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**CHAPTER NO. 1**

**COLLIGATIVE PROPERTIES OF DILUTE SOLUTIONS**

 **PART - I**

**BY**

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**COLLIGATIVE PROPERTIES OF DILUTE SOLUTIONS**

**1.1 Introduction:**

In this chapter we will study about the solutions and their properties. Solutions are a solid is dissolved in a liquid. The solid is referred toas the solute and the liquid as the solvent.Properties of solutions that depend on the number of molecules present and not on the kind of molecules are called colligative properties. These properties include boiling point elevation, freezing point depression, and osmotic pressure. “A colligative property is a property of a solution that is dependent on the ratio between the total number of solute particles (in the solution) to the total number of solvent particles.”  The word “colligative” has been adapted or taken from the Latin word “colligatus” which translates to “bound together”. In the context of defining a solution, colligative properties help us understand how the properties of the solution are linked to the concentration of solute in the solution.

**1.2 Solution:**

solution is a homogeneous mixture of two or moresubstances on molecular level. The constituent of themixture present in a smaller amount is called the Solute

and the one present in a larger amount is called the Solvent.Composition of a solution can be described by expressing its concentration. The latter can be expressed either qualitatively or quantitatively. For example, qualitatively we can say that the solution is dilute (i.e., relatively very small quantity of solute) or it is concentrated (i.e., relatively very large quantity of solute). But in real life these kinds of description can add to lot of confusion and thus the need for a quantitative description of the solution.

**1.2.1. Concentration of a Solution:**

The concentration of a solution is defined as “The amountof solute present in a given amount of solution”.

Concentration is generally expressed as the quantity ofsolute in a unit volume of solution.

Concentration = Quantityof solute/Volumeof solution

A solution containing a relatively low concentration ofsolute is called **Dilute solution.** A solution of high concentrationis called **Concentrated solution.**

**1.2.2. Types of Solutions:**

The common solutions that we come across are those where the solute is a solid and the solvent

is a liquid. In fact, substance in any three states of matter (solid, liquid, gas) can act as solute or

solvent. Thus there are **seven types of solutions** whose examples are listed in Table 1.2.1.

**Table 1.2.1: Types and Examples of Solutions:**

|  |  |  |  |
| --- | --- | --- | --- |
| **Sr. No.** | **State of Solute**  | **State of Solvent**  | **Example** |
| 1 | Gas  | Gas  | Air |
| 2 | Gas | Liquid (Carbonated drinks) | Oxygen in water, CO2 in water |
| 3 | Gas | Solid | Adsorption of H2 by palladium |
| 4 | Liquid | Liquid | Alcohol in water |
| 5 | Liquid | Solid | Mercury in silver |
| 6 | Solid  | Liquid | Sugar, Salt |
| 7 | Solid | Solid (Steel) | Metal alloys : Carbon in iron |

There are several ways by which we can describe the concentration of the solution quantitatively.

**(i) Mass percentage (w/w):** The mass percentage of a component of a solution is defined as:

Mass % of a component = $\frac{Mass of the component in the solution }{Total mass of the solution} x 100$…..(1.1)

 For example, if a solution is described by 10% glucose in water by mass, it means that 10 g of glucose is dissolved in 90 g of water resulting in a 100 g solution. Concentration described by mass percentage is commonly used in industrial chemical applications. For example, commercial bleaching solution contains 3.62 mass percentage of sodium hypochlorite in water.

**(ii) Volume percentage (V/V):** The volume percentage is defined as:

Volume % of a component =$\frac{ Volume of the component }{Total volume of solution} x 100$……..(1.2)

For example, 10% ethanol solution in water means that 10 mL of ethanol is dissolved in water such that the total volume of the solution is 100 mL. Solutions containing liquids are commonly expressed in this unit. For example, a 35% (v/v) solution of ethylene glycol, an antifreeze, is used in cars for cooling the engine. At this concentration the antifreeze lowers the freezing point of water to 255.4K (–17.6°C).

**(iii) Mass by volume percentage (w/V):** Another unit which is commonly used in medicine and pharmacy is mass by volume percentage. It is the mass of solute dissolved in 100 mL of the solution.

**(iv) Parts per million:** When a solute is present in trace quantities, it is convenient to express concentration in parts per million (ppm) and is defined as: Parts per million =

= $\frac{Number of parts of the component}{Total number of parts of all components of the solution} x $10-6………..(1.3)

As in the case of percentage, concentration in parts per million can also be expressed as mass to mass, volume to volume and mass to volume. A litre of sea water (which weighs 1030 g) contains about 6 × 10–3 g of dissolved oxygen (O2 ). Such a small concentration is also expressed as 5.8 g per 106 g (5.8 ppm) of sea water. The concentration of pollutants in water or atmosphere is often expressed in terms of µg mL–1 or ppm.

**(v) Mole fraction:** Commonly used symbol for mole fraction is x and subscript used on the right-hand side of x denotes the component. It is defined as: Mole fraction of a component =

= $\frac{Number of moles of the component }{Total number of moles of all components}$……….(1.4)

For example, in a binary mixture, if the number of moles of A and B are nAand nB respectively, the mole fraction of A will be

xA= $\frac{nA}{nA+nB}$……………….(1.5)

For a solution containing i number of components, we have:

xi =$\frac{ni}{n1+n2+n3+…ni}$ = $\frac{ni}{∑ni}$ ………………(1.6)

It can be shown that in a given solution sum of all the mole fractions is unity, i.e. x1 + x2 + .................. + xi = 1

Mole fraction unit is very useful in relating some physical properties of solutions, say vapour pressure with the concentration of the solution and quite useful in describing the calculations involving gas mixtures.

**(vi) Molarity:** Molarity (M) is defined as number of moles of solute dissolved in one litre (or one cubic decimetre) of solution, =

Molarity (M) = $\frac{Moles of solute}{Volume of solution in litre }$ ……………...(1.7)

For example, 0.25 mol L–1 (or 0.25 M) solution of NaOH means that 0.25 mol of NaOH has been dissolved in one litre (or one cubic decimetre).

**(vii) Molality:** Molality (m) is defined as the number of moles of the solute per kilogram (kg) of the solvent and is expressed as:

Molality (m) =$\frac{Moles of solute}{Mass of solvent in kg }$ ……………… (1.8)

 For example, 1.00 mol kg–1 (or 1.00 m) solution of KCl means that 1 mol (74.5 g) of KCl is dissolved in 1 kg of water. Each method of expressing concentration of the solutions has its own merits and demerits. Mass %, ppm, mole fraction and molality are independent of temperature, whereas molarity is a function of temperature. This is because volume depends on temperature and the mass does not.

**(viii) Normality:** Normality of a solution (symbol N) is defined as number of equivalents of solute per litre of thesolution.

Normality (N) = $\frac{Equivalents of solute}{Volume of solution in litres}$ …………(1.9)

Thus, when 40g of NaOH (eq. wt. = 40) is dissolved in one litre of solvent, normality of the solutionis one and the solution is called 1*N* (one-normal).

**Problem 1.**Calculate the mole fraction of ethylene glycol (C2H6O2) in a solution containing 20% of C2H6O2 by mass.

**Solution:**

Assume that we have 100g of solution (one can start with any amount of solution because the results obtained will be the same).

Solution will contain 20g of ethylene glycol and 80g of water. Molar mass of C2H6O2 = 12 × 2 + 1 × 6 + 16 × 2 = 62gmol–1

Moles of C2H6O2=$\frac{20g}{62gmole-1}$ = 0.322 mol

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

Xglycerol = $\frac{Moles of C2H6O2 }{Moles of C2H6O2+Moles of H2 O}$

 = $\frac{0.322 Mol}{0.322 Mol+4.444 mol}$ = 0.068

Similarly, Xwater= $\frac{4.444 mol}{ 4.444 mol+ 0.322 Mol}$ = 0.932

Mole fraction of water can also be calculated as: 1 – 0.068 = 0.932

**Problem 2.** Calculate the molarity of a solution containing 5g of NaOH in 450 mL solution.

Solution: Moles of NaOH = $\frac{5g}{40g mol-1}$ = 0.125mol

Volume of the solution in litres = 450 mL / 1000 mL L-1 Using equation (1.8),

Molarity =$\frac{ 0.125mol× 1000 mLL-1}{450 mL }$ = 0.278 M

 = 0.278 mol L–1

= 0.278 mol dm–3

**Problem 3.** Calculate molality of 2.5g of ethanoic acid (CH3COOH) in 75g of benzene. Molar mass of C2H4O2 : 12 × 2 + 1 × 4 + 16 × 2 = 60gmol–1

Moles of C2H4O2 =$\frac{2.5g}{60gmol-1}$ = 0.0417 mol

Mass of benzene in kg = 75 g/1000 g kg–1 = 75 10–3 kg

Molality of C2H4O2= $\frac{Moles of C2H4O2}{kg of Benzene}$ = $\frac{0.0417 mol x1000g kg-1}{75g}$=

= 0.556 mol kg–1

**1.3 Colligative Properties:**

The properties that depend on the number of solute particles irrespective of their nature relative to the total number of particles present in the solution are called colligative properties.

There are four colligative properties:

1. Relative Lowering of vapour Pressure
2. Elevation in Boiling Point
3. Depression in freezing point
4. Osmotic pressure

**1.3.1 Relative Lowering of vapour Pressure:**

When a non-volatile solute is added to a solvent, the vapour pressure decreases.

The lowering of vapour pressure w.r.t. the vapour pressure of the pure solvent is called “Relative lowering in vapour pressure”.If *p* is the vapour pressure of the solvent and *ps*that of the solution, the lowering of vapour pressureis (*p* – *ps*). This lowering of vapour pressure relative to the vapour pressure of the pure solvent is

termed the **Relative lowering of Vapour pressure.** Thus,

Relative Lowering of Vapour Pressure =$\frac{P-Ps}{P}$

According to Raoult’s Law,The relative lowering of the vapour pressure of a dilute solution is equal to the mole fraction of the solute present in dilute solution.

Raoult’s Law can be expressed mathematically in the form:

$\frac{P-Ps}{P}$ = $\frac{n}{n+N}$

where *n* = number of moles or molecules of solute

*N* = number of moles or molecules of solvent.

**1.3.2 Derivation of Raoult’s Law:**

The vapour pressure of the pure solvent is caused by the number of molecules evaporating fromits surface. When a nonvolatile solute is dissolved in solution, the presence of solute molecules inthe surface blocks a fraction of the surface where no evaporation can take place.This causes the lowering of the vapour pressure. The vapour pressure of the solution is, therefore,determined by the number of molecules of the solvent present at any time in the surface which isproportional to the mole fraction. That is,

Ps $α\frac{N}{n+N}$

where *N* = moles of solvent and *n* = moles of solute.

Or Ps = k $\frac{N}{n+N}$……………(1.10)

*k* is proportionality factor.

In case of pure solvent *n* = 0 and hence,

Mole fraction of solvent = $\frac{N}{n+N}$ = $\frac{N}{0+N}$ = 1

Now from equation (1.10), the vapour pressure *p* = *k*

Therefore the equation (1.10) assumes the form

Ps = P $\frac{N}{n+N}$

$\frac{Ps}{p}$ = $\frac{N}{n+N}$

1- $\frac{Ps}{p}$ = 1- $\frac{N}{n+N}$

$\frac{P-Ps}{p}$ = $\frac{n}{n+N}$

This is Raoult’s Law.

**Problem1.**Calculate the vapour pressure lowering caused by the addition of 100 g ofsucrose (mol mass = 342) to 1000 g of water if the vapour pressure of pure water at 25°C is 23.8 mmHg.

**Solution:**

Using Raoult’s Law Equation

$\frac{P-Ps}{p}$ = $\frac{ΔP}{P}=\frac{n}{n+N}$…………….(1.10)

where Δ*P*= lowering of vapour pressure

*p* = vapour pressure of water = 23.8 mm Hg

*n* = moles of sucrose =100/342 = 0.292 moles

*N* = moles of water= 1000/18 = 55.5 moles

Substituting values in equation (1.10)

$$\frac{ΔP}{23.8}= \frac{0.292}{0.292+55.5}$$

Δ*P = 23.8 x* $\frac{0.292}{55.792}$ *=* 0.125mm

Thus the lowering of vapour pressure = **0.125 mm Hg**

**1.3.3 Ideal Solutions and Deviations from Raoult’s Law:**

A solution which obeys Raoult’s law strictly is called an **Ideal solution.** A solution which showsdeviations from Raoult’s law is called a **Nonideal** or **Real solution.**Suppose the molecules of the solvent and solute are represented by A and B respectively.

 Nowlet γAB be the attractive force between A and B, and γAA between A and A. IfγAB = γAAthe solution will show the same vapour pressure as predicted by Raoult’s law and it is an idealsolution.

However, ifγAB>γAAmolecule A will escape less readily and the vapour pressure will be less than that predicted byRaoult’s law (**Negative deviation**). On the other hand, ifγAB<γAA. A molecule will escape from the solution surface more readily and the vapour pressure of the solutionwill be higher than predicted by Raoult’s law **(Positive deviation).**In very dilute solutions of nonelectrolytes, the solvent and solute molecules are very much alikein both molecular size and molecular attractions. Thus such solutions tend to approach the idealbehaviour and obey Raoult’s law fairly accurately.

**1.4 Elevation of Boiling Point:**

When a liquid is heated, its vapour pressure rises and when it equals the atmospheric pressure,the liquid boils. The addition of a non volatile solute lowers the vapour pressure and consequentlyelevates the boiling point as the solution has to be heated to a higher temperature to make its vapourpressure become equal to atmospheric pressure. If *T*b is the boiling point of the solvent and *T* is the

boiling point of the solution, the difference in the boiling points (Δ*T*) is called the **elevation of boilingpoint.**

T – Tb = Δ*T*

The vapour pressure curves of the pure solvent, and solutions (1) and (2) with differentconcentrations of solute are shown in Fig.1.4.1.

1Atmosphere

A B C

D

E

Tb

T1

T2

P

P1

P2

Temperature K

Vapour Pressure

solvent

Solution 1

Solution 2

For dilute solutions, the curves *BD* and *CE* are parallel and straight lines approximately. Thereforefor similar triangles *ACE* and *ABD*, we have

$\frac{AB}{AC}= \frac{AD}{AE}$ or

$$\frac{T1-Tb}{T2-Tb}= \frac{p-p1}{p-p2}$$

where *p* – *p*1 and *p* – *p*2 are lowering of vapour pressure for solution 1 and solution 2 respectively.

Hence **the elevation of boiling point is directly proportional to the lowering of vapour pressure.**

Or ΔT $∝$P-Ps …………………….(1.11)

**1.4.1 Determination of Molecular Mass from Elevation of Boiling Point:**

Since *p* is constant for the same solvent at a fixed temperature, from (1) we can writeΔT $∝\frac{P-Ps}{P}$ …………………………(1.12)

But from Raoult’s Law for dilute solutions,

$\frac{P-Ps}{P} ∝\frac{wM}{Wm}$ ………………………………..(1.13)

Since *M* (mol mass of solvent) is constant, from (1.13)

$\frac{P-Ps}{P} ∝\frac{w}{Wm}$ ……………………………..(1.14)

From (1.12) and (1.14)

ΔT $∝ \frac{w}{M} x \frac{w}{Wm}$

ΔT = Kb x $\frac{w}{M} x \frac{1}{W}$ ………………………(1.15)

where *Kb*is a constant called **Boiling point constant or Ebulioscopic constant of molal elevationconstant.** If *w*/*m* = 1, *W* = 1, *Kb*= Δ*T*. Thus,

**Molal elevation constant may be defined as the boiling-point elevation produced when 1 mole ofsolute is dissolved in one kg (1000 g) of the solvent.**

If the mass of the solvent (*W*) is given in grams, it has to be converted into kilograms. Thus theexpression (1.15) assumes the form

ΔT = Kb x $\frac{w}{M} x\frac{1}{w/1000}$

Hence m = $\frac{1000 x Kb x w}{ΔT x W}$ ……………………..(1.16)

where Δ*T* = elevation of boiling point; *Kb*= molal elevation constant; *w* = mass of solute in grams;*m* = mol mass of solute; and *W* = mass of solvent in grams.