^{-1}$ the boiling point of this solution will be

- (a) 102°C (b) 103°C
 (c) 101°C (d) 100°C (NEET 2016)

B17. Which one of the following is incorrect for an ideal solution?

- (a) $\Delta H_{\text{mix}} = 0$
 (b) $\Delta V_{\text{mix}} = 0$
 (c) $\Delta P = P_{\text{obs}} - P_{\text{calculated by Raoult's law}} = 0$
 (d) $\Delta G_{\text{mix}} = 0$ (NEET 2016)

B18. The van't Hoff factor (*i*) for a dilute aqueous solution of the strong electrolyte barium hydroxide is

- (a) 0 (b) 1
 (c) 2 (d) 3 (NEET 2016)

Answers

- B3.** (d) **B4.** (d) **B5.** (b) **B6.** (c) **B7.** (c) **B8.** (d) **B9.** (d) **B10.** (d) **B11.** (c) **B12.** (c) **B13.** (b)
B14. (b) **B15.** (c) **B16.** (c) **B17.** (d) **B18.** (d)

Competition File

B19. If molality of the dilute solution is doubled, the value of molal depression constant (K_f) will be
 (a) halved (b) tripled
 (c) unchanged (d) doubled (NEET 2017)

B20. Consider the following aqueous solutions and assume 100% ionization of electrolytes
 (I) 0.1 m urea (II) 0.04 m $\text{Al}_2(\text{SO}_4)_3$
 (III) 0.05 m CaCl_2 (IV) 0.005 m NaCl

The correct statement regarding the above solutions is
 (a) freezing point will be lowest for solution I
 (b) freezing point will be highest for solution IV
 (c) vapour pressure will be highest for solution II
 (d) osmotic pressure will be highest for solution III

(Kerala P.M.T. 2007)

B21. The temperature at which 10% aqueous solution (w/v) of glucose will exhibit the osmotic pressure of 16.4 atm is ($R = 0.082 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$).
 (a) 360°C (b) 180 K
 (c) 90 K (d) 300 K

(Kerala P.M.T. 2008)

B22. At 300 K the vapour pressure of an ideal solution containing 1 mole of liquid A and 2 moles of liquid B is 500 mm of Hg. The vapour pressure of the solution increases by 25 mm of Hg if one more mole of B is added to the above ideal solution at 300 K. Then vapour pressure of A in its pure state is
 (a) 300 mm of Hg (b) 40 mm of Hg
 (c) 500 mm of Hg (d) 600 mm of Hg
 (e) 200 mm of Hg

(Kerala PMT 2009)

B23. Henry's law constant of oxygen is $1.4 \times 10^{-3} \text{ mol L}^{-1} \text{ atm}^{-1}$ at 298 K. How much of oxygen is dissolved in 100 mL at 298 K when the partial pressure of oxygen is 0.5 atm?
 (a) 1.4 g (b) 3.2 g
 (c) 22.4 mg (d) 2.24 mg
 (e) 3.2 mg

(Kerala PMT 2009)

B24. The solubility of a gas in water at 300 K under a pressure of 100 atmospheres is $4 \times 10^{-3} \text{ kg L}^{-1}$. Therefore, the mass of the gas in kg dissolved in 250 mL of water under a pressure of 250 atmospheres at 300 K is
 (a) 2.5×10^{-3} (b) 2.0×10^{-3}
 (c) 1.25×10^{-3} (d) 5.0×10^{-3}
 (e) 3×10^{-3}

(Kerala PMT 2010)

B25. Which one of the following statements is false?
 (a) Raoult's law states that the vapour pressure of a component over a binary solution of volatile liquids is directly proportional to its mole fraction.
 (b) Two sucrose solutions of the same molality prepared in different solvents will have the same depression of freezing point.

(c) The correct order of osmotic pressures of 0.01 M solution of each compound is $\text{BaCl}_2 > \text{KCl} > \text{CH}_3\text{COOH} >$ glucose.
 (d) In the equation osmotic pressure $p = MRT$, M is the molarity of the solution.

(e) The molecular weight of NaCl determined by colligative property measurement is less than its theoretical molecular weight. (Kerala P.M.T. 2011)

B26. Equimolar aqueous solutions of NaCl and BaCl_2 are prepared. If the freezing point of NaCl is -2°C , the freezing point of BaCl_2 solution is expected to be

(a) -2°C (b) -3°C
 (c) -1.5°C (d) -1.66°C (A.M.U. Med. 2013)

B27. The degree of ionization of HF in 0.100 m aqueous solution is (freezing point of the solution = -0.197°C and K_f for water = 1.86°C)
 (a) 6% (b) 12%
 (c) 3% (d) 9%

B28. The partial pressure of nitrogen in air is 0.76 atm. and its Henry's law constant is $7.6 \times 10^4 \text{ atm}$ at 300 K. What is the mole fraction of N_2 in the solution obtained when air is bubbled through water at 300 K?
 (a) 1×10^{-4} (b) 2×10^{-4}
 (c) 1×10^{-5} (d) 2×10^{-5}

(e) 1×10^{-6} (Kerala PMT 2014)

B29. The experimental and calculated elevation in boiling points of an electrolyte AB in its aqueous solution at a given concentration are 0.81 K and 0.54 K respectively. The percentage ionization of the electrolyte at this concentration is

(a) 20 (b) 40
 (c) 50 (d) 60
 (e) 80

(Kerala PMT 2014)

B30. An electrolyte (AB) is 100% ionized in 10% aqueous solution. What is the osmotic pressure (atm) of a 10% solution of the electrolyte at 300 K, if molecular weight of AB is 200 g mol^{-1} ?
 (a) 200 (b) 100
 (c) 246 (d) 24.6

B31. The density of 2.0 M solution of a solute is 1.2 g mL^{-1} . If the molecular mass of the solute is 100 g mol^{-1} , then the molality of the solution is

(a) 2.0 m (b) 1.2 m
 (c) 1.0 m (d) 0.6 m
 (e) 2.4 m

(Kerala PMT 2015)

Answers

- B19.** (c) **B20.** (b) **B21.** (e) **B22.** (a) **B23.** (d) **B24.** (a) **B25.** (b) **B26.** (b) **B27.** (a) **B28.** (c)
B29. (c) **B30.** (d) **B31.** (a)

Competition File

B32. The correct equation for the degree of association ' α ' of an associating solute, ' n ' molecules of which undergoes association in solution, is

- | | |
|-----------------------------------|-----------------------------------|
| (a) $\alpha = \frac{n(i-1)}{1-n}$ | (b) $\alpha = \frac{i(n-1)}{1+n}$ |
| (c) $\alpha = \frac{i(n+1)}{1-n}$ | (d) $\alpha = \frac{i(n+1)}{n-1}$ |
| (e) $\alpha = \frac{n(1-i)}{1-n}$ | |

(Kerala PMT 2015)

B33. The vapour pressure of a solvent at 293 K is 100 mm Hg. Then the vapour pressure of a solution containing 1 mole of a strong electrolyte (AB_2) in 99 moles of the solvent at 293 K is (assume complete dissociation of solute)

- | | |
|---------------|---------------|
| (a) 103 mm Hg | (b) 99 mm Hg |
| (c) 97 mm Hg | (d) 101 mm Hg |
| (e) 98 mm Hg | |

(Kerala PMT 2015)

B34. The correct order of osmotic pressure of 0.01 M aqueous solution of the following is

- | |
|--------------------------------|
| (a) Sucrose > CH_3COOH > KCl |
| (b) CH_3COOH > Sucrose > KCl |
| (c) Sucrose > KCl > CH_3COOH |
| (d) KCl > Sucrose > CH_3COOH |
| (e) KCl > CH_3COOH > Sucrose |

(Kerala PMT 2015)

JEE (Main) & Other State Boards' Engineering Entrance

B35. A 5.25% solution of a substance is isotonic with a 1.5% solution of urea (molar mass = 60 g mol⁻¹) in the same solvent. If the densities of both the solutions are assumed to be equal to 1.0 g cm⁻³, molar mass of the substance will be

- | | |
|-------------------------------|-------------------------------|
| (a) 90.0 g mol ⁻¹ | (b) 115.0 g mol ⁻¹ |
| (c) 105.0 g mol ⁻¹ | (d) 210.0 g mol ⁻¹ |

(A.I.E.E. 2007)

B36. The density (in g mL⁻¹) of a 3.60 M sulphuric acid solution that is 29% H_2SO_4 (molar mass = 98 g mol⁻¹) by mass will be

- | | |
|----------|----------|
| (a) 1.64 | (b) 1.88 |
| (c) 1.22 | (d) 1.95 |

(A.I.E.E. 2007)

B37. At 80°C, the vapour pressure of pure liquid 'A' is 520 mm Hg and that of pure liquid 'B' is 1000 mm Hg. If a mixture of solution of 'A' and 'B' boils at 80°C and 1 atm pressure, the amount of 'A' in the mixture is (1atm = 760 mm Hg):

- | | |
|--------------------|--------------------|
| (a) 50 mol percent | (b) 52 mol percent |
| (c) 34 mol percent | (d) 48 mol percent |

(A.I.E.E. 2008)

B38. The vapour pressure of pure water at 20°C is 17.5 mm Hg. If 18 g of glucose ($C_6H_{12}O_6$) is added to 178.2 g of water at 20°C, the vapour pressure of resulting solution will be

- | | |
|------------------|------------------|
| (a) 17.325 mm Hg | (b) 17.675 mm Hg |
| (c) 15.750 mm Hg | (d) 16.500 mm Hg |

(A.I.E.E. 2008)

B39. Two liquids X and Y form an ideal solution. At 300 K, vapour pressure of the solution containing 1 mole of X and 3 mole of Y is 550 mm Hg. At the same temperature, if 1 mole of Y is further added to this solution, vapour pressure (in mm Hg) of X and Y in their pure states will be, respectively

- | | |
|-----------------|-----------------|
| (a) 200 and 300 | (b) 300 and 400 |
| (c) 400 and 600 | (d) 500 and 300 |

B40. If sodium sulphate is considered to be completely dissociated into cations and anions in aqueous solution, the change in freezing point of water (ΔT_f), when 0.01 mol of sodium sulphate is dissolved in 1 kg of water is ($K_f = 1.86 \text{ K kg mol}^{-1}$)

- | | |
|--------------|--------------|
| (a) 0.0744 K | (b) 0.0186 K |
| (c) 0.0372 K | (d) 0.0558 K |

B41. On mixing, heptane and octane form an ideal solution. At 373 K, the vapour pressures of the two liquid components (heptane and octane) are 105 kPa and 45 kPa respectively. Vapour pressure of the solution obtained by mixing 25.0 g of heptane and 35 g of octane will be (molar mass of heptane = 100 g mol⁻¹ and of octane = 114 g mol⁻¹):

- | | |
|--------------|---------------|
| (a) 96.2 kPa | (b) 144.5 kPa |
| (c) 72.0 kPa | (d) 36.1 kPa |

B42. A 5.2 molal aqueous solution of methyl alcohol, CH_3OH , is supplied. What is the mole fraction of methyl alcohol in the solution?

- | | |
|-----------|-----------|
| (a) 0.086 | (b) 0.050 |
| (c) 0.100 | (d) 0.190 |

B43. Ethylene glycol is used as an antifreeze in a cold climate. Mass of ethylene glycol which should be added to 4 kg of water to prevent it from freezing at -6 °C will be (K for water = 1.86 K kg mol⁻¹, and molar mass of ethylene glycol = 62 g mol⁻¹)

- | | |
|--------------|--------------|
| (a) 400.00 g | (b) 304.60 g |
| (c) 804.32 g | (d) 204.30 g |

B44. The degree of dissociation (α) of a weak electrolyte, A_xB_y is related to Van't Hoff factor (i) by the expression :

- | | |
|------------------------------------|----------------------------------|
| (a) $\alpha = \frac{x+y-1}{i-1}$ | (b) $\alpha = \frac{x+y+1}{i-1}$ |
| (c) $\alpha = \frac{i-1}{(x+y-1)}$ | (d) $\alpha = \frac{i-1}{x+y+1}$ |

(A.I.E.E. 2011)

Answers

- B32.** (a) **B33.** (c) **B34.** (e) **B35.** (d) **B36.** (c) **B37.** (a) **B38.** (a) **B39.** (c) **B40.** (d) **B41.** (c)
B42. (a) **B43.** (c) **B44.** (c)

Competition File

- B45.** The molality of a urea solution in which 0.0100 g of urea, $[(\text{NH}_2)_2\text{CO}]$ is added to 0.3000 dm³ of water at STP is :
 (a) 5.55×10^{-4} m (b) 33.3 m
 (c) 3.33×10^{-2} m (d) 0.555 m (A.I.E.E.E. 2011)
- B46.** A 5% solution of cane sugar (molar mass 342) is isotonic with 1% of a solution of an unknown solute. The molar mass of unknown solute in g/mol is
 (a) 171.2 (b) 68.4
 (c) 34.2 (d) 136.2 (A.I.E.E.E. 2011)
- B47.** The density of a solution prepared by dissolving 120 g of urea (mol. mass = 60 u) in 1000 g of water is 1.15 g/mL. The molarity of this solution is
 (a) 1.78 M (b) 1.02 M
 (c) 2.05 M (d) 0.50 M (A.I.E.E.E. 2012)
- B48.** K_f for water is 1.86 K kg mol⁻¹. If your automobile radiator holds 1.0 kg of water, how many grams of ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$) must you add to get the freezing point of the solution lowered to -2.8°C ?
 (a) 93 g (b) 39 g
 (c) 27 g (d) 72 g (A.I.E.E.E. 2012)
- B49.** The molarity of a solution obtained by mixing 750 mL of 0.5 M HCl with 250 mL of 2M HCl will be
 (a) 0.875 M (b) 1.00 M
 (c) 1.75 M (d) 0.975 M (JEE Main 2013)
- B50.** Consider separate solutions of 0.500M $\text{C}_2\text{H}_5\text{OH}_{(aq)}$, 0.100 M $\text{Mg}_3(\text{PO}_4)_{2(aq)}$, 0.250 M $\text{KBr}_{(aq)}$ and 0.125 M $\text{Na}_3\text{PO}_4{}_{(aq)}$ at 25°C . Which statement is true about these solutions, assuming all salts to be strong electrolytes?
 (a) 0.500 M $\text{C}_2\text{H}_5\text{OH}_{(aq)}$ has the highest osmotic pressure.
 (b) They all have the same osmotic pressure.
 (c) 0.100 M $\text{Mg}_3(\text{PO}_4)_{2(aq)}$ has the highest osmotic pressure.
 (d) 0.125 M $\text{Na}_3\text{PO}_4{}_{(aq)}$ has the highest osmotic pressure. (JEE Main 2014)
- B51.** The vapour pressure of acetone at 20°C is 185 torr. When 1.2 g of a non-volatile substance was dissolved in 100 g of acetone at 20°C , its vapour pressure was 183 torr. The molar mass (g mol⁻¹) of the substance is
 (a) 128 (b) 488
 (c) 32 (d) 64 (JEE Main 2015)
- B52.** 18 g glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) is added to 178.2 g water. The vapour pressure of water (in torr) for this aqueous solution is
 (a) 7.6 (b) 76.0
 (c) 752.4 (d) 759.0 (JEE Main 2016)
- B53.** The freezing point of benzene decreases by 0.45°C when 0.2 g of acetic acid is added to 20 g of benzene. If acetic acid associates to form a dimer in benzene, percentage association of acetic acid in benzene will be: (K_f for benzene = 5.12 K kg mol⁻¹)
 (a) 64.6% (b) 80.4%
 (c) 74.6% (d) 94.6% (JEE Main 2017)
- B54.** For 1 molal aqueous solution of the following compounds, which one will show the highest freezing point?
 (a) $[\text{Co}(\text{H}_2\text{O})_6]\text{Cl}_3$
 (b) $[\text{Co}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2\cdot\text{H}_2\text{O}$
 (c) $[\text{Co}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl}\cdot 2\text{H}_2\text{O}$
 (d) $[\text{Co}(\text{H}_2\text{O})_3\text{Cl}_3]\cdot 3\text{H}_2\text{O}$ (JEE Main 2018)
- B55.** Two liquids X and Y form an ideal solution. The mixture has a vapour pressure of 400 mm at 300 K when mixed in the molar ratio of 1:1 and a vapour pressure of 350 mm when mixed in the molar ratio of 1:2 at the same temperature. The vapour pressures of the two pure liquids X and Y respectively are
 (a) 250 mm, 550 mm
 (b) 350 mm, 450 mm
 (c) 350 mm, 700 mm
 (d) 500 mm, 500 mm
 (e) 550 mm, 250 mm (Kerala P.E.T. 2008)
- B56.** A 6% solution of urea is isotonic with
 (a) 0.05 M solution of glucose
 (b) 6% solution of glucose
 (c) 25% solution of glucose
 (d) 1 M solution of glucose (Karnataka C.E.T. 2009)
- B57.** The difference between the boiling point and freezing point of an aqueous solution containing sucrose (molecular wt. = 342 g mol⁻¹) in 100 g of water is 105°C . If K_f and K_b of water are 1.86 and 0.51 K kg mol⁻¹ respectively, the weight of sucrose in solution is about
 (a) 34.2 g (b) 342 g
 (c) 7.2 g (d) 72 g
 (e) 68.4 g (Kerala PET 2009)
- B58.** The amount of solute (molar mass 60 g mol⁻¹) that must be added to 180 g of water so that the vapour pressure of water is lowered by 10% is
 (a) 30 g (b) 60 g
 (c) 120 g (d) 12 g
 (e) 24 g (Kerala PET 2010)
- B59.** A solution containing 1.8 g of a compound (empirical formula CH_2O) in 40 g of water is observed to freeze at -0.465°C . The molecular formula of the compound is (K_f of water = 1.86 kg K mol⁻¹)
 (a) $\text{C}_2\text{H}_4\text{O}_2$ (b) $\text{C}_3\text{H}_6\text{O}_3$
 (c) $\text{C}_4\text{H}_8\text{O}_4$ (d) $\text{C}_5\text{H}_{10}\text{O}_5$
 (e) $\text{C}_6\text{H}_{12}\text{O}_6$ (Kerala P.E.T. 2011)

Answers

- B45.** (a) **B46.** (b) **B47.** (c) **B48.** (a) **B49.** (a) **B50.** (b) **B51.** (d) **B52.** (c) **B53.** (d) **B54.** (d)
B55. (e) **B56.** (d) **B57.** (d) **B58.** (b) **B59.** (e)

Competition File

- B60.** 58.5 g of NaCl and 180 g of glucose were separately dissolved in 1000 mL of water. Identify the correct statement regarding the elevation of boiling point (b.pt.) of the resulting solutions.
- NaCl solution will show higher elevation of b.pt.
 - Glucose solution will show higher elevation of b.pt.
 - Both the solutions will show equal elevation of b.pt.
 - The b.pt. of elevation will be shown by neither of the solutions.
- (W.B.J.E.E. 2012)
- B61.** Freezing point of an aqueous solution is -0.186°C . If the values of K_b and K_f of water are respectively $0.52 \text{ K kg mol}^{-1}$ and $1.86 \text{ K kg mol}^{-1}$, then the elevation of boiling point of the solution in K is
- 0.52
 - 1.04
 - 1.34
 - 0.134
 - 0.052
- (Kerala P.E.T. 2012)
- B62.** The mass of a non-volatile solute of molar mass 40 g mol^{-1} that should be dissolved in 114 g of octane to lower its vapour pressure by 20% is
- 8 g
 - 11.4 g
 - 9.8 g
 - 12.8 g
- (Karnataka C.E.T. 2012)
- B63.** The vapour pressures of two liquids A and B in their pure states are in ratio of 1 : 2. A binary solution of A and B contains A and B in the mole proportion of 1 : 2. The mole fraction of A in the vapour phase of the solution will be
- 0.33
 - 0.2
 - 0.25
 - 0.52
- (Karnataka C.E.T. 2012)
- B64.** The measured freezing point depression for a 0.1 m aqueous CH_3COOH solution is 0.19°C . The acid dissociation constant K_a at this concentration will be (Given K_p , the molal cryoscopic constant = $1.86 \text{ K kg mol}^{-1}$)
- 4.76×10^{-5}
 - 4×10^{-5}
 - 8×10^{-5}
 - 2×10^{-5}
- (W.B. JEE 2013)
- B65.** The vapour pressure of pure benzene and toluene at a particular temperature are 100 mm and 50 mm respectively. Then the mole fraction of benzene in vapour phase in contact with equimolar solution of benzene and toluene is
- 0.67
 - 0.75
 - 0.33
 - 0.50
 - 0.20
- (Kerala P.E.T. 2013)
- B66.** An aqueous solution containing 3 g of a solute of molar mass 111.6 g mol^{-1} in a certain mass of water freezes at -0.125°C . The mass of water in grams present in the solution is ($K_f = 1.86 \text{ K kg mol}^{-1}$)
- 300
 - 600
 - 500
 - 400
 - 250
- (Kerala PET 2014)
- B67.** A solution of 1.25 g of P in 50 g of water lowers freezing point by 0.3°C . Molar mass of P is 94 and K_f (water) = $1.86 \text{ K kg mol}^{-1}$. The degree of association of P if it forms dimers in water is
- 80%
 - 60%
 - 65%
 - 75%
- (Karnataka CET 2014)
- B68.** Van't Hoff factor of centimolar solution of $\text{K}_3[\text{Fe}(\text{CN})_6]$ is 3.333. Calculate the per cent dissociation of $\text{K}_3[\text{Fe}(\text{CN})_6]$.
- 33.33
 - 0.78
 - 78
 - 23.33
- (MH-CET 2015)
- B69.** After adding non-volatile solute freezing point of water decreases to -0.186°C . Calculate ΔT_b if $K_f = 1.86 \text{ K kg mol}^{-1}$ and $K_b = 0.521 \text{ K kg mol}^{-1}$
- 0.0521 K
 - 0.0186 K
 - 0.521 K
 - 1.86 K
- (Karnataka CET 2015)
- B70.** 0.06% (w/v) aqueous solution of urea is isotonic with
- 0.6% glucose solution
 - 0.1 M glucose solution
 - 0.06% glucose solution
 - 0.01 M glucose solution
- (Karnataka CET 2015)
- B71.** Which of the following aqueous solutions has the highest freezing point?
- 0.01 m NaCl
 - 0.01 m Na_2SO_4
 - 0.1 m Sucrose
 - 0.1 m NaCl
- (Karnataka CET 2015)
- B72.** A solution containing 2.44 g of solute dissolved in 75 g of water boiled at 100.413°C . What will be the molar mass of the solute? (K_b for water = $0.52 \text{ K kg mol}^{-1}$)
- 40.96 g mol^{-1}
 - 20.48 g mol^{-1}
 - 81.92 g mol^{-1}
 - None of these
- (A.M.U. 2015)
- B73.** If P° and P are the vapour pressures of the pure solvent and solution and n_1 and n_2 are the moles of solute and solvent respectively in the solution, then the correct relation between P and P° is
- $P^\circ = P \left[\frac{n_1}{n_1 + n_2} \right]$
 - $P^\circ = P \left[\frac{n_2}{n_1 + n_2} \right]$
 - $P = P^\circ \left[\frac{n_2}{n_1 + n_2} \right]$
 - $P = P^\circ \left[\frac{n_1}{n_1 + n_2} \right]$
- (WB JEE 2016)
- B74.** Calculate the molality of a solution that contains 51.2 g of naphthalene, (C_{10}H_8) in 500 mL of carbon tetrachloride. The density of CCl_4 is 1.60 g/mL.
- 0.250 m
 - 0.500 m
 - 0.750 m
 - 0.840 m
 - 1.69 m
- (Kerala PET 2016)
- B75.** 31 g of ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$) is mixed with 500 g of solvent (K_f of the solvent is 2 K kg mol^{-1}). What is the freezing point of the solution in K? (freezing point of solvent = 273 K).
- 272
 - 271
 - 270
 - 274
 - 275
- (Kerala PET 2016)

Answers

- B60.** (a) **B61.** (e) **B62.** (a) **B63.** (b) **B64.** (b) **B65.** (a) **B66.** (d) **B67.** (a) **B68.** (b) **B69.** (a)
B70. (d) **B71.** (a) **B72.** (a) **B73.** (c) **B74.** (b) **B75.** (b)

Competition File

B76. Osmotic pressure of the solution can be increased by
 (a) increasing the temperature of the solution
 (b) decreasing the temperature of the solution
 (c) increasing the volume of the vessel
 (d) diluting the solution. (Karnataka C.E.T. 2016)

B77. The molarity of 3 M solution of methanol if the density of the solution is 0.9 g cm^{-3} is
 (a) 3.73 (b) 3.0
 (c) 3.33 (d) 3.1
 (e) 3.2 (Kerala PET 2017)

B78. The freezing point of equimolar aqueous solutions will be highest for
 (a) $\text{C}_6\text{H}_5\text{NH}_3\text{Cl}$ (b) AgNO_3
 (c) $\text{Ca}(\text{NO}_3)_2$ (d) $\text{La}(\text{NO}_3)_3$
 (e) D-fructose (Kerala PET 2017)

B79. Assuming the compounds to be completely dissociated in aqueous solution, identify the pair of the solutions that can be expected to be isotonic at the same temperature.
 (a) 0.01 M Urea and 0.01 M NaCl
 (b) 0.02 M NaCl and 0.01 M Na_2SO_4
 (c) 0.03 M NaCl and 0.02 M MgCl_2
 (d) 0.01 M Sucrose and 0.02 M glucose (WB JEE 2017)

B80. The Van't Hoff factor ' i ' accounts for
 (a) extent of dissolution of solute
 (b) extent of dissociation of solute
 (c) extent of mobility of solute
 (d) extent of solubility of solute (Karnataka CET 2017)

B81. What will be the percentage of dimerization of 61 g of benzoic acid in 1000 g of a solvent and producing a depression in freezing point of 2°C ? Consider K_f to be 6.
 (a) 72% (b) 67%
 (c) 43% (d) 28% (J.K. CET 2018)

B82. Calculate the molarity of a solution of 30 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 4.3 L of solution. Consider atomic mass of Co = 59u, N = 14u, O = 16u, H = 1u
 (a) 0.023 M (b) 0.23 M
 (c) 0.046 M (d) 0.46 M (J.K. CET 2018)

B83. Which of the following aqueous solution should have the highest boiling point?
 (a) 1.0 M NaOH (b) 1.0 M Na_2SO_4
 (c) 1.0 M NH_4NO_3 (d) 1.0 M KNO_3 (Karnataka CET 2018)

B84. Isotonic solutions are having the same
 (a) surface tension (b) vapour pressure
 (c) osmotic pressure (d) viscosity. (Karnataka CET 2018)

B85. If 1 mol of NaCl solute is dissolved into 1 kg of water, at what temperature will water boil at 1.013 bar? (K_b of water is $0.52 \text{ K kg mol}^{-1}$).
 (a) 373.15 K (b) 373.67 K
 (c) 374.19 K (d) 373.19 K
 (e) 375 K (Kerala PET 2018)

JEE (Advance) for IIT Entrance

B86. The elevation in boiling point of a solution of 13.44 g of CuCl_2 in 1 kg of water using following information will be

(molecular wt. of CuCl_2 = 134.4, K_b = $0.52 \text{ K molal}^{-1}$).

- (a) 0.16 (b) 0.05
 (c) 0.1 (d) 0.2 (I.I.T. 2005)

B87. When 20 g of naphthoic acid ($\text{C}_{11}\text{H}_8\text{O}_2$) is dissolved in 50 g of benzene ($K = 1.72 \text{ K kg mol}^{-1}$) a freezing point depression of 2 K is observed. The Van't Hoff factor ' i ' is
 (a) 0.5 (b) 1
 (c) 2 (d) 3 (I.I.T. 2007)

B88. The Henry's law constant for the solubility of N_2 gas in water at 298 K is $1.0 \times 10^5 \text{ atm}$. The mole fraction of N_2 in air is 0.8. The number of moles of N_2 from air dissolved in 10 moles of water at 298 K and 5 atm pressure is
 (a) 4.0×10^{-4} (b) 4.0×10^{-5}
 (c) 5.0×10^{-4} (d) 4.0×10^{-6} (IIT-JEE 2009)

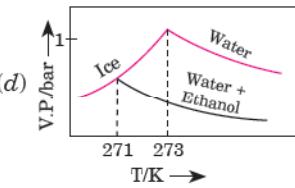
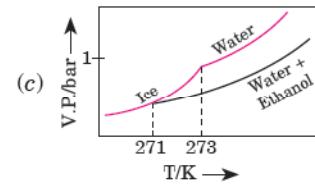
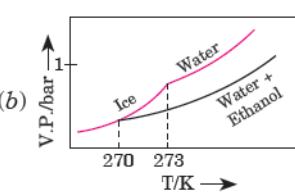
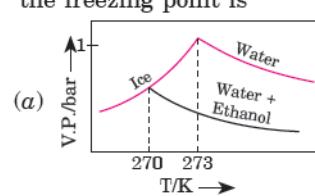
B89. Dissolving 120g of urea (mol. wt. 60) in 1000 g of water gave a solution of density 1.15 g/mL . The molarity of the solution is
 (a) 1.78 M (b) 2.00 M
 (c) 2.05 M (d) 2.22 M (I.I.T. 2011)

B90. The freezing point (in $^\circ\text{C}$) of a solution containing 0.1 g of $\text{K}_3[\text{Fe}(\text{CN})_6]$ (mol. wt. 329) in 100 g of water ($K_f = 1.86 \text{ K kg mol}^{-1}$) is
 (a) -2.3×10^{-2} (b) -5.7×10^{-2}
 (c) -5.7×10^{-3} (d) -1.2×10^{-2} (I.I.T. 2011)

B91. For a dilute solution containing 2.5 g of a non-volatile non-electrolyte solution in 100 g of water, the elevation in boiling point at 1 atm pressure is 2°C . Assuming concentration of solute is much lower than the concentration of solvent, the vapour pressure (mm of Hg) of the solution is (take $K_b = 0.76 \text{ K kg mol}^{-1}$)
 (a) 724 (b) 740
 (c) 736 (d) 718 (I.I.T. J.E.E. 2012)

B92. Pure water freezes at 273 K and 1 bar. The addition of 34.5 g of ethanol to 500 g of water changes the freezing point of the solution. Use the freezing point depression constant of water as 2 K kg mol^{-1} . The figures shown below represent plots of vapour pressure (V.P.) versus temperature (T). (Molecular weight of ethanol is 46 g mol^{-1})

Among the following, the option representing change in the freezing point is



(JEE Advance 2017)

Answers

- | | | | | | | | | | |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| B76. (a) | B77. (a) | B78. (e) | B79. (c) | B80. (b) | B81. (b) | B82. (a) | B83. (b) | B84. (c) | B85. (c) |
| B86. (a) | B87. (a) | B88. (a) | B89. (c) | B90. (a) | B91. (a) | B92. (b) | | | |

Competition File

C MULTIPLE CHOICE QUESTIONS with more than one correct answers

C1. Colligative properties of a solution are

- (a) independent of the nature of solute
- (b) inversely proportional to molecular mass of solute
- (c) proportional to concentration of solute
- (d) independent of the amount of solvent.

C2. Non-ideal solutions showing negative deviations are:

- (a) acetone + ethyl alcohol
- (b) acetic acid + pyridine
- (c) chloroform + benzene
- (d) carbon tetrachloride + toluene

C3. Which of the following form nearly ideal solution?

- (a) Chlorobenzene + Bromobenzene
- (b) Hexane + Heptane (c) Ethanol + Cyclohexane
- (d) Acetic acid + Pyridine

C4. In the depression in freezing point experiment, it is observed that

- (a) the vapour pressure of the solution is less than that of pure solvent.
- (b) the vapour pressure of the solution is more than that of pure solvent
- (c) only solute molecules solidify at the freezing point.
- (d) only solvent molecules solidify at the freezing point.

C5. For 0.5 m aqueous solution of KCl, the important physical properties at 27°C are $K_f(\text{water}) = 1.86 \text{ K m}^{-1}$, $K_b(\text{water}) = 0.512 \text{ K m}^{-1}$

- (a) freezing point of solution = -3.72°C
- (b) boiling point of solution = 100.512°C
- (c) osmotic pressure = 3.76 atm
- (d) observed molecular mass = 37.25 (approx. assuming degree of dissociation = 1).

C6. Which of the following statements is/are wrong?

- (a) The value of colligative property decreases when solute undergoes dissociation.
- (b) For AlCl₃, the Van't Hoff factor is 3.
- (c) Solvent rises from soil to the top of a tall tree due to osmosis.
- (d) Aqueous solution of NaCl freezes at lower temperature than water.

C7. Benzene and naphthalene form an ideal solution at room temperature. For this process, the true statement(s) is (are)

- (a) ΔG is positive (b) ΔS_{system} is positive
- (c) $\Delta S_{\text{surroundings}} = 0$ (d) $\Delta H = 0$

(JEE Advance 2013)

C8. The solution which is isotonic with 6% (m/v) solution of urea is / are:

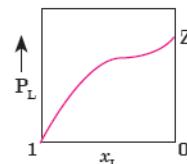
- (a) 18% (m/v) solution of glucose
- (b) 0.5 M solution of BaCl₂
- (c) 1M solution of sucrose
- (d) 1M solution of acetic acid

C9. Mixture(s) showing positive deviation from Raoult's law at 35°C is (are)

- (a) carbon tetrachloride + methanol
- (b) carbon disulphide + acetone
- (c) benzene + toluene
- (d) phenol + aniline.

(JEE Advance 2016)

C10. For a solution formed by mixing liquids L and M, the vapour pressure of L plotted against the mole fraction of M in solution is shown in the following figure. Here x_L and x_M represent mole fractions of L and M, respectively, in the solution. The correct statement (s) applicable to this system is (are)



- (a) attractive intermolecular interactions between L–L in pure liquid L and M–M in pure liquid M are stronger than those between L–M when mixed in solution.
- (b) the point Z represents vapour pressure of pure liquid M and Raoult's law is obeyed when $x_L \rightarrow 0$
- (c) the point Z represents vapour pressure of pure liquid M and Raoult's law is obeyed when $x_L = 0$ to $x_L = 1$
- (d) the point Z represents vapour pressure of pure liquid L and Raoult's law is obeyed when $x_L \rightarrow 1$

(JEE Advance 2017)

Answers

- | | | | | | | | |
|--------------------------|----------------------|---------------------|---------------------|---------------------|---------------------|--------------------------|---------------------|
| C1. (a), (b), (c) | C2. (b), (c) | C3. (a), (b) | C4. (a), (d) | C5. (b), (d) | C6. (a), (b) | C7. (b), (c), (d) | C8. (a), (c) |
| C9. (a), (b) | C10. (a), (d) | | | | | | |

Competition File

D MULTIPLE CHOICE QUESTIONS *based on the given passage/comprehension*

Passage I.

Vapour pressure of a liquid or a solution is the pressure exerted by the vapour in equilibrium with the liquid or solution at a particular temperature. It depends upon the nature of the liquid and temperature. According to Raoult's law, in a solution, the vapour pressure of a component at a given temperature is equal to the mole fraction of that component in solution multiplied by the vapour pressure of that component in the pure state. The solutions in which each component obeys Raoult's law are called ideal solutions. There are two types of non-ideal solutions, showing positive deviations and negative deviations from ideal behaviour.

Answer the following questions :

- D1.** The vapour pressure of a pure liquid A is 40 mm of Hg at 300 K. The vapour pressure of this liquid in solution with liquid B is 32 mm of Hg. The mole fraction of A in solution obeying Raoult's law is
(a) 0.6 (b) 0.5 (c) 0.2 (d) 0.8

D2. Which of the following statements is correct for non-ideal solutions ?
(a) For solutions showing -ve deviations, ΔV_{mixing} and ΔH_{mixing} are +ve.
(b) For solutions showing negative deviations, the interactions between the components are greater than the pure components.
(c) For solutions showing +ve deviations, $\Delta V_{\text{mixing}} = +ve$ but $\Delta H_{\text{mixing}} = +ve$.
(d) For solutions showing -ve deviations, $\Delta V_{\text{mixing}} = -ve$ but $\Delta H_{\text{mixing}} = +ve$.

D3. Vapour pressure of a solution of heptane and octane is given by the equation:
 $p(\text{sol.}) \text{ (mm Hg)} = 35 + 65x$, where x is the mole fraction of heptane. Vapour pressure of pure octane is
(a) 100 mm Hg (b) 35 mm Hg
(c) 30 mm Hg (d) 1.86 mm Hg

D4. If liquid A and B form ideal solution, then
(a) $\Delta G_{\text{mix}} = 0$ (b) $\Delta H_{\text{mixing}} = 0$
(c) $\Delta G_{\text{mix}} = 0$, $\Delta S_{\text{mix}} = 0$ (d) $\Delta S_{\text{mixing}} = 0$

Passage II

A solution of glucose (molar mass = 180 g mol⁻¹) has been prepared at 298 K by dissolving 7.2 g of glucose in 100 g of water. K_f for water is 1.86 K m⁻¹ and vapour pressure of water at 298 K is 0.024 atm.

Answers

Passage-I. D1. (d) D2. (b) D3. (b) D4. (b)
Passage-III. D9. (b)

Answer the following questions :

- D5. The freezing point of the solution at 298 K will be
(a) $-0.744\text{ }^{\circ}\text{C}$ (b) $-0.372\text{ }^{\circ}\text{C}$
(c) $-0.186\text{ }^{\circ}\text{C}$ (d) $-0.093\text{ }^{\circ}\text{C}$

D6. The vapour pressure of the solution at 298 K will be
(a) 0.0220 atm (b) 0.238 atm
(c) 0.0238 atm (d) 0.220 atm

D7. The amount of sodium chloride that should be dissolved in the same amount of water to get the same freezing point will be
(a) 11.79 g (b) 1.179 g
(c) 2.34 g (d) 23.4 g

D8. If on dissolving the above amount of sodium chloride in same amount of water, the freezing point is found to be $-0.698\text{ }^{\circ}\text{C}$, the percentage dissociation is
(a) 72% (b) 80%
(c) 92% (d) 88%

Passage III

The equations derived for colligative properties are based on the assumption that solutions are dilute and solute molecules do not dissociate or associate in solution. Discrepancies in determination of molar masses or measuring colligative properties arise when the solute dissociates or associates on dissolving in a solvent. This is because due to association or dissociation of solute molecules in the solution, the number of molecules undergo a change. Van't Hoff introduced a factor called Van't Hoff factor ' i ' to express the extent of association or dissociation of solute in solution as :

$$i = \frac{\text{Normal molar mass}}{\text{Observed molar mass}}$$

Inclusion of ' i ' modifies the equations for colligative properties as :

$$\frac{\Delta p}{p} = i x_{\text{solute}} \quad \Delta T_f = i K_f m$$

$$\Delta T_b = i K_b m \quad \pi = i c R T$$

Answer the following questions :

Competition File

D10. 0.2 m aqueous solution of a weak acid (HX) is 20% dissociated. The boiling point of this solution is (K_b for water = 0.52 Km^{-1})

- (a) 101.04°C (b) 100.104°C
 (c) 100.1248°C (d) 100.52°C

D11. Which of the following equimolar solution is expected to have lowest freezing point?

- (a) 0.5 M H_3PO_4 (b) 0.5 M Na_3PO_4
 (c) 0.5 M NaCl (d) 0.5 M Aniline

D12. The elevation in boiling point for 1 M urea, 1 M glucose, 1 M NaCl and 1 M K_2SO_4 are in the ratio :

- (a) $1 : 1 : 2 : 3$ (b) $3 : 2 : 1 : 1$
 (c) $1 : 2 : 3 : 4$ (d) $2 : 2 : 3 : 4$

D13. The average osmotic pressure of human blood is 7.8 bar at 37°C . The concentration of aqueous NaCl solution that could be used in the blood stream is

- (a) 7.8 mol L^{-1} (b) 1.5 mol L^{-1}
 (c) 0.075 mol L^{-1} (d) 0.15 mol L^{-1}

Answers

Passage-III. D10. (c) D11. (b) D12. (a) D13. (d)

Assertion Reason Type Questions

The questions given below consist of an Assertion and Reason. Use the following key to choose the appropriate answer.

- (a) If both assertion and reason are CORRECT and reason is the CORRECT explanation of the assertion.
- (b) If both assertion and reason are CORRECT but, reason is NOT THE CORRECT explanation of the assertion.
- (c) If assertion is CORRECT but, reason is INCORRECT.
- (d) If assertion is INCORRECT but, reason is CORRECT.
- (e) If both assertion and reason are INCORRECT.

1. Assertion : ΔH_{mix} and ΔV_{mix} are zero for the ideal solution.

Reason : The interactions between the particles of the components of a solution are almost identical as between particles in the liquids.

2. Assertion : Increasing pressure on water decreases its freezing point.

Reason : Density of water is maximum at 273 K.

3. Assertion : 0.1 M glucose solution has higher increment in the freezing point than 0.1 M urea solution.

Reason : K_f for both has different values.

4. Assertion : Cooking time in pressure cookers is reduced.

Reason : Boiling point inside the pressure cooker is raised.

5. Assertion : The sum of mole fractions of all components of a solution is unity.

Reason : Mole fraction is independent of temperature.

6. Assertion : Sodium chloride is used to clear snow on the roads.

Reason : Sodium chloride depresses the freezing point of water.

7. Assertion : Osmotic pressure of 0.1 M urea solution is less than that of 0.1 M NaCl solution.

Reason : Osmotic pressure is not a colligative property.

8. Assertion : Elevation in boiling point for two isotonic solutions may not be same.

Reason : Boiling point depends upon the concentration of the solute.

9. Assertion : Iodine is more soluble in CCl_4 than in water.

Reason : Non-polar solutes are more soluble in non-polar solvents

10. Assertion : Camphor is usually used in molecular mass determination.

Reason : Camphor has low cryoscopic constant and therefore, causes greater depression in freezing point.

Answers

1. (a) 2. (c) 3. (e) 4. (a) 5. (b) 6. (a) 7. (c) 8. (e) 9. (a) 10. (c)

Competition File

Matrix Match Type Questions

Each question contains statements given in two columns. Match the statements in column I with statements in column II.

Each question contains statements given in two columns, which have to be matched. Statements in Column I are labelled as A, B, C and D whereas statements in Column II are labelled as p, q, r and s. Match the entries of Column I with appropriate entries of Column II. Each entry in Column I may have one or more than one correct option from Column II. The answers to these questions have to be appropriate bubbled as illustrated in the following example.

If the correct matches are A-q, A-r, B-p, B-s, C-r, C-s and D-q, then the correctly bubbled matrix will look like the following:

	p	q	r	s
A	<input checked="" type="radio"/>	<input checked="" type="radio"/>	<input checked="" type="radio"/>	<input type="radio"/>
B	<input checked="" type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input checked="" type="radio"/>
C	<input type="radio"/>	<input checked="" type="radio"/>	<input checked="" type="radio"/>	<input type="radio"/>
D	<input type="radio"/>	<input checked="" type="radio"/>	<input checked="" type="radio"/>	<input checked="" type="radio"/>

1. Match the behaviour of solutions in Column I with the examples listed in Column II.

Column I	Column II
(A) Show ideal behaviour	(p) Water + Nitric acid
(B) Show -ve deviation from ideal behaviour	(q) Benzene + Acetone
(C) Show +ve deviation from ideal behaviour	(r) n-hexane + n-heptane
(D) Non-ideal solution	(s) Carbon tetrachloride + chloroform

2. Match the type of solutions in Column I with the characteristic property mentioned in Column II.

Column I	Column II
(A) Solution in which solute undergoes association	(p) Van't Hoff factor will be less than 1 observed
(B) Solution in which solute dissociation	(q) observed molecular mass will be more than normal value
(C) Solution containing non-electrolyte	(r) colligative property will be more than normal value
(D) 0.1M solution of benzoic acid in benzene	(s) Van't Hoff factor will be equal to 1.

Answers

- | | | | |
|---------------------|-----------|---------------|-------------------|
| (1) : (A) – (r) | (B) – (p) | (C) – (q) (s) | (D) – (p) (q) (s) |
| (2) : (A) – (p) (q) | (B) – (r) | (C) – (s) | (D) – (p) (q) |

Integer type or Numerical Value Type Questions

Integer Type: The answer to each of the following question is a single-digit-integer ranging from 0 to 9.

1. How many of the following solutions show negative deviation from ideal behaviour?

Chloroform + diethyl ether, acetone + aniline, water + nitric acid, acetone + ethyl alcohol, acetone + carbon disulphide, chloroform + nitric acid.

2. The depression in freezing point for 1 M urea, 0.5 M glucose, 1 M NaCl, and 1M K₂SO₄ are in the ratio x : 1 : y : z, The value of x + z is

3. At a certain temperature, the vapour pressure (in mm Hg) of CH₃OH and C₂H₅OH solution is represented as:

$$p = 126x + 142$$

where x is the mole fraction of CH₃OH. The vapour of solution containing equimoles of CH₃OH and C₂H₅OH is y + 200 mm Hg. The value of y is

4. An electrolyte A₂B₃ ionizes in water upto 75%. The van't Hoff factor for it is
5. The depression in freezing point expected for 0.6 m Al₂(SO₄)₃ solution will be 'n' times compared with 0.2 m Na₂SO₄ solution. The value of n is
6. 29.2% (w/w) HCl stock solution has a density of 1.25 g mL⁻¹. The molecular weight of HCl is 36.5 g mol⁻¹. The volume (mL) of stock solution required to prepare 200 mL of 0.4 M HCl is (I.I.T. 2012)
7. MX₂ dissociates into M²⁺ and X⁻ ions in an aqueous solution, with a degree of dissociation (α) of 0.5. The ratio of the observed depression of freezing point of the aqueous solution to the value of the depression of freezing point in the absence of ionic dissociation is.

(JEE Advance 2014)

Answers

- | | | | | | | |
|------|------|------|------|------|------|------|
| 1. 4 | 2. 8 | 3. 5 | 4. 4 | 5. 5 | 6. 8 | 7. 2 |
|------|------|------|------|------|------|------|

Competition File

8. If the freezing point of a 0.01 molal aqueous solution of a cobalt (III) chloride-ammonia complex (which behaves as a strong electrolyte) is -0.0558°C , the number of chloride (s) in the coordination sphere of the complex is [K_f of water = 1.86 K kg mol⁻¹]

(JEE Advance 2015)

9. The mole fraction of a solute in a solution is 0.1. At 298 K, molarity of this solution is the same as its molality. Density of this solution at 298 K is 2.0 g cm⁻³. The ratio of the molecular weights of the solute and solvent, $\left(\frac{\text{MW}_{\text{solute}}}{\text{MW}_{\text{solvent}}}\right)$, is

(JEE Advance 2016)

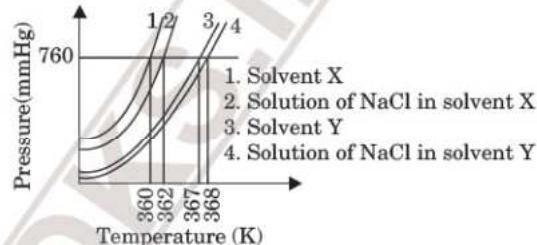
Numerical Value Type: Give the correct numerical value (in decimal notation truncated/rounded off to the second decimal place).

10. Liquids A and B form ideal solution over the entire range of composition. At temperature T, enquimolar binary solution of liquids A and B has vapour pressure 45 torr. At the same temperature, a new solution of A and B having mole fractions x_A

and x_B respectively has vapour pressure of 22.5 torr. The value of x_A/x_B in the new solution is

(Given that the vapour pressure of pure liquid A is 20 torr at temperature T.) *(JEE Advance 2018)*

11. The plot given below shows P—T curves (where P is the pressure and T is the temperature) for two solvents X and Y and isomolal solutions of NaCl in these solvents. NaCl completely dissociates in both the solvents.



On addition of equal number of moles of a non-volatile solute S in equal amount (in kg) of these solvents, the elevation of boiling point of solvent X is three times that of solvent Y. Solute S is known to undergo dimerization in these solvents. If the degree of dimerization is 0.7 in solvent Y, the degree of dimerization in solvent X is

(JEE Advance 2018)

Answers

8. 1 9. 9 10. 19.00 11. 0.05



NCERT

Multiple Choice Questions (Type-I)

1. Which of the following units is useful in relating concentration of solution with its vapour pressure?
 - (a) mole fraction
 - (b) parts per million
 - (c) mass percentage
 - (d) molality
2. On dissolving sugar in water at room temperature solution feels cool to touch. Under which of the following cases dissolution of sugar will be most rapid?
 - (a) Sugar crystals in cold water.
 - (b) Sugar crystals in hot water.
 - (c) Powdered sugar in cold water.
 - (d) Powdered sugar in hot water.

Exemplar Problems

Objective Questions

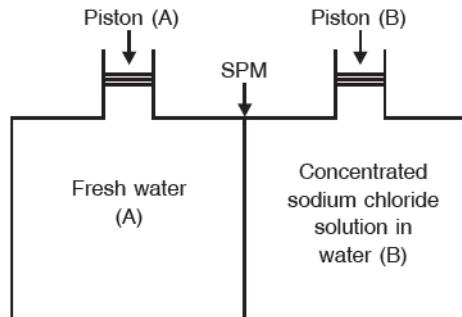
3. At equilibrium the rate of dissolution of a solid solute in a volatile liquid solvent is _____.
 (a) less than the rate of crystallisation
 (b) greater than the rate of crystallisation
 (c) equal to the rate of crystallisation
 (d) zero
4. A beaker contains a solution of substance 'A'. Precipitation of substance 'A' takes place when small amount of 'A' is added to the solution. The solution is _____.
 (a) saturated (b) supersaturated
 (c) unsaturated (d) concentrated

Answers

1. (a) 2. (d) 3. (c) 4. (b)

Competition File

5. Maximum amount of a solid solute that can be dissolved in a specified amount of a given liquid solvent does **not** depend upon _____.
 (a) Temperature (b) Nature of solute
 (c) Pressure (d) Nature of solvent
6. Low concentration of oxygen in the blood and tissues of people living at high altitude is due to _____.
 (a) low temperature
 (b) low atmospheric pressure
 (c) high atmospheric pressure
 (d) both low temperature and high atmospheric pressure
7. Considering the formation, breaking and strength of hydrogen bond, predict which of the following mixtures will show a positive deviation from Raoult's law?
 (a) Methanol and acetone.
 (b) Chloroform and acetone.
 (c) Nitric acid and water.
 (d) Phenol and aniline.
8. Colligative properties depend on _____.
 (a) the nature of the solute particles dissolved in solution.
 (b) the number of solute particles in solution.
 (c) the physical properties of the solute particles dissolved in solution.
 (d) the nature of solvent particles.
9. Which of the following aqueous solutions should have the highest boiling point?
 (a) 1.0 M NaOH (b) 1.0 M Na_2SO_4
 (c) 1.0 M NH_4NO_3 (d) 1.0 M KNO₃
10. The unit of ebullioscopic constant is _____.
 (a) K kg mol⁻¹ or K (molality)⁻¹
 (b) mol kg K⁻¹ or K⁻¹(molality)
 (c) kg mol⁻¹ K⁻¹ or K⁻¹(molality)⁻¹
 (d) K mol kg⁻¹ or K (molality)
11. In comparison to a 0.01 M solution of glucose, the depression in freezing point of a 0.01 M MgCl₂ solution is _____.
 (a) the same (b) about twice
 (c) about three times (d) about six times
12. An unripe mango placed in a concentrated salt solution to prepare pickle, shrivels because _____.
 (a) it gains water due to osmosis.
 (b) it loses water due to reverse osmosis.
 (c) it gains water due to reverse osmosis.
 (d) it loses water due to osmosis.
13. At a given temperature, osmotic pressure of a concentrated solution of a substance _____.
 (a) is higher than that of a dilute solution.
 (b) is lower than that of a dilute solution.
 (c) is same as that of a dilute solution.
 (d) cannot be compared with osmotic pressure of dilute solution.
14. Which of the following statements is false?
 (a) Two different solutions of sucrose of same molality prepared in different solvents will have the same depression in freezing point.
 (b) The osmotic pressure of a solution is given by the equation $\pi = cRT$ (where c is the molarity of the solution).
 (c) Decreasing order of osmotic pressure for 0.01 M aqueous solutions of barium chloride, potassium chloride, acetic acid and sucrose is $\text{BaCl}_2 > \text{KCl} > \text{CH}_3\text{COOH} > \text{sucrose}$.
 (d) According to Raoult's law, the vapour pressure exerted by a volatile component of a solution is directly proportional to its mole fraction in the solution.
15. The values of Van't Hoff factors for KCl, NaCl and K₂SO₄, respectively, are _____.
 (a) 2, 2 and 2 (b) 2, 2 and 3
 (c) 1, 1 and 2 (d) 1, 1 and 1
16. Which of the following statements is **false**?
 (a) Units of atmospheric pressure and osmotic pressure are the same.
 (b) In reverse osmosis, solvent molecules move through a semipermeable membrane from a region of lower concentration of solute to a region of higher concentration.
 (c) The value of molal depression constant depends on nature of solvent.
 (d) Relative lowering of vapour pressure, is a dimensionless quantity.
17. Value of Henry's constant K_H _____.
 (a) increases with increase in temperature.
 (b) decreases with increase in temperature.
 (c) remains constant.
 (d) first increases then decreases.
18. The value of Henry's constant K_H is _____.
 (a) greater for gases with higher solubility.
 (b) greater for gases with lower solubility.
 (c) constant for all gases.
 (d) not related to the solubility of gases.
19. Consider the figure given below and mark the correct option.

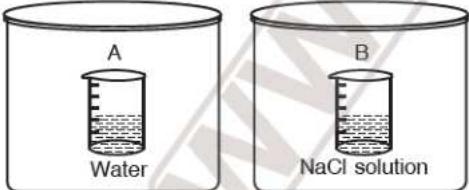


- (a) water will move from side (A) to side (B) if a pressure lower than osmotic pressure is applied on piston (B).
 (b) water will move from side (B) to side (A) if a pressure greater than osmotic pressure is applied on piston (B).

Answers

- | | | | | | | | | |
|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| 5. (c) | 6. (b) | 7. (a) | 8. (b) | 9. (b) | 10. (a) | 11. (c) | 12. (d) | 13. (a) |
| 14. (a) | 15. (b) | 16. (b) | 17. (a) | 18. (b) | 19. (b) | | | |

Competition File

- (c) water will move from side (B) to side (A) if a pressure equal to osmotic pressure is applied on piston (B).
 (d) water will move from side (A) to side (B) if pressure equal to osmotic pressure is applied on piston (A).
20. We have three aqueous solutions of NaCl labelled as 'A', 'B' and 'C' with concentrations 0.1M, 0.01M and 0.001M, respectively. The value of van't Hoff factor for these solutions will be in the order _____.
 (a) $i_A < i_B < i_C$ (b) $i_A > i_B > i_C$
 (c) $i_A = i_B = i_C$ (d) $i_A < i_B > i_C$
21. On the basis of information given below mark the correct option.
Information:
 (A) In bromoethane and chloroethane mixture, intermolecular interactions of A-A and B-B type are nearly same as A-B type interactions.
 (B) In ethanol and acetone mixture A-A or B-B type intermolecular interactions are stronger than A-B type interactions.
 (C) In chloroform and acetone mixture A-A or B-B type intermolecular interactions are weaker than A-B type interactions.
 (a) Solution (B) and (C) will follow Raoult's law.
 (b) Solution (A) will follow Raoult's law.
 (c) Solution (B) will show negative deviation from Raoult's law.
 (d) Solution (C) will show positive deviation from Raoult's law.
22. Two beakers of capacity 500 mL were taken. One of these beakers, labelled as "A", was filled with 400 mL water whereas the beaker labelled "B" was filled with 400 mL of 2 M solution of NaCl. At the same temperature both the beakers were placed in closed containers of same material and same capacity as shown in figure given below:
- 
- At a given temperature, which of the following statement is correct about the vapour pressure of pure water and that of NaCl solution.
 (a) vapour pressure in container (A) is more than that in container (B).
 (b) vapour pressure in container (A) is less than that in container (B).
- (c) vapour pressure is equal in both the containers.
 (d) vapour pressure in container (B) is twice the vapour pressure in container (A).
23. If two liquids A and B form minimum boiling azeotrope at some specific composition then _____.
 (a) A-B interactions are stronger than those between A-A or B-B.
 (b) vapour pressure of solution increases because more number of molecules of liquids A and B can escape from the solution.
 (c) vapour pressure of solution decreases because less number of molecules of only one of the liquids escape from the solution.
 (d) A-B interactions are weaker than those between A-A or B-B.
24. 4L of 0.02 M aqueous solution of NaCl was diluted by adding one litre of water. The molality of the resultant solution is _____.
 (a) 0.004 (b) 0.008
 (c) 0.012 (d) 0.016
25. On the basis of information given below mark the correct option.
Information : On adding acetone to methanol some of the hydrogen bonds between methanol molecules break.
 (a) At specific composition, methanol-acetone mixture will form minimum boiling azeotrope and will show positive deviation from Raoult's law.
 (b) At specific composition, methanol-acetone mixture forms maximum boiling azeotrope and will show positive deviation from Raoult's law.
 (c) At specific composition, methanol-acetone mixture will form minimum boiling azeotrope and will show negative deviation from Raoult's law.
 (d) At specific composition, methanol-acetone mixture will form maximum boiling azeotrope and will show negative deviation from Raoult's law.
26. K_H value for Ar(g), CO₂(g), HCHO(g) and CH₄(g) are 40.39, 1.67, 1.83×10^{-5} and 0.413 respectively. Arrange these gases in the order of their increasing solubility.
 (a) HCHO < CH₄ < CO₂ < Ar
 (b) HCHO < CO₂ < CH₄ < Ar
 (c) Ar < CO₂ < CH₄ < HCHO
 (d) Ar < CH₄ < CO₂ < HCHO

Answers

Competition File

Multiple Choice Questions (Type-II)

Note : In the following questions two or more options may be correct.

27. Which of the following factor (s) affect the solubility of a gaseous solute in the fixed volume of liquid solvent?

- (i) nature of solute (ii) temperature (iii) pressure
- (a) (i) and (iii) at constant T
- (b) (i) and (ii) at constant P
- (c) (ii) and (iii) only
- (d) (iii) only

28. Intermolecular forces between two benzene molecules are nearly of same strength as those between two toluene molecules. For a mixture of benzene and toluene, which of the following are **not** true?

- (a) $\Delta_{mix} H = \text{zero}$ (b) $\Delta_{mix} V = \text{zero}$
- (c) These will form minimum boiling azeotrope.
- (d) These will not form ideal solution.

29. Relative lowering of vapour pressure is a colligative property because _____.

- (a) It depends on the concentration of a non electrolyte solute in solution and does not depend on the nature of the solute molecules.
- (b) It depends on number of particles of electrolyte solute in solution and does not depend on the nature of the solute particles.
- (c) It depends on the concentration of a non electrolyte solute in solution as well as on the nature of the solute molecules.
- (d) It depends on the concentration of an electrolyte or non electrolyte solute in solution as well as on the nature of solute molecules.

30. Van't Hoff factor 'i' is given by the expression _____.

- (a) $i = \frac{\text{Normal molar mass}}{\text{Abnormal molar mass}}$
- (b) $i = \frac{\text{Abnormal molar mass}}{\text{Normal molar mass}}$
- (c) $i = \frac{\text{Observed colligative property}}{\text{Calculated colligative property}}$
- (d) $i = \frac{\text{Calculated colligative property}}{\text{Observed colligative property}}$

31. Isotonic solutions must have the same _____.

- (a) solute
- (b) density
- (c) elevation in boiling point
- (d) depression in freezing point

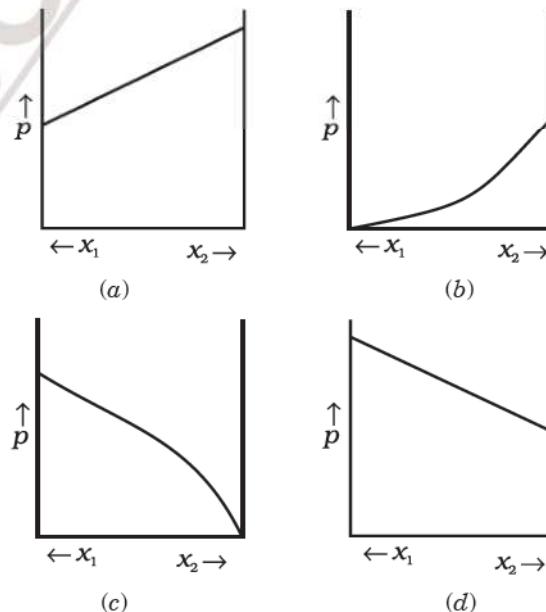
32. Which of the following binary mixtures will have same composition in liquid and vapour phase?

- (a) Benzene – Toluene
- (b) Water – Nitric acid
- (c) Water – Ethanol
- (d) n-Hexane – n-Heptane

33. In isotonic solutions _____.

- (a) solute and solvent both are same.
- (b) osmotic pressure is same.
- (c) solute and solvent may or may not be same.
- (d) solute is always same solvent may be different.

34. For a binary ideal liquid solution, the variation in total vapour pressure versus composition of solution is given by which of the curves?



35. Colligative properties are observed when _____.

- (a) a non volatile solid is dissolved in a volatile liquid.
- (b) a non volatile liquid is dissolved in another volatile liquid.
- (c) a gas is dissolved in non volatile liquid.
- (d) a volatile liquid is dissolved in another volatile liquid.

Answers

- 27. (a), (b) 28. (c), (d) 29. (a),(b) 30. (a),(c) 31. (c),(d) 32. (b),(c) 33. (b),(c) 34. (a),(d) 35. (a),(b)**

Competition File

Matching Type Questions

Note : In the following questions match the items given in Column I and Column II.

36. Match the items given in Column I and Column II.

Column I	Column II
(a) Saturated solution	(i) Solution having same osmotic pressure at a given temperature as that of given solution.
(b) Binary solution	(ii) A solution whose osmotic pressure is less than that of another.
(c) Isotonic solution	(iii) Solution with two components.
(d) Hypotonic solution	(iv) A solution which contains maximum amount of solute that can be dissolved in a given amount of solvent at a given temperature.
(e) Solid solution	(v) A solution whose osmotic pressure is more than that of another.
(f) Hypertonic solution	(vi) A solution in solid phase.

37. Match the items given in Column I with the type of solutions given in Column II.

Column I	Column II
(a) Soda water	(i) A solution of gas in solid
(b) Sugar solution	(ii) A solution of gas in gas
(c) German silver	(iii) A solution of solid in liquid
(d) Air	(iv) A solution of solid in solid
(e) Hydrogen gas in palladium	(v) A solution of gas in liquid
	(vi) A solution of liquid in solid

38. Match the laws given in Column I with expressions given in Column II.

Column I	Column II
(a) Raoult's law	(i) $\Delta T_f = K_f m$
(b) Henry's law	(ii) $\pi = cRT$
(c) Elevation of boiling point	(iii) $p = x_1 p_1^o + x_2 p_2^o$
(d) Depression in freezing point	(iv) $\Delta T_b = K_b m$
(e) Osmotic pressure	(v) $p = K_H x$

39. Match the terms given in Column I with expressions given in Column II.

Column I	Column II
(a) Mass percentage	(i) $\frac{\text{Number of moles of the solute component}}{\text{Volume of solution in litres}}$
(b) Volume percentage	(ii) $\frac{\text{Number of moles of a component}}{\text{Total number of moles of all the components}}$
(c) Mole fraction	(iii) $\frac{\text{Volume of the solute component in solution}}{\text{Total volume of solution}} \times 100$
(d) Molality	(iv) $\frac{\text{Mass of the solute component in solution}}{\text{Total mass of the solution}} \times 100$
(e) Molarity	(v) $\frac{\text{Normal molar mass}}{\text{Abnormal molar mass}}$

Answers

36. (a)→(iv); (b)→(iii); (c)→(i); (d)→(ii); (e)→(vi); (f)→(v)

37. (a)→(v); (b)→(iii); (c)→(iv); (d)→(ii); (e)→(i);

38. (a)→(iii); (b)→(v); (c)→(iv); (d)→(i); (e)→(ii);

39. (a)→(iv); (b)→(iii); (c)→(ii); (d)→(v); (e)→(i);

Competition File

Assertion and Reason Type Questions

Note : In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

- (a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
 - (b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
 - (c) Assertion is correct statement but reason is wrong statement.
 - (d) Assertion and reason both are incorrect statements.
 - (e) Assertion is wrong statement but reason is correct statement.
- 40. Assertion :** Molarity of a solution in liquid state changes with temperature.

Reason : The volume of a solution changes with change in temperature.

- 41. Assertion :** When methyl alcohol is added to water, boiling point of water increases.

Reason : When a volatile solute is added to a volatile solvent elevation in boiling point is observed.

- 42. Assertion :** When NaCl is added to water a depression in freezing point is observed.

Reason : The lowering of vapour pressure of a solution causes depression in the freezing point.

- 43. Assertion :** When a solution is separated from the pure solvent by a semipermeable membrane, the solvent molecules pass through it from pure solvent side to the solution side.

Reason : Diffusion of solvent occurs from a region of high concentration solution to a region of low concentration solution.

Answers

40. (a) 41. (d) 42. (a) 43. (c)

Hints & Explanations for Difficult Objective Type Questions

A. mcq with only one correct answer

A1. (b) :

$$\begin{aligned} \text{Mass of solution} &= 500 \times 1.05 = 525 \text{ g} \\ \text{Mass of urea} &= 6 \text{ g} \\ \text{Mass of solvent} &= 525 - 6 = 519 \text{ g} \\ \text{Molality} &= \frac{6/60}{519} \times 1000 \\ &= 0.1927 \text{ m} \end{aligned}$$

A2. (c) : $M_1V_1 + M_2V_2 \equiv M_3V_3$
 $1 \times 2.5 + 0.5 \times 3 \equiv M_3 \times 5.5$ (Total solution = 5.5 L)
 $2.5 + 1.5 = M_3 \times 5.5$
 $\therefore M_3 = \frac{4}{5.5} = 0.73 \text{ M}$

A3.(c): Let volume of 4N HCl used = x mL
Volume of 10 N HCl used = $(1000 - x)$ mL
 $N_1V_1 + N_2V_2 = N_3V_3$
 $4 \times x + 10 \times (1000 - x) = 6 \times 1000$
 $6x = 4000$
 $x = \frac{4000}{6} = 666.7 \text{ mL}$

$$\begin{aligned} \text{Vol. of 4 N HCl used} &= 0.67 \text{ L} \\ \text{Vol. of 10 N HCl used} &= 1 - 0.67 \\ &= 0.33 \text{ L} \end{aligned}$$

A4. (d) : Let a mole of CH_3OH and b mole of water be present in the solution.

$$\text{Mass of water} = b \times 18$$

Molality of solution

$$= \frac{a}{b \times 18} \times 1000 = 4.5$$

or $\frac{a}{b} = \frac{18 \times 4.5}{1000} = 0.081$

Mole fraction of CH_3OH

$$= \frac{a}{a+b} \text{ or } \frac{1}{1+b/a}$$

$$= \frac{1}{1 + \frac{1}{0.081}} = \frac{1}{1 + 12.34} = 0.075$$

A5. (a) : 3 Molar solution of NaCl means that 3 mol of NaCl is dissolved in 1000 mL of solution.

$$\text{Mass of 3 M NaCl solution} = 1.25 \times 1000 = 1250 \text{ g}$$

$$\text{Mass of 3 mole NaCl} = 3 \times 58.5 = 175.5 \text{ g}$$

$$\text{Mass of solvent} = 1250 - 175.5 = 1074.5 \text{ g}$$

$$\text{Molality} = \frac{3}{1074.5} \times 1000 = 2.79 \text{ m}$$

A6. (b) : Moles of solute = 2.5

$$\text{Moles of water} = \frac{1000}{18} = 55.6$$

$$\text{Mole fraction of solute} = \frac{2.5}{2.5 + 55.6} = 0.043$$

A7. (c) : 4.27 M H_2SO_4 (*aq*) means that 4.27 moles of H_2SO_4 are present in 1000 mL of solution.

$$\text{Mass of solution} = 1000 \times 1.25 = 1250 \text{ g}$$

$$\text{Mass of 4.27 moles of } \text{H}_2\text{SO}_4 = 4.27 \times 98 = 418.46 \text{ g}$$

Competition File

Mass of water present = $1250 - 418.46 = 831.54$ g

$$\text{Molality} = \frac{4.27 \times 1000}{831.54} = 5.135 \text{ m}$$

A8. (d) : 7M solution of KOH means 7 moles of KOH in 1000 mL of solution.

Wt. of KOH = $7 \times 56 = 392$ g in 1000 mL

Since the solution is 40% by weight, it means that 40g of KOH is present in 100 g of solution.

392 g of KOH is present in $\frac{100}{40} \times 392 = 980$ g

$$\text{Density} = \frac{980}{1000} = 0.98 \text{ g mL}^{-1}$$

A9. (c) : Suppose x mL of 12M HCl to be mixed with $(1000-x)$ mL of 4 M HCl.

$$M_1V_1 + M_2V_2 = M_3V_3$$

$$12 \times x + 4(1000-x) = 6 \times 1000$$

$$12x + 4000 - 4x = 6000$$

$$8x = 2000$$

$$x = \frac{2000}{8} = 250 \text{ mL}$$

Volume of 12 M HCl required = 250 mL

Volume of 4 M HCl required = $1000 - 250 = 750$ mL

A10. (d) : Moles of $\text{H}_2\text{SO}_4 = \frac{80}{98}$ mol

Volume of solution = $\frac{100}{1.8} = 55.5$ mL

Molarity of solution = $\frac{80 \times 1000}{98 \times 55.5} = 14.7$ M

Now

$$M_1V_1 = M_2V_2$$

$$14.7 \times V_1 = 0.2 \times 1000$$

$$V_1 = \frac{0.2 \times 1000}{14.7} = 13.60 \text{ mL}$$

A11. (c) : Mole fraction of A = $1 - 0.2 = 0.8$

$$p_A^\circ \times x_A + p_B^\circ \times x_B = p$$

$$p_A^\circ = 70 \text{ torr}; p_B^\circ = ?; p = 84 \text{ torr}$$

$$70 \times 0.8 + p_B^\circ \times 0.2 = 84$$

$$p_B^\circ \times 0.2 = 84 - 56 = 28 \text{ torr}$$

$$p_B^\circ = \frac{28}{0.2} = 140 \text{ torr}$$

A12. (a) : $y_A = \frac{p_A^\circ \times x_A}{p_{\text{total}}}$

plot of y_A vs $1/p_{\text{total}}$ is linear

A13. (a) : According to Raoult's law

$$p_A = x_A p_A^\circ = \frac{1}{3} \times 45 = 15 \text{ torr}$$

$$p_B = x_B p_B^\circ = \frac{2}{3} \times 36 = 24 \text{ torr}$$

Total pressure = $15 + 24 = 39$ torr

The observed pressure is less than expected value and hence it shows negative deviation.

A15. (a) : The mole fraction of the gas in the solution,

$$x = \frac{p}{K_H} = \frac{1}{1000 \times 10^3} = 10^{-5} \text{ bar}$$

If n is the number of moles of gas in a solution of 1 L of water contains 55.5 mol, then

$$x = \frac{n}{n + 55.5} \approx \frac{n}{55.5} \approx 1.00 \times 10^{-5}$$

$$\therefore n = 55.5 \times 10^{-5} = 55.5 \times 10^{-2} \text{ millimoles.}$$

$$\text{or } = 0.55 \text{ millimoles}$$

A16. (a) :

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

$$p_{O_2} = 0.2 \text{ atm}, K_H = 4.34 \times 10^4 \text{ atm}$$

$$0.2 = 4.34 \times 10^4 \times x_{O_2}$$

$$x_{O_2} = \frac{0.2}{4.34 \times 10^4} = 4.61 \times 10^{-6}$$

$$\text{Now } x_{O_2} = \frac{n_{O_2}}{n_{O_2} + n_{H_2O}} = \frac{n_{O_2}}{n_{H_2O}}$$

$$\text{For 1 litre water, } n_{H_2O} = 55.55.$$

$$x_{O_2} = \frac{n_{O_2}}{n_{H_2O}} = \frac{n_{O_2}}{55.55} = 4.61 \times 10^{-6}$$

$$\text{or } n_{O_2} = 4.61 \times 10^{-6} \times 55.55 \\ = 2.56 \times 10^{-4} \text{ M.}$$

A17. (d) : For equimolar solution of X and Y

$$x_X = 0.5, x_Y = 0.5$$

$$p_X = 0.5 \times 200 = 100 \text{ torr}$$

$$p_Y = 0.5 \times 100 = 50 \text{ torr}$$

$$p_{\text{total}} = 100 + 50 = 150 \text{ torr}$$

Mole fraction of component X in vapour phase,

$$\gamma_X = \frac{100}{150} = 0.67$$

A18. (b) : In solution,

$$\text{if } x_A = x, x_B = 2x$$

$$p_A^\circ = p, p_B^\circ = 2p$$

$$p_A = x \times p, p_B = 2x \times 2p = 4xp$$

$$p_{\text{total}} = xp + 4xp = 5xp$$

Mole fraction in vapour phase,

$$y_B = \frac{p_B}{p_{\text{total}}} = \frac{4xp}{5xp} = 0.8$$

Competition File

A19. (a) : The vapour pressure of A is more than that of B. Therefore, boiling point of A is less than that of B i.e., $T_A^\circ < T_b^\circ$.

(a) represents the azeotrope of minimum boiling point.

A20. (b) : Let the mole fraction of P be x

Mole fraction of Q = $1 - x$

$$450x = 200(1-x)$$

$$650x = 200$$

$$x = \frac{200}{650} = 0.308$$

A21. (a) : $\Delta T_b = K_b \times m$

or $m = \frac{\Delta T_b}{K_b} = \frac{0.126}{2.52} = 0.05 \text{ m}$

A22. (a) : $\pi = cRT$

$$= 0.2 \times 0.082 \times 300 = 4.92 \text{ atm}$$

A23. (c) : The two solutions have same osmotic pressure,

$$\frac{5}{180} RT = \frac{2.5 RT}{M}$$

or $M = \frac{2.5}{5} \times 180 = 90 \text{ g mol}^{-1}$

A24. (d) : $\Delta T_b = \frac{K_b \times 1000 \times w_B}{w_A \times M_B}$

Since K_b and w_A are same for two solutions,

$$\frac{\Delta T_b}{\Delta T'_b} = \frac{w_B \times M_B'}{w_B' \times M_B}$$

$$\Delta T_b \text{ (urea)} = 0.25^\circ, w_B = 1\text{g}, M_B = 60$$

$$\Delta T'_b \text{ (glucose)} = ?, w_B = 3\text{g}, M_B' = 180$$

$$\therefore \frac{0.25}{\Delta T'_b} = \frac{1 \times 180}{3 \times 60}$$

or $\Delta T'_b = 0.25^\circ$

∴ Boiling point of solution = $100 + 0.25 = 100.25^\circ\text{C}$

A25. (a) : $\Delta T_b = 0.01^\circ, w_A = 100 \text{ g}, K_b = 0.50, M_B = 342$

$$\Delta T_b = \frac{K_b \times 1000 \times w_B}{w_A \times M_B}$$

or $w_B = \frac{\Delta T_b \times w_A \times M_B}{K_b \times 1000}$

$$= \frac{0.01 \times 100 \times 342}{0.50 \times 1000} = 0.684 \text{ g}$$

$$\text{No. of molecules} = \frac{0.684}{342} \times 6.023 \times 10^{23} \\ = 1.2 \times 10^{21}$$

A26. (a) : For first solution,

$$\frac{10}{p_A^\circ} = 0.2$$

For second solution

$$\frac{20}{p_A^\circ} = x_2$$

$$\therefore \frac{10}{20} = \frac{0.2}{x_2} \text{ or } x_2 = 0.4$$

$$\text{Mole fraction of solvent} = 1 - 0.4 = 0.6$$

A27. (d) : Molar mass of macro-molecules (proteins, colloids, etc.) can be determined with greater accuracy by finding osmotic pressure because the magnitude of this colligative property is comparatively large even in dilute solutions.

A28. (d) : $\Delta T_b = 100.512 - 100 = 0.512^\circ$

$$m = \frac{\Delta T_b}{K_b} = \frac{0.512}{0.512} = 1 \text{ m}$$

$$\Delta T_f = K_f \times m = 1.86 \times 1 = 1.86^\circ$$

$$\text{Freezing point of solution} = 0 - 1.86 = - 1.86^\circ \text{ C}$$

A29. (c) : A is solute and B is solvent.

$$p_B = p_B^\circ - \frac{10}{100} p_B^\circ = 0.9 p_B^\circ$$

$$M_B = \frac{30}{100} M_A = 0.30 M_A$$

$$\frac{p_B^\circ - 0.9 p_B^\circ}{p_B^\circ} = x_A = \frac{w_A \times M_B}{M_A \times w_B}$$

$$\frac{p_B^\circ - 0.9 p_B^\circ}{p_B^\circ} = \frac{w_A \times 0.30 M_A}{w_B \times M_A}$$

$$0.1 = \frac{w_A}{w_B} \times 0.3$$

or $\frac{w_B}{w_A} = \frac{0.3}{0.1} = 3.0$

A30. (c) : $\Delta T_b = \frac{K_b \times 1000 \times w_B}{w_A \times M_B}$

$$= \frac{0.52 \times 1000 \times 0.6}{100 \times 60} = 0.052$$

∴ Boiling point of solution : $373 + 0.052 = 373.052 \text{ K}$

A31. (a) : It depends upon the number of particles.

NaCl (2 particles, Na^+ , Cl^-), BaCl_2 (3 particles, Ba^{2+} , 2Cl^-) and glucose (non-electrolyte)

A32. (c) : The simple inspection of the question shows that (d) should be the correct choice because CaCl_2 will give 3 mol of ions for 1 mol of CaCl_2 dissolved (assuming it to be completely dissociated). However, in the given question, the amounts are given in grams. If we assume that m grams of all the substances are dissolved in 1000 g of solvent then,

Molal conc. of NaCl in solution

$$= \frac{m}{58.5} \times 2 = 0.034 \text{ m}$$

Molal conc. of ions of CaCl_2 in solution

$$= \frac{m}{11} \times 3 = 0.027 \text{ m}$$

∴ Molal conc. of NaCl in solution is more than molal conc. of CaCl_2 solution.

Competition File

A33. (d) : They give same number of ions



Initial	1 mol	-	-
After dissociation	$1-\alpha$	α	2α

$$\text{Total moles} = 1 - \alpha + \alpha + 2\alpha = 1 + 2\alpha$$

$$i = 1 + 2\alpha \text{ or } \alpha$$

$$= \frac{i-1}{2} = \frac{2.74-1}{2} = 0.87 \text{ or } 87\%.$$



Molal conc. in solution

$$\begin{aligned} &= m(1-0.20) + 0.20 m + 0.20 m \\ &= 1.20 m \end{aligned}$$

and

$$m = 0.2$$

$$\begin{aligned} \Delta T_f &= K_f \times m \\ &= 1.86 \times 1.20 (0.2) \\ &= 0.446 = 0.45 \end{aligned}$$

\therefore Freezing point of solution = -0.45°C .

A36. (b) : For two solutions A and B

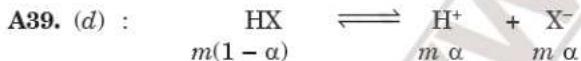
$$\frac{\pi(A)}{\pi(B)} = \frac{c(A)}{c(B)}$$

$$c(B) = 0.1 \text{ M}, c(A) = 0.05 \times 3 = 0.15 \text{ M}$$

$$\begin{aligned} \frac{\pi(A)}{p} &= \frac{0.15}{0.1} = 1.5 \\ \therefore \pi(A) &= 1.5 p \end{aligned}$$

A37. (c) : It is the ratio of number of particles in solution
Urea = 1, common salt = 2, sodium sulphate = 3

A38. (a) : Colligative properties are directly proportional to the number of particles. $\text{Al}_2(\text{SO}_4)_3$ will give 5 particles and therefore, depression in freezing point will be almost 5 times than for non-electrolyte.



$$\text{Total molality} = m(1-\alpha) + m\alpha + m\alpha = m(1+\alpha)$$

$$\Delta T_f = K_f m (1+\alpha) = 1.86 \times 0.2 \times (1+0.3) = 0.48^\circ$$

\therefore Freezing point of solution = -0.48°C .

A40. (c) : $\pi = i CRT$

$$(1) \pi(0.15 \text{ M urea}) = 1 \times 0.15 RT = 0.15 RT$$

$$(2) \pi(0.05 \text{ M CaCl}_2) = 3 \times 0.05 RT = 0.15 RT$$

$$(3) \pi(0.1 \text{ M MgSO}_4) = 2 \times 0.1 RT = 0.2 RT$$

$$(4) \pi(0.15 \text{ M glucose}) = 1 \times 0.15 RT = 0.15 RT$$

\therefore (1), (2) and (4) are isotonic.

A41. (b) : Mole fraction of component A in vapour phase

$$\begin{aligned} y_A &= \frac{p_A}{p_{\text{total}}} = \frac{p_A^\circ x_A}{p_A^\circ x_A + p_B^\circ x_B} = \frac{p_A^\circ x_A}{p_A^\circ x_A + p_B^\circ (1-x_A)} \\ &= \frac{p_A^\circ x_A}{x_A (p_A^\circ - p_B^\circ) + p_B^\circ} \end{aligned}$$

$$\frac{1}{y_A} = \frac{x_A (p_A^\circ - p_B^\circ) + p_B^\circ}{x_A p_A^\circ}$$

$$= \frac{p_A^\circ - p_B^\circ}{p_A^\circ} + \frac{p_B^\circ}{x_A p_A^\circ}$$

$$\therefore \text{Plot of } \frac{1}{y_A} \text{ against } \frac{1}{p_A^\circ} \text{ gives straight line with slope } = \frac{p_B^\circ}{p_A^\circ}$$

A42. (c) : For binary solution showing positive deviations during mixing, entropy increases to maximum and free energy decreases to minimum. $\Delta H_{\text{mix}} > 0$.

A43. (a) : Loss in weight of solution $\propto p_A = 2.5 \text{ g}$

$$\begin{aligned} \text{Loss in weight of solvent (water)} &\propto p_A^\circ - p_A = 0.06 \\ p_A^\circ &= (p_A^\circ - p_A) + p_A = 0.06 + 2.5 = 2.56 \text{ g} \end{aligned}$$

$$\frac{p_A^\circ - p_A}{p_A^\circ} = \frac{w_B \times M_A}{M_B \times w_A}$$

$$\frac{0.06}{2.56} = \frac{5 \times 18}{M_B \times 80}$$

$$M_B = \frac{5 \times 18 \times 2.56}{80 \times 0.06} = 48 \text{ g mol}^{-1}$$

B. mcq from Competitive Examinations

B1. (a) : 98% H_2SO_4 by mass means 98 g of H_2SO_4 are present in 100 g of solution

$$\text{Volume of solution} = \frac{100}{1.80} = 55.56 \text{ mL}$$

$$\text{Molarity of solution} = \frac{98/98}{55.56} \times 1000 = 18.0 \text{ M}$$

$$\begin{aligned} \text{Now, } M_1 V_1 &= M_2 V_2 \\ 18.0 \times V_1 &= 0.1 \times 1000 \\ V_1 &= \frac{0.1 \times 1000}{18.0} = 5.55 \text{ mL.} \end{aligned}$$

B2. (d) : $\Delta T_f = iK_f m (i = 1.20)$

$$= 1.2 \times 1.86 \times 0.5 = 1.12 \text{ K.}$$

B3. (d) : The number of moles produced by 1 mole of ionic compound

$$\Delta T_f = iK_f m, i = \Delta T_f / K_f m$$

$$\Delta T_f = 0 - (-0.00732)$$

$$= 0.00732 \text{ }^\circ\text{C}$$

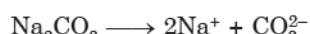
$$K_f = 1.86 \text{ }^\circ\text{C/m}$$

$$m = 0.0020$$

$$i = \frac{0.00732}{1.86 \times 0.0020}$$

$$= 1.968 \approx 2$$

B4. (d) : Molarity of solution = $\frac{25.3 \times 1000}{106 \times 250}$
 $= 0.955 \text{ M}$



$$[\text{Na}^+] = 2 \times 0.955 \text{ M} = 1.910 \text{ M}$$

$$[\text{CO}_3^{2-}] = 0.955 \text{ M.}$$

Competition File

B5. (b) : According to Raoult's law

$$p_s = p^\circ x_A \quad (x_A = \text{mole fraction of solvent})$$

On addition of water the mole fraction of water in the solution increases, therefore vapour pressure increases.

B6. (c) : $\Delta T_f = K_f m$

$$\text{Molality, } m = \frac{6.85/342}{100} \times 1000 = 0.2$$

$$\therefore \Delta T_f = 1.86 \times 0.2 = 0.372$$

$$\therefore \text{Freezing point of solution} = 0 - 0.372 \\ = -0.372^\circ\text{C.}$$

B7. (c) : For dissociation, $i > 1$

For association, $i < 1$

B8. (d) : According to Raoult's law

$$p = x_A p_A + x_B p_B$$

For binary solution, $x_A + x_B = 1$ or $x_B = 1 - x_A$

$$\begin{aligned} p &= x_A p_A + (1 - x_A) p_B \\ &= x_A p_A + p_B - x_A p_B \end{aligned}$$

$$\text{or} \quad = p_B + x_A(p_A - p_B)$$

B9. (d) : Moles of urea $= \frac{6.02 \times 10^{20}}{6.02 \times 10^{23}} = 1 \times 10^{-3}$

$$\text{Molarity} = \frac{1 \times 10^{-3}}{100} \times 1000 = 0.01 \text{ M}$$

B10. (d) : Molarity $= \frac{\text{Moles of HNO}_3}{\text{Volume of solution}} \times 1000$

$$2 = \frac{\text{Mass}/63}{250} \times 1000$$

$$\text{Mass of HNO}_3 = \frac{2 \times 250 \times 63}{1000} = 31.5 \text{ g}$$

$$\text{Mass of HNO}_3 \text{ required for 70% solution} = \frac{31.5 \times 100}{70} \\ = 45.0 \text{ g.}$$

B11. (c) : Largest freezing point depression is shown by solute having largest (same 0.1 m concentration) value of Van't Hoff factor (i).

$$\Delta T_f = i K_f m$$

$$i(\text{KCl}) = 2; i(\text{C}_6\text{H}_{12}\text{O}_6) = 1;$$

$$i[\text{Al}_2(\text{SO}_4)_3] = 5; i(\text{K}_2\text{SO}_4) = 3$$

B12. (c) : $\Delta T_b = i K_b m$

or $\Delta T_b \propto i$ for equimolar solution

$\therefore 'i'$ of solution X > $'i'$ of solution Y

This is possible if X undergoes dissociation.

B13. (b) : For $\text{Al}_2(\text{SO}_4)_3 \rightleftharpoons 2\text{Al}^{3+} + 3\text{SO}_4^{2-}$, $i = 5$

Now $\text{Al}(\text{NO}_3)_3 \rightarrow \text{Al}^{3+} + 3\text{NO}_3^-$; $i = 4$

$\text{K}_4[\text{Fe}(\text{CN})_6] \rightarrow 4\text{K}^+ + [\text{Fe}(\text{CN})_6]^{4-}$; $i = 5$

$\text{K}_2\text{SO}_4 \rightarrow 2\text{K}^+ + \text{SO}_4^{2-}$; $i = 3$

$\text{K}_3[\text{Fe}(\text{CN})_6] \rightarrow 3\text{K}^+ + [\text{Fe}(\text{CN})_6]^{3-}$; $i = 4$

B14. (b) : 1.00 m solution means that 1 mol of solute is present in 1000 g of water.

$$\text{Moles of solute} = 1$$

$$\text{Moles of water} = \frac{1000}{18} = 55.55$$

$$\text{Mole fraction of solute} = \frac{1}{1 + 55.55} = 0.0177$$

B15. (c) : Mole fraction of benzene (x_b) $= \frac{1}{2}$

$$\text{Mole fraction of toluene} (x_t) = \frac{1}{2}$$

$$\text{Vapour pressure of benzene} (p_b) = 12.8 \times \frac{1}{2} = 6.4 \text{ kPa}$$

$$\text{Vapour pressure of toluene} (p_t) = 3.85 \times \frac{1}{2} = 1.925 \text{ kPa}$$

$$\begin{aligned} \text{Total vapour pressure of solution} (p) &= 6.4 + 1.925 \\ &= 8.325 \text{ kPa} \end{aligned}$$

$$\text{Mole fraction of benzene in vapour phase} = \frac{6.4}{8.325} = 0.77$$

$$\text{Mole fraction of toluene in vapour phase} = \frac{1.925}{8.325} = 0.23$$

The vapour will contain higher percentage of benzene.

B16. (c) : $\frac{p^\circ - p_s}{p^\circ} \approx \frac{n_B}{n_A} = \frac{w_B \times M_A}{M_B \times w_A}$

$$\frac{760 - 732}{760} = \frac{6.5 \times 18}{M_B \times 100}$$

$$\frac{28}{760} = \frac{6.5 \times 18}{M_B \times 100}$$

$$M_B = \frac{6.5 \times 18 \times 760}{28 \times 100} = 31.76$$

$$\text{Now, } \Delta T_b = \frac{K_b \times w_B \times 1000}{w_A \times M_B} = \frac{0.52 \times 6.5 \times 1000}{100 \times 31.76} = 1.06$$

$$\therefore \text{Boiling point of solution} = 100 + 1.06 = 101.06^\circ\text{C} \\ \approx 101^\circ\text{C}$$

B18. (d) : $\text{Ba(OH)}_2 \rightleftharpoons \text{Ba}^{2+} + 2\text{OH}^-$
 $i = 3$

B19. (c) : The value of molal depression constant (K_f) is constant for a particular solvent. Therefore, it will be unchanged when molality of the dilute solution is doubled.

B21. (e) : $\pi = \frac{nRT}{V}$

$$16.4 = \frac{10}{180} \times 0.082 \times T \\ = \frac{10}{180} \times \frac{100}{1000}$$

$$\begin{aligned} \text{or} \quad T &= \frac{16.4 \times 100 \times 180}{10 \times 1000 \times 0.082} \\ &= 360 \text{ K} \end{aligned}$$

Competition File

B22. (a) : According to Raoult's law

$$p = p_A^\circ x_A + p_B^\circ x_B$$

$$p = 500 \text{ mm Hg}, x_A = \frac{1}{3}, x_B = \frac{2}{3}$$

$$500 = \frac{1}{3} p_A^\circ + \frac{2}{3} p_B^\circ$$

$$\text{or } 1500 = p_A^\circ + 2 p_B^\circ \quad \dots(i)$$

On adding 1 mole of B,

$$p = 525 \text{ mm Hg}, x_A = \frac{1}{4}, x_B = \frac{3}{4}$$

$$525 = \frac{1}{4} p_A^\circ + \frac{3}{4} p_B^\circ$$

$$\text{or } 2100 = p_A^\circ + 3 p_B^\circ \quad \dots(ii)$$

Subtracting (i) from (ii)

$$600 = p_B^\circ$$

$$\therefore 1500 = p_A^\circ + 2 \times 600$$

$$\therefore p_A^\circ = 300 \text{ mm Hg.}$$

B23. (d) : $p = \frac{1}{K} \times \text{Solubility}$

Solubility = K_p

$$= 0.5 \times 1.4 \times 10^{-3} \text{ mol/L}$$

$$= 0.5 \times 1.4 \times 10^{-3} \times 32 \text{ g/L}$$

$$= 22.4 \times 10^{-3} \text{ g/L}$$

Amount dissolved in 100 mL

$$\begin{aligned} &= \frac{22.4 \times 10^{-3}}{10} \\ &= 2.24 \times 10^{-3} \text{ g} = 2.24 \text{ mg.} \end{aligned}$$

B26. (b) : $\Delta T_f = i K_f m$

For NaCl, $\Delta T_f = 2, i = 2$

$$2 = 2 \times K_f \times m$$

For BaCl₂, $\Delta T_f = ?, i = 3$

$$\Delta T_f = 3 \times K_f \times m$$

Since K_f and m are same (equimolar solution)

$$\frac{\Delta T_f}{2} = \frac{3}{2} \text{ or } \Delta T_f = 3$$

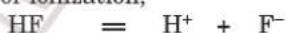
\therefore Freezing point of BaCl₂ solution = $0 - 3 = -3^\circ\text{C}$.

B27. (a) : $\Delta T_f = K_f \times m = 1.86 \times 0.100 = 0.186$

$$\Delta T_f (\text{observed}) = 0.197$$

$$i = \frac{0.197}{0.186} = 1.06$$

If α is the degree of ionization,



$$\text{Initial moles} \quad 1 \quad 0 \quad 0$$

$$\text{After ionization} \quad 1 - \alpha \quad \alpha \quad \alpha$$

Total number of moles after ionization

$$= 1 - \alpha + \alpha + \alpha = 1 + \alpha.$$

$$i = \frac{1 + \alpha}{1} = 1.06 \text{ or } \alpha = 0.6 \text{ or } 6\%$$

B28. (c) : According to Henry's law,

$$p(\text{N}_2) = x_{\text{H}} \times x(\text{N}_2)$$

$$0.76 \text{ atm} = 7.6 \times 10^4 \text{ atm} \times x(\text{N}_2)$$

$$\therefore x(\text{N}_2) = 1 \times 10^{-5}$$

B29. (c) : $\text{AB} \rightleftharpoons \text{A}^+ + \text{B}^-$

$$\text{Initial} \quad 1 \rightleftharpoons 0 \quad 0$$

$$\text{At equ.} \quad 1 - \alpha \quad \alpha \quad \alpha$$

$$\text{Total moles} = 1 - \alpha + \alpha + \alpha = 1 + \alpha$$

$$i = \frac{1 + \alpha}{1}$$

$$i = \frac{\text{Observed colligative property}}{\text{Normal colligative property}}$$

$$= \frac{0.81}{0.54} = 1.5$$

$$\therefore 1 + \alpha = 1.5$$

$$\text{or } \alpha = 0.5 \quad \text{or } 50\%$$

B30. (d) : $\text{AB} \rightleftharpoons \text{A}^+ + \text{B}^-$

$$\pi = i \frac{w_B}{M_B} \times \frac{RT}{V}$$

$$\text{or } \pi = 2 \times \frac{10}{200} \times \frac{0.0821 \times 300}{100/1000} = 24.6 \text{ atm}$$

B31. (a) : 2 M solution means that 2 moles of solute are present in 1000 mL of solution.

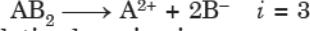
$$\text{Wt. of solution} = 1000 \times 1.2 = 1200 \text{ g}$$

$$\text{Wt. of solute} = 2 \times 100 = 200 \text{ g}$$

$$\text{Wt. of solvent} = 1200 - 200 = 1000 \text{ g}$$

$$\text{Molality} = \frac{2 \times 1000}{1000} = 2 \text{ m}$$

B33. (c) : For complete dissociation of electrolyte AB₂,



Relative lowering in vapour pressure,

$$\frac{p^\circ - p}{p^\circ} = i \times \frac{n_2}{n_1 + n_2}$$

$$\frac{100 - p}{100} = 3 \times \frac{1}{1 + 99}$$

$$100 - p = \frac{3 \times 100}{100} = 3$$

$$\therefore p = 100 - 3 = 97 \text{ mm Hg}$$

B34. (e) : $\pi = iCRT$

$$\text{or } \pi \propto i$$

Hence, KCl > CH₃COOH > Sucrose
(Strong electrolyte) (Weak acid) (Non electrolyte)

B35. (d) : For isotonic solution, C₁ = C₂

$$\frac{5.25}{M} = \frac{1.5}{60} \text{ or } M = 210 \text{ g mol}^{-1}$$

B36. (c) : 29% H₂SO₄ by mass means that 29 g H₂SO₄ are present in 100 g of the solution. If d g mL⁻¹ is the density of the solution, then

$$\text{Volume} = \frac{100}{d}$$

$$\text{Moles of H}_2\text{SO}_4 = \frac{29}{98}$$

$$\text{Molarity} = \frac{29/98 \times 1000}{100/d} = 3.60$$

$$\text{or } d = \frac{3.60 \times 100 \times 98}{1000 \times 29} = 1.22 \text{ g mL}^{-1}$$

B37. (a) : $p_{\text{total}} = p_A^\circ x_A + p_B^\circ x_B$

$$760 = 520 x_A + 1000 (1 - x_A)$$

Competition File

$$\begin{aligned} 760 &= 520 x_A + 1000 - 1000 x_A \\ 480 x_A &= 240 \\ x_A &= 0.5 \text{ or Moles of A = 50\%.} \end{aligned}$$

B38. (a) : Moles of glucose = $\frac{18}{180} = 0.1$

$$\text{Moles of water} = \frac{178.2}{18} = 9.9$$

$$\frac{p^{\circ} - p}{p^{\circ}} = \frac{0.1}{0.1 + 9.9}$$

$$\frac{17.5 - p}{17.5} = \frac{0.1}{10}$$

$$17.5 - p = \frac{0.1 \times 17.5}{10} = 0.175$$

$$p = 17.5 - 0.175$$

$$= 17.325 \text{ mm Hg}$$

B39. (c) : According to Raoult's law

$$p = p_Y^{\circ} x_X + p_X^{\circ} x_Y$$

$$\text{Initially, } p = 550 \text{ mm Hg, } x_X = \frac{1}{4}, \quad x_Y = \frac{3}{4}$$

$$550 = p_X^{\circ} \cdot \frac{1}{4} + p_Y^{\circ} \cdot \frac{3}{4} \quad \dots(i)$$

On adding 1 mole of Y

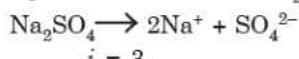
$$p = 560 \text{ mm Hg, } x_X = \frac{1}{5}, \quad x_Y = \frac{4}{5}$$

$$560 = p_X^{\circ} \cdot \frac{1}{5} + p_Y^{\circ} \cdot \frac{4}{5} \quad \dots(ii)$$

Solving eq. (i) and (ii), $p_X^{\circ} = 400 \text{ mm Hg}$

$$p_Y^{\circ} = 600 \text{ mm Hg.}$$

B40. (d) : For complete dissociation of Na_2SO_4



$$i = 3$$

$$m = \frac{0.01}{1} \times 1 = 0.01$$

$$\Delta T_f = iK_f m$$

$$= 3 \times 1.86 \times 0.01$$

$$\Delta T_f = 0.0558 \text{ K.}$$

B41. (c) :

$$n_h = \frac{25}{100} = 0.25$$

$$n_o = \frac{35}{114} = 0.307$$

$$x_h = \frac{0.25}{0.25 + 0.307} = 0.45$$

$$x_o = 1 - 0.45 = 0.55$$

$$p = x_h p_h^{\circ} + x_o p_o^{\circ}$$

$$= 0.45 \times 105 + 0.55 \times 45$$

$$= 47.25 + 24.75$$

$$= 72 \text{ k Pa.}$$

B42. (a) : 5.2 molal solution means that 5.2 moles of solute (CH_3OH) are present in 1000 g of water

$$\text{Moles of CH}_3\text{OH, } n_{\text{CH}_3\text{OH}} = 5.2$$

$$\text{Moles of water, } n_{\text{water}} = \frac{1000}{18} = 55.56$$

$$x_{\text{CH}_3\text{OH}} = \frac{5.2}{5.2 + 55.56} = 0.086.$$

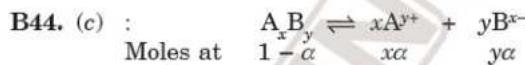
B43. (c) :

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

$$6 = \frac{1.86 \times 1000 \times w_2}{4000 \times 62}$$

$$w_2 = \frac{6 \times 4000 \times 62}{1.86 \times 1000} = 800 \text{ g.}$$

B44. (c) :



Moles at equi :

Total no. of moles = $1 - \alpha + x\alpha + y\alpha$

$$i = \frac{1 - \alpha + x\alpha + y\alpha}{1}$$

$$\therefore (i - 1) = \alpha(x + y - 1)$$

$$\therefore \alpha = \frac{i - 1}{(x + y - 1)}.$$

B45. (a) : Density of water at 25°C = 1 g/mL

Volume of water = $0.3 \times 1000 = 300 \text{ mL}$

Mass of water = $300 \times 1 = 300 \text{ g}$

$$\text{Moles of urea} = \frac{0.01}{60}$$

$$\text{Molality} = \frac{0.01 \times 1000}{60 \times 300} = 5.55 \times 10^{-4} \text{ m.}$$

B46. (b) :

$$\pi_1 = \pi_2$$

$$C_1 = C_2$$

$$\frac{5}{342} = \frac{1}{M}$$

$$\therefore M = \frac{342}{5} = 68.4.$$

B47. (c) : Mass of urea = 120 g

$$\text{Moles of urea} = \frac{120}{60} = 2$$

Mass of solution = $1000 + 120 = 1120 \text{ g}$

$$\text{Volume of solution} = \frac{1120}{1.15}$$

$$\text{Molarity} = \frac{2}{1120} \times 1000 = 2.05 \text{ M}$$

B48. (a) : $\Delta T_f = 0 - (-2.8) = 2.8$

Mass of solvent = 1 kg = 1000 g

$$\Delta T_f = \frac{K_f \times 1000 \times w_B}{w_A \times M_B}$$

$$2.8 = \frac{1.86 \times 1000 \times w_B}{1000 \times 62}$$

$$w_B = \frac{2.8 \times 1000 \times 62}{1.86 \times 1000} = 93.3 \text{ g.}$$

B49. (a) : $M_1 V_1 + M_2 V_2 = M_3 V_3$

$$0.5 \times 750 + 2 \times 250 = M_3 \times 1000$$

$$M_3 = \frac{375 + 500}{1000} = 0.875 \text{ M.}$$

B50. (b) : Osmotic pressure,

$$\pi = icRT$$

$$\pi [\text{C}_2\text{H}_5\text{OH}] = 1 \times 0.500 \text{ RT} = 0.5 \text{ RT}$$

$$\pi [\text{Mg}_3(\text{PO}_4)_2] = 5 \times 0.100 \text{ RT} = 0.5 \text{ RT}$$

$$\pi [\text{K Br}] = 2 \times 0.250 \text{ RT} = 0.5 \text{ RT}$$

Competition File

$$\pi [\text{Na}_3\text{PO}_4] = 4 \times 0.125 \text{ RT} = 0.5 \text{ RT}$$

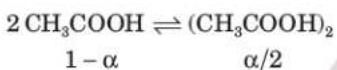
Therefore, all have some osmotic pressure.

$$\begin{aligned} \text{B51. (d)} : \quad \frac{p^\circ - p_s}{p^\circ} &= x_B = \frac{n_B}{n_A + n_B} \approx \frac{n_B}{n_A} \\ &\approx \frac{w_B \times M_A}{w_A \times M_B} \\ \frac{185 - 183}{185} &= \frac{1.2 \times 58}{100 \times M_2} \\ \therefore M_2 &= \frac{1.2 \times 58 \times 185}{2 \times 100} = 64.38 \approx 64 \end{aligned}$$

$$\text{B52. (c)} : \text{At } 1 \text{ atm, the vapour pressure of water, } p^\circ = 760 \text{ torr.} \\ w_B = 18 \text{ g; } M_B = 180 \text{ g mol}^{-1}; w_A = 178.2 \text{ g; } p_A = ?$$

$$\begin{aligned} \therefore \frac{p_A^\circ - p_A}{p_A^\circ} &= \frac{w_B M_A}{w_A M_B} \\ \text{or } \frac{760 - p_A}{760} &= \frac{18 \times 18}{178.2 \times 180} \\ \text{or } \frac{760 - p_A}{760} &= 0.0101 \\ \text{or } p_A &= 752.3 \text{ torr} \end{aligned}$$

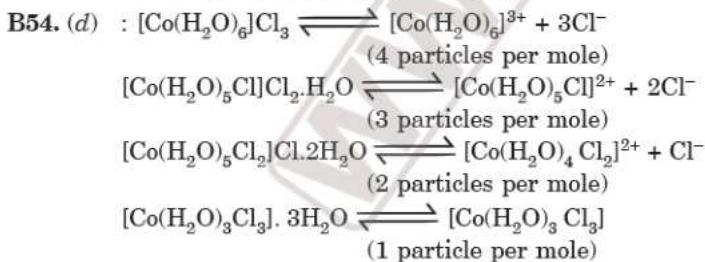
$$\begin{aligned} \text{B53. (d)} : \quad \Delta T_f &= \frac{i \times K_f \times 1000 \times w_B}{w_A \times M_B} \\ 0.45 &= \frac{i \times 5.12 \times 1000 \times 0.2}{20 \times 60} \\ i &= \frac{0.45 \times 20 \times 60}{5.12 \times 1000 \times 0.2} = 0.527 \end{aligned}$$



$$\text{Total number of moles} = 1 - \alpha + \alpha/2 = 1 - \alpha/2$$

$$\begin{aligned} i &= \frac{1 - \alpha/2}{1} = 0.527 \\ -\alpha/2 &= 0.527 - 1 = -0.473 \\ \alpha &= 0.473 \times 2 = 0.946 \end{aligned}$$

\therefore Percentage association = 94.6%



Now $\Delta T_f \propto i$ (no. of particles)

So, $[\text{Co}(\text{H}_2\text{O})_3\text{Cl}_3] \cdot 3\text{H}_2\text{O}$ will have minimum depression in freezing point and hence maximum freezing point.

$$\text{B55. (e)} : n_X = n_Y = 1 \text{ or } \frac{n_X}{n_Y} = 1$$

$$x_X = \frac{1}{1+1} = \frac{1}{2}, X_Y = \frac{1}{1+1} = \frac{1}{2}$$

$$p = p_X^\circ \times x_X + p_Y^\circ \times x_Y = 400 \text{ mm}$$

$$\text{or } \frac{1}{2} p_X^\circ + \frac{1}{2} p_Y^\circ = 400 \text{ mm} \quad \dots(i)$$

When $\frac{n_X'}{n_Y'} = \frac{1}{2}$ at the same temperature

$$x_{X'} = \frac{1}{3} \text{ and } x_{Y'} = \frac{2}{3}$$

$$\therefore p' = p_X^\circ \times x_{X'} + p_Y^\circ \times x_{Y'} = 350 \text{ mm}$$

$$\text{or } \frac{1}{3} p_X^\circ + \frac{2}{3} p_Y^\circ = 350 \text{ mm} \quad \dots(ii)$$

Solving (i) and (ii) $p_X^\circ = 550 \text{ mm}$, $p_Y^\circ = 250 \text{ mm}$.

$$\text{B56. (d)} : \left(\frac{6 \times 1000}{60 \times 100} \right)_{\text{urea}} = C_{\text{glucose}}$$

$$\therefore C_{\text{glucose}} = 1 \text{ M}$$

B57. (d) : Let w be the mass of sucrose dissolved in 100 g of water

$$\text{Molality, } m = \frac{w}{342} \times \frac{1000}{100}$$

$$= 0.0292 w$$

$$\begin{aligned} \Delta T_f &= K_f \times m \\ &= 1.86 \times 0.0292 w \end{aligned}$$

$$\begin{aligned} \Delta T_b &= K_b \times m \\ &= 0.51 \times 0.0292 w \end{aligned}$$

$$T_f = 0 - 1.86 \times 0.0292 w$$

$$T_b = 100 + 0.51 \times 0.0292 w$$

$$\begin{aligned} T_b - T_f &= 100 + 0.51 \times 0.0292 w \\ &- 0 + 1.86 \times 0.0292 w \\ &= 100 + 0.0692 w \end{aligned}$$

$$105 = 100 + 0.0692 w$$

$$0.0692 w = 5$$

$$\begin{aligned} w &= \frac{5}{0.0692} \\ &= 72.2 \approx 72 \text{ g.} \end{aligned}$$

$$\text{B58. (b)} : \frac{p_A^\circ - p_A}{p_A^\circ} = \frac{w_B M_A}{w_A M_B}$$

$$\therefore \frac{10}{100} = \frac{w_B \times 18}{180 \times 60}$$

$$\therefore w_B = \frac{10}{100} \times \frac{180 \times 60}{18} = 60 \text{ g}$$

$$\text{B59. (e)} : M_2 = \frac{1000 \times K_f \times w_2}{w_1 \times \Delta T_f}$$

$$\begin{aligned} \Delta T_f &= 0 - (-0.465) = 0.465 \\ &= \frac{1000 \times 1.86 \times 1.8}{40 \times 0.465} = 180 \end{aligned}$$

$$\text{Empirical formula mass} = 12 + 2 \times 1 + 16 = 30$$

$$\begin{aligned} n &= \frac{\text{Molecular mass}}{\text{Empirical formula mass}} \\ &= \frac{180}{30} = 6 \end{aligned}$$

\therefore Molecular formula $(\text{CH}_2\text{O})_6 = \text{C}_6\text{H}_{12}\text{O}_6$.

Competition File

B60. (a) : Molality of NaCl = $\frac{58.5/58.5}{1000} \times 1000 = 1 \text{ m}$
 (for water = 1000 mL = 1000 g
 ∵ density of water = 1)

Molality of glucose
 $= \frac{180/180}{1000} \times 1000 = 1 \text{ m}$

i for NaCl = 2, i for glucose = 1

$$\Delta T_b = i \times K_b \times m$$

∴ ΔT_b for NaCl > ΔT_b for glucose.

B61. (e) : $\frac{\Delta T_f}{\Delta T_b} = \frac{K_f}{K_b}$
 $\Delta T_f = 0 - (-0.186) = 0.186^\circ\text{C}$
 $\frac{0.186}{\Delta T_b} = \frac{1.86}{0.52}$
 or $\Delta T_b = \frac{0.186 \times 0.52}{1.86} = 0.052$

B62. (a) : $\frac{p_A^\circ - p_A}{p_A^\circ} = \frac{20}{100} = x_B$

Let mass of non volatile solute be added = x g

$$\frac{x}{40} = \frac{20}{100} \approx \frac{x}{40}$$

$$\frac{x}{40} + \frac{114}{114} = \frac{20}{100} \approx \frac{114}{114}$$

$$\text{or } \frac{x}{40} \times 1 = \frac{20}{100} \therefore x = \frac{40 \times 20}{100} = 8 \text{ g}$$

B63. (b) : Let vapour pressure of A be p so that vapour pressure of B is $2p$.

Total vapour pressure of solution.

$$= p \times \frac{1}{3} + 2p \times \frac{2}{3} = \frac{5p}{3}$$

In vapour phase, mole fraction of A is

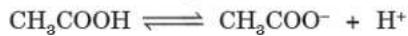
$$y_A = \frac{\frac{p}{5}}{\frac{5p}{3}} = 0.20$$

B64. (b) : $\Delta T_f = 0.19, m = 0.1, K_f = 1.86 \text{ Km}^{-1}$

$$\Delta T_f = i K_f \times m \text{ or } i = \frac{\Delta T_f}{K_f \times m}$$

$$= \frac{0.19}{1.86 \times 0.1} = 1.02$$

If α is the degree of dissociation,



Initial moles	1	0	0
After dissociation	$1 - \alpha$	α	α

Total number of moles after dissociation

$$= 1 - \alpha + \alpha + \alpha = 1 + \alpha.$$

$$i = \frac{1+\alpha}{1} = 1.02 \text{ or } \alpha = 0.02$$

$$K_a = c\alpha^2 = 0.1 \times (0.02)^2 = 4 \times 10^{-5}$$

B65. (a) : For equimolar solution, $x_b = x_t = 0.5$
 $p_b = x_b \times p_b^0 = 0.5 \times 100 = 50 \text{ mm}$
 $p_t = x_t \times p_t^0 = 0.5 \times 50 = 25 \text{ mm}$
 Total vapour pressure, $p_{\text{total}} = 50 + 25 = 75 \text{ mm}$
 Mole fraction of benzene in vapour phase,

$$y_b = \frac{p_b}{p_{\text{total}}} = \frac{50}{75} = 0.67$$

B66. (d) : $\Delta T_f = 0 - (-0.125) = 0.125^\circ\text{C}$
 $\Delta T_f = \frac{K_f \times w_B \times 1000}{M_B \times w_A}$
 $0.125 = \frac{1.86 \times 3 \times 1000}{111.6 \times w_A}$
 $w_A = 400 \text{ g}$

B67. (a) : As P undergoes association:
 $2P \rightleftharpoons P_2$
 If α is the degree of association
 Initial 1 0
 After association $1 - \alpha$ $\alpha/2$

$$\text{Total number of moles} = 1 - \alpha + \alpha/2 = 1 - \frac{\alpha}{2}$$

$$i = \frac{1 - \alpha/2}{1}$$

Now, observed molar mass,

$$M_B = \frac{1000 \times K_f \times w_B}{w_A \times \Delta T_f}$$

$$= \frac{1000 \times 1.86 \times 1.25}{50 \times 0.3} = 155$$

$$i = \frac{\text{Normal molar mass}}{\text{Observed molar mass}}$$

$$= \frac{94}{155} = 0.606$$

$$1 - \frac{\alpha}{2} = 0.606$$

$$-\frac{\alpha}{2} = 0.606 - 1$$

$$= -0.394$$

$$\alpha = 0.788 \text{ or } 78.8\%$$

$$\simeq 80\%$$

B68. (b) : $\text{K}_3[\text{Fe}(\text{CN})_6] \rightleftharpoons 3\text{K}^+ + [\text{Fe}(\text{CN})_6]^{3-}$

If α is the degree of dissociation, then

$$1 - \alpha \quad 3\alpha \quad \alpha$$

$$\text{Total moles after dissociation} = 1 - \alpha + 3\alpha + \alpha = 1 + 3\alpha$$

$$i = \frac{1 + 3\alpha}{1} = 3.333$$

$$3\alpha = 3.333 - 1 = 2.333$$

$$\alpha = \frac{2.333}{3} = 0.78 \text{ or } 78\%$$

B69. (d) : Molarity of 0.06% (w/v) aqueous solution of urea is molarity = $\frac{0.06}{60} \times \frac{1000}{100} = 0.01 \text{ M}$

Competition File

As osmotic pressure, $\pi = cRT$,

0.01 M solution of urea will be isotonic with 0.01 M glucose solution.

B71. (a) : For 0.01 M NaCl

$$\Delta T_f = 2 \times 0.01 K_f = 0.02 K_f \quad (\because i = 2)$$

For 0.01 M Na_2SO_4

$$\Delta T_f = 3 \times 0.01 K_f = 0.03 K_f \quad (\because i = 3)$$

For 0.1 M sucrose

$$\Delta T_f = 0.1 K_f \quad (\because i = 1)$$

For 0.1 M NaCl

$$\Delta T_f = 2 \times 0.1 K_f = 0.2 K_f \quad (\because i = 2)$$

Therefore, the depression in freezing point will be minimum in 0.01 M NaCl solution and hence its freezing point will be highest.

B72. (a) : $\Delta T_b = 373.413 - 373 = 0.413 \text{ K}$

$$K_b = 0.52$$

$$\Delta T_b = \frac{K_b \times 1000 \times w_B}{M_B \times w_A}$$

$$0.413 = \frac{0.52 \times 1000 \times 2.44}{M_B \times 75}$$

$$\therefore M_B = \frac{0.52 \times 1000 \times 2.44}{0.413 \times 75} = 40.96 \text{ g mol}^{-1}$$

B73. (c) : According to Raoult's law

$$p = p^\circ x_{\text{solute}} \quad \text{or} \quad p = p^\circ \left[\frac{n_2}{n_1 + n_2} \right]$$

B74. (b) : Mass of $\text{CCl}_4 = 500 \times 1.6 = 800 \text{ g}$

$$\text{Molecular mass of naphthalene } (\text{C}_{10}\text{H}_8) = 10 \times 12 + 8 \times 1 = 128$$

$$\therefore \text{Molality} = \frac{51.2 \times 1000}{128 \times 800} = 0.500 \text{ m}$$

$$\text{B75. (b)} : \Delta T_f = \frac{K_f \times w_B \times 1000}{w_A \times M_B} = \frac{2 \times 31 \times 1000}{500 \times 62} = 2 \text{ K}$$

Freezing point of solution = $273 - 2 = 271 \text{ K}$

B77. (a) : 3 M solution of methanol means that 3 moles of methanol are present in 1 L or 1000 cm^3 of solution.

$$\text{Mass of solution} = 1000 \times 0.9 = 900 \text{ g}$$

$$\text{Molar mass of methanol } \text{CH}_3\text{OH} = 12 + 4 \times 1 + 16 = 32 \text{ g mol}^{-1}$$

$$\text{Mass of methanol} = 3 \times 32 = 96 \text{ g}$$

$$\text{Mass of water} = 900 - 96 = 804 \text{ g}$$

$$\text{Molality} = \frac{3 \times 1000}{804} = 3.73 \text{ m}$$

B78. (e) : D-Fructose does not ionise and therefore, $i = 1$. It will have minimum depression in freezing point and hence highest freezing point.

B79. (c) : For isotonic solutions, $\pi_1 = \pi_2$

Where $\pi = icRT$

For the given solutions at the same temperature, T and R are constant

(a) For urea, $i = 1$, $\pi = 1 \times 0.01 \text{ RT}$

For NaCl, $i = 2$, $\pi = 2 \times 0.01 \text{ RT}$

(b) For NaCl, $i = 2$, $\pi = 2 \times 0.02 \text{ RT}$

For Na_2SO_4 , $i = 3$, $\pi = 3 \times 0.02 \text{ RT}$

(c) For NaCl, $i = 2$, $\pi = 2 \times 0.03 \text{ RT}$

For MgCl_2 , $i = 3$, $\pi = 3 \times 0.02 \text{ RT}$

$\therefore \pi(\text{NaCl}) = \pi(\text{MgCl}_2)$: isotonic

(d) For sucrose, $i = 1$, $\pi = 1 \times 0.01 \text{ RT}$

For glucose, $i = 1$, $\pi = 1 \times 0.02 \text{ RT}$

B80. (b) : Van't Hoff factor (i) expresses the extent of dissociation of solute in the solution.

$$\begin{aligned} \text{B81. (b)} : \Delta T_f &= i K_f m \\ &= \frac{i \times K_f \times w_B \times 1000}{M_B \times w_A} \end{aligned}$$

$$w_B = 61 \text{ g}, w_A = 100 \text{ g}, M_B = 122$$

$$2 = \frac{i \times 6 \times 61 \times 1000}{122 \times 1000}$$

$$i = \frac{2 \times 122 \times 1000}{6 \times 61 \times 1000} = 0.67$$

Benzoic acid dimerises as



$$\text{Initial} \quad 1 \quad 0$$

$$\text{after association} \quad 1-\alpha \quad \alpha/2$$

$$\text{Total moles after association} = 1 - \alpha + \alpha/2 = 1 - \alpha/2$$

$$i = \frac{1 - \alpha/2}{1} = 0.67$$

$$1 - \alpha/2 = 0.67$$

$$-\alpha/2 = 0.67 - 1 = -0.33$$

$$\alpha = 0.66 \text{ or } 66\%$$

B82. (a) : Molar mass = $59 + 14 \times 2 + 12 \times 16 + 12 \times 1 = 291$

$$\text{Moles of } \text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} = \frac{30}{291}$$

$$\text{Molarity} = \frac{30}{291 \times 4.3} = 0.023 \text{ M}$$

B83. (b) : $\Delta T_b = i K_b m$

Since concentration (m) is same,

$$\Delta T_b \propto i$$

$$i(\text{for NaOH}) = 2, i(\text{for } \text{Na}_2\text{SO}_4) = 3$$

$$i(\text{for } \text{NH}_4\text{NO}_3) = 2, i(\text{for } \text{KNO}_3) = 2$$

So, elevation in boiling point will be maximum for Na_2SO_4 solution and hence 1.0M Na_2SO_4 will have highest boiling point.

B85. (c) : Molality of NaCl solution = 1 m

Competition File

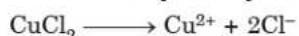
$i = 2$ for NaCl

$$\Delta T_b = i K_b m = 2 \times 0.52 \times 1 = 1.04$$

$$\text{Boiling point of solution} = 373.15 + 1.04 = 374.19\text{K}$$

B86. (a) :

$$\Delta T_b = i K_b \cdot m$$



$$m = \frac{13.44}{134.4} = 0.1 \text{ m}$$

Assuming 100% ionization, $i = 3$

$$\begin{aligned}\Delta T_b &= 3 \times 0.52 \times 0.1 \\ &= 0.156 \text{ or } \approx 0.16\end{aligned}$$

B87. (a) :

$$\Delta T_f = i K_f \times m$$

$$\begin{aligned}m &= \frac{20}{172} \times 1000 \\ &= \frac{50}{2} = i \times 1.72 \times 2.326 \\ i &= \frac{2}{1.72 \times 2.326} = 0.50.\end{aligned}$$

B88. (a) :

$$P_{N_2} = K_H \times x_{N_2} \text{ (dissolved)}$$

$$P_{N_2}^{\circ} = x_{N_2} \text{ (air)}$$

$$\text{Hence } x_{N_2} = \frac{x_{N_2} (\text{air}) \cdot p}{K_H} = \frac{0.8 \times 5}{10^5} = 4 \times 10^{-5}$$

$$\text{Moles of N}_2 \text{ in 1 mole of water} = 4 \times 10^{-5}$$

$$\text{Moles of N}_2 \text{ in 10 moles of water} = 4 \times 10^{-4}$$

B89. (c) : Total mass of solution = $1000 + 120 = 1120$ g

$$\text{Volume of solution} = \frac{1120}{1.15} = 973.9$$

$$\text{Molarity} = \frac{120/60}{973.9} \times 1000 = 2.05 \text{ M.}$$

B90. (a) : $K_3[\text{Fe}(\text{CN})_6] \rightleftharpoons 3\text{K}^+ + [\text{Fe}(\text{CN})_6]^{3-}$

Here $i = 4$

$$\begin{aligned}\Delta T_f &= \frac{i \times K_f \times 1000 \times w_2}{w_1 \times M_2} \\ &= \frac{4 \times 1.86 \times 1000 \times 0.1}{100 \times 329} = 2.3 \times 10^{-2}\end{aligned}$$

$$\begin{aligned}\text{Freezing point} &= 0 - 2.3 \times 10^{-2} \\ &= -2.3 \times 10^{-2} \text{ }^\circ\text{C.}\end{aligned}$$

B91. (a) :

$$\begin{aligned}M_B &= \frac{K_b \times 1000 \times w_B}{\Delta T_b \times w_A} \\ &= \frac{0.76 \times 1000 \times 2.5}{2 \times 100} = 9.5\end{aligned}$$

$$\frac{p_A^0 - p_A}{p_A^0} = x_2 = \frac{n_2}{n_1} \text{ (as } n_2 \ll n_1\text{)}$$

$$\frac{p_A^0 - p_A}{p_A^0} = \frac{w_2 / M_2}{w_1 / M_1}$$

$$\frac{760 - p_A}{760} = \frac{2.5 / 9.5}{100 / 18} = 0.0474$$

$$760 - p_A = 0.0474 \times 760 = 36$$

$$\text{or } p_A = 760 - 36 = 724 \text{ mm.}$$

B92. (b) : As T increases, the vapour pressure increases. Therefore, options (a) and (d) are not correct.

$$\begin{aligned}\Delta T_f &= \frac{K_f \times w_B \times 1000}{M_B \times w_A} \\ &= \frac{2 \times 34.5 \times 1000}{46 \times 500} = 3\text{K}\end{aligned}$$

$$\Delta T_f = 273(\text{K}) - T_f = 3\text{K}$$

$$\text{or } T_f = 273 - 3 = 270\text{K}$$

Therefore, option (b) is correct.

C. mcq with more than one correct answer

C4. (a, d) : When a solute is added to a solvent, its vapour pressure becomes less and during freezing, only solvent molecules solidify. Therefore, statements (a) and (d) are correct.

C7. (b, c, d) : For an ideal solution

- (i) $\Delta G < 0$ for mixing
- (ii) $\Delta S_{\text{system}} > 0$ because disorder increases
- (iii) $\Delta S_{\text{surv}} = 0$; no heat is exchanged in case of ideal solution
- (iv) $\Delta H_{\text{mixing}} = 0$

Therefore, statements b, c and d are correct.

C8. (a, c) : Osmotic pressure of urea solution,

$$C = 6 \text{ g}/100 \text{ cm}^3 = 60 \text{ g/L}$$

$$\pi (\text{urea}) = \frac{60}{60} \text{ RT} = 1\text{RT}$$

$$(a) C (\text{glucose}) = 18\text{g}/100 \text{ cm}^3 = 180 \text{ g/l}$$

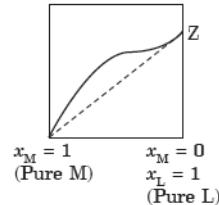
$$\pi (\text{glucose}) = \frac{180}{180} \text{ RT} = 1\text{RT}$$

$$(b) \pi (\text{BaCl}_2) = 3 \times 0.5 \text{ RT} = 1.5 \text{ RT} (i = 3)$$

$$(c) \pi (\text{Sucrose}) = 1\text{RT} = \text{RT}$$

$$(d) \pi (\text{acetic acid}) = 2 \times 1 \times \text{RT} = 2\text{RT} (i = 2)$$

C10. (a, d) :



There is positive deviation from ideal solution as indicated by graph above dotted line. Therefore, L-M interactions are less than L-L and M-M interactions. Point-Z represents vapour pressure of pure liquid L. At $x_L \rightarrow 1$, the solution is very dilute of M in L and is nearly ideal. Therefore, it obeys Raoult's law ($p_L = x_L p_L^0$).

D. mcq based on passage/comprehension

Passage I

D1. (d) : $p_A = x_A \times p_A^0$ or $32 = x_A \times 40$

$$\text{or } x_A = \frac{32}{40} = 0.8$$

Competition File

D3. (b) : For pure octane, $x = 0$

$$\therefore p(\text{sol}) = p(\text{octane}) = 35 + 65 \times 0 = 35 \text{ mm of Hg}$$

D4. (b) : For ideal solutions, $\Delta H_{\text{mixing}} = 0$

Passage II.

D5. (a) : Molarity of solution = $\frac{7.2/180}{100} \times 1000 = 0.4$

$$\Delta T_f = K_f \times m = 1.86 \times 0.4 = 0.744$$

$$\text{Freezing point of solution} = 0 - 0.744 = -0.744^\circ\text{C}$$

D6. (c) : $\frac{p_A^o - p_A}{p_A^o} = \frac{w_B/M_B}{w_A/M_A}$

$$\frac{0.024 - p_A}{0.024} = \frac{7.2/180}{100/18}$$

$$0.024 - p_A = 0.024 (0.0072) = 0.0001728$$

$$\therefore p_A = 0.024 - 0.0001728 = 0.0238 \text{ atm}$$

D7. (b) : $\Delta T_f = i K_f m$

$$0.744 = 2 \times 1.86 \times m$$

$$\text{or } m = 0.2$$

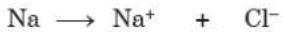
$$\text{Amount of NaCl to be dissolved} = 0.2 \times 58.5 = 11.7 \text{ g} \\ \text{in 1000 g or 1.179 g in 100 g.}$$

D8. (d) : Molality of solution = 0.2 m

$$\Delta T_f (\text{calculated}) = 1.86 \times 0.2 = 0.372$$

$$\Delta T_f (\text{observed}) = 0.698$$

$$\therefore i = \frac{0.698}{0.372} = 1.88$$



It α is the degree of dissociation,

$$\begin{array}{ccccccccc} 1-\alpha & & \alpha & & \alpha \\ \text{Total moles} & = & 1-\alpha+\alpha+\alpha & = & 1+\alpha \end{array}$$

$$i = \frac{1+\alpha}{1} = 1.88$$

$$\therefore \alpha = 0.88 \text{ or } 88\%$$

Passage III.

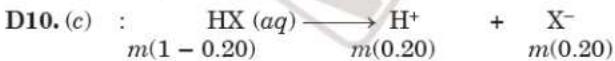
D9. (b) : For two solutions

$$\frac{\pi(A)}{\pi(B)} = \frac{c(A)}{c(B)}$$

$$c(B) = 0.1 \text{ M}, c(A) = 0.02 \times 4 = 0.08 \text{ M}$$

$$\frac{\pi(A)}{p} = \frac{0.08}{0.1} = 0.8$$

$$\therefore \pi(A) = 0.8p$$



$$m(1-0.20) \quad m(0.20) \quad m(0.20)$$

$$\text{Molal conc. of soln.} = m(1-0.20) + 0.20 m + 0.20 m \\ = 1.20 m$$

$$\Delta T_b = K_b \times m \\ = 0.52 \times 1.20 (0.2) = 0.1248$$

$$\text{Boiling point} = 100.1248^\circ\text{C}$$

D11. (b) : $\text{Na}_3\text{PO}_4 \rightleftharpoons 3\text{Na}^+ + \text{PO}_4^{3-}$ (produces 4 ions)

D13. (d) : NaCl sol. used should be isotonic with blood stream.

For NaCl, $i = 2$, $\pi = icRT$

$$\text{or } c = \frac{\pi}{iRT} = \frac{7.8 \text{ bar}}{2 \times 0.083 \text{ bar L K}^{-1} \text{ mol}^{-1} \times 310 \text{ K}} \\ = 0.15 \text{ mol L}^{-1}$$

Assertion Reason Type Questions

3. (e) : **Correct assertion** : 0.1 M glucose and 0.1 M urea solution have same freezing point.

Correct reason : Both have the same molar concentration of the solute and are non-associated non-electrolytes.

4. (a) : Reason is correct explanation of assertion.

5. (b) : Both assertion and reason are correct but reason is not correct explanation of assertion.

7. (c) : **Correct reason** : NaCl is an electrolyte and dissociates to give two ions. Therefore, osmotic pressure of 0.1 M NaCl is almost double than that of 0.1 M urea solution.

8. (e) : **Correct assertion** : Elevation in boiling point of two isotonic solutions is the same.

Correct reason : Elevation in boiling point depends upon the concentration of the solute.

10. (c) : **Correct reason** : Camphor has large K_f value and therefore, causes greater depression in freezing point.

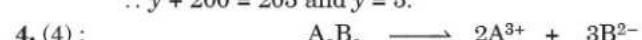
Integer type or Numerical Value Type Questions

1. (4) : Chloroform + diethylether, acetone + aniline, water + nitric acid, chloroform + nitric acid.

2. (8) : $2 : 1 : 4 : 6 \therefore x+z = 2+6 = 8$.

3. (5) : $p^\circ(\text{C}_2\text{H}_5\text{OH}) = 142, p^\circ(\text{CH}_3\text{OH}) = 126 + 142 = 268$

$$p_{\text{solution}} = 142 \times 0.5 + 268 \times 0.5 = 71 + 134 = 205 \\ \therefore y + 200 = 205 \text{ and } y = 5.$$



$$\begin{array}{cccccc} \text{Initial} & 1 & 0 & 0 \\ \text{After} & 1-0.75 & 1.5 & 2.25 \\ \text{ionization} & = 0.25 \end{array}$$

$$\text{Total moles after ionization} = 0.25 + 1.5 + 2.25 = 4$$

$$\therefore i = \frac{4}{1} = 4.$$

5. (5) : $\Delta T_f = iK_f \times m$

For 0.6 m $\text{Al}_2(\text{SO}_4)_3$,

$$\Delta T_f = 5 \times K_f \times 0.6 = 3.0 \text{ K} (i = 5)$$

For 0.2 m Na_2SO_4 ,

$$\Delta T_f = 3 \times K_f \times 0.2 = 0.6 \text{ K} (i = 3)$$

Thus, ΔT_f for $\text{Al}_2(\text{SO}_4)_3$ solution is 5 times that for Na_2SO_4 solution.

6. (8) : Mass of HCl = 29.2 g

$$\text{Volume of solution} = \frac{100 \text{ g}}{1.25} = 80 \text{ mL}$$

$$\text{Molarity of solution} = \frac{\text{g mol}}{\text{Volume of solution}} \times 1000$$

$$= \frac{29.2/36.5}{80} \times 1000 = 10 \text{ M}$$

Competition File

Using

$$M_1 V_1 = M_2 V_2$$

$$10 \times V_1 = 200 \times 0.4$$

$$\therefore V_1 = \frac{200 \times 0.4}{10} = 8$$



If α is the degree of dissociation

$$1 - \alpha \quad \alpha \quad 2\alpha$$

Total moles after dissociation

$$= 1 - \alpha + \alpha + 2\alpha = 1 + 2\alpha$$

$$i = \frac{1 + 2\alpha}{1} = 1 + 2\alpha \\ = 1 + 2 \times 0.5 = 2$$



Given: $m = 0.01$ molal, $\Delta T_f = 0 - (0.0558^\circ) = 0.0558^\circ C$

$$K_f = 1.86 \text{ K kg mol}^{-1}$$

$$i = \frac{\Delta T_f}{K_f \times m} = \frac{0.0558}{1.86 \times 0.01} = 3$$

Since three ions are produced by the complex, the molecular formula of the complex is $[Co(NH_3)_5Cl]Cl_2$. Thus, the number of Cl^- ions in the coordination sphere is only one.

9. (9) : Mole fraction of solute 0.1 means that 1 mol of solution has 0.1 mol of solute and 0.9 mol of solvent.

If M_1 is molar mass of solute and M_2 is molar mass of solvent, then

$$\text{Mass of solvent} = 0.9 \times M_2$$

$$\text{Molality} = \frac{0.1}{0.9 M_2} \times 1000$$

$$\text{Volume of solution} = \frac{\text{Mass of solute} + \text{Mass of solvent}}{\text{Density}}$$

$$= \frac{0.1 M_1 + 0.9 M_2}{2}$$

$$\text{Molarity} = \frac{0.1}{(0.1 M_1 + 0.9 M_2)} \times 2 \times 1000$$

Since molality = molarity

$$\frac{0.1}{0.9 M_2} \times 1000 = \frac{0.1 \times 2 \times 1000}{0.1 M_1 + 0.9 M_2}$$

$$\frac{100}{0.9 M_2} = \frac{200}{0.1 M_1 + 0.9 M_2}$$

$$10 M_1 + 90 M_2 = 180 M_2$$

$$10 M_1 = 90 M_2 \quad \therefore \frac{M_1}{M_2} = 9$$

10. (19.00) : Refer Advanced Level Problems; Problem. 6 (page 33)

11. (0.05) : Refer Advanced Level Problems; Problem 19 (page 64)

NCERT Exemplar Problems : MCQs Type-I

1. (a) : $\frac{p_A^\circ - p_A}{p_A^\circ} = x_B$ (mole fraction of solute)

2. (d) : Since the solution is cool to touch, the dissolution is endothermic. Therefore, high temperature will favour dissolution. Further, powdered sugar has large surface area and is favourable for dissolution.

3. (c) : At equilibrium, rate of dissolution = rate of crystallisation.

4. (b) : In super saturated solution, substance starts precipitating.

6. (b) : According to Henry's law, solubility of oxygen in blood and tissues of people is low because of low atmospheric pressure. However, temperature of human body remains constant.

7. (a) : Solution of methanol and acetone will show positive deviation because intermolecular H-bonds of methanol will break when acetone is dissolved in it. As a result, rate of evaporation increases.

9. (b) : 1.0 M Na_2SO_4 because $i = 3$.

11. (c) : 0.01 M glucose ($i = 1$) and 0.01 M $MgCl_2$ ($i = 3$)

Since $\Delta T_f = i K_f m$, $MgCl_2$ will show about three times depression in freezing point.

14. (a) : Depression in freezing point depends upon the nature of the solvent.

15. (b) : $KCl \rightarrow K^+ + Cl^-$ ($i = 2$), $NaCl \rightarrow Na^+ + Cl^-$ ($i = 2$),
 $K_2SO_4 \rightarrow 2K^+ + SO_4^{2-}$ ($i = 3$).

18. (b) : $p_A = K_H x_A$ or $K_H = \frac{p_A}{x_A}$

Hence, lower the value of x_A (solubility), greater will be the value of K_H at the same partial pressure and at the same temperature.

19. (b) : It represents reverse osmosis.

22. (a) : Vapour pressure decreases when a non-volatile solute is dissolved in it.

24. (d) : $M_1 V_1 = M_2 V_2$; $0.02 \times 4 = M_2 \times 5 \therefore M_2 = 0.016$

26. (c) : Lower the value of K_H , higher is the solubility.

NCERT Exemplar Problems : MCQs Type-II

28. (c, d) : They will form ideal solution and therefore $\Delta_{mix} H = 0$. The statement (c) and (d) are not true.

31. (c, d) : Isotonic solutions have same molar concentration and hence have same elevation in boiling point and same depression in freezing point.

32. (b, c) : These are non-ideal solutions, which form azeotropic mixtures and have same composition in liquid phase and vapour phase.

34. (a, d) : $p = p_A^\circ x_A + p_B^\circ x_B$

This shows that solutions (a) and (d) are possible depending upon which component is more volatile.



Unit Practice Test

for Board Examination

Time Allowed : 2 Hrs.

Maximum Marks : 35

1. State the condition resulting in reverse osmosis. (1)
2. 2.5 g each of two solutes X and Y (molar mass of X > Y) are dissolved separately in 50 g each of the same solvent. Which will show greater elevation in boiling point? (1)
3. Write the mathematical form of Raoult's law of relative lowering of vapour pressure. (1)
4. What is the value of van't Hoff factor for a compound which undergoes tetramerisation in an organic solvent ? (1)
5. How is the molarity of a solution different from its molality ? (1)
6. Why does solution of ethanol and cyclohexane show positive deviation from Raoult's law. (2)
7. Why do gases always tend to be less soluble in liquids as the temperature is raised? (2)
8. How many grams of potassium chloride should be added to 1.5 kg of water to lower its freezing point to -7.5°C ? K_f for water = $1.86^{\circ}\text{C kg mol}^{-1}$. (2)
9. Sodium chloride solution boils at higher temperature than water, while it freezes at lower temperature than water. Explain. (2)
10. Why is the freezing point depression of 0.1 M KCl solution nearly twice that of 0.1 M sucrose solution? (2)
11. A solution contains 0.8960 g of K_2SO_4 in 500 mL solution. Its osmotic pressure is found to be 0.690 atm at 27°C . Calculate the value of Van't Hoff factor. ($R = 0.082 \text{ L atm K}^{-1} \text{ mol}^{-1}$) (3)
12. State Raoult's law. How would you distinguish between ideal and non-ideal solutions with the help of the law. (3)
13. Why do we get sometimes abnormal molar masses of the substances by using colligative properties of the solutions? State the factors with suitable examples which bring abnormality in results. (3)
14. Two aqueous solutions containing respectively 7.5 g of urea (molar mass = 60) and 42.57 g of substance X in 100 g of water freeze at the same temperature. Calculate the molecular mass of X. (3)
15. 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. (3)
16. (a) What is relative lowering in vapour pressure? Show that relative lowering in vapour pressure is a colligative property. (1)

 (b) Calculate the normal freezing point of a sample of sea water containing 3.8 % NaCl and 0.12% MgCl_2 by mass. Given $K_f = 1.86 \text{ K kg mol}^{-1}$, molar mass of NaCl = 58.5 and MgCl_2 = 95 g mol $^{-1}$. (2)

 (c) Calculate the volume of 80% H_2SO_4 by weight (density = 1.8 g/mol) required to prepare 1L of 0.2 M solution. (2)

► To check your performance, see HINTS AND SOLUTIONS TO SOME QUESTIONS at the end of Part I of the book.

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