Dilute solutions: Colligative properties (Part 1)

CHE-CC 204(sem II)

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Dilute solutions

- When the amount of component relative to the other component in a solution is small i.e. the conc. of one of the component is small in the solution, the solution is termed as ‘dilute solution’.

- The dilute solution of non volatile solute exhibits properties which depends only on the conc. of the solute, and do not depend upon its nature.

- These properties are collectively called colligative properties. In general, for dilute solutions, colligative properties is proportional to the mole fraction of the solute.

COLLIGATIVE PROPERTIES

COLLIGATIVE PROPERTIES Depend on the number of solute particles in solution but not on the identity of the solute.

There are four type of colligative properties:

- Vapor pressure lowering
- Boiling point elevation
- Freezing point depression
- Osmotic pressure

EXAMPLES

0.5 m solution of $Pb(NO_3)_2$

0.5 m Pb^{2+} and 1.0 m NO^{3-} $\rightarrow$ 1.5 m total ions

0.5 m $HC_2H_3O_2$(acetic acid)

$HC_2H_3O_2 \leftrightarrow H^+ + C_2H_3O_2^-$

solution is between 0 and 1.0 m in total ions

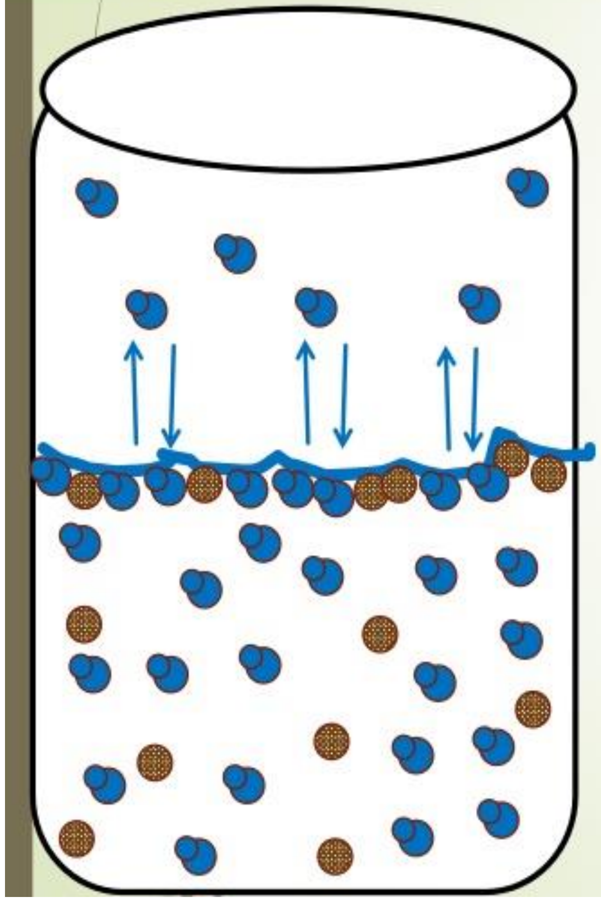
solution is between 0.5 and 1.0 m in all species

Vapor pressure lowering

Raoult's Law $$\underset{\text{vapor pressure of solution}}{P_A} = \underset{\text{mole fraction of solvent}}{X_A}\ \underset{\text{vapor pressure pure solvent}}{P_A^{o}}$$

- vapor pressure lowering is a colligative property — its depends on the conc. but not on the nature of the solute

Raoult's Law



The vapor pressure of the solution depends on the **mole fraction of the solvent**.

$$\chi_{\mathbf{solvent}} = \frac{\text{moles } \mathbf{solvent}}{\text{moles solute} + \text{moles solvent}}$$

Liquid molecule

Nonvolatile solute

RAOULT’S LAW EXAMPLE 1

- Calculate total vapor pressure of a liquid at room temperature that is composed of a mixture of benzene and toluene. The mole fractions of benzene and toluene are

  X_{ben} = 0.33and X_{tol} = 0.67

  Benzene; P^0_{Ben} = 75 torr

  Toluene ; P^0_{tol} = 22 torr

  $P_A = X_A P_A^O$

Determination of Molecular weight of non volatile substance by lowering of vapor pressure .

- $p \,\alpha\, x_2$
- $p = p^o x_1$___________________(1)

For binary solution $X_1 + X_2 = 1$

$$X_2 = 1 - X_1$$

$$X_1 = 1 - X_2 \text{ \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ } (2)$$

Substitute the value X_1 in equation (1)

$$p = p^o x_1$$

$$p = p^o (1 - X_2)$$

$$p = p^o - p^o X_2$$

$$X_2 = (p^o - p)/p^o \text{ \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ } (3)$$

mole fraction of solute is known as relative lowering of vapor pressure . This is Raoult's Law.

Determination of Molecular weight of non volatile substance by lowering of vapor pressure (contd).

- Relative lowering of vapor pressure is a colligative properties as its depend only on the mole fraction of the solute.
- Mole fraction of the solute $x_2 = n_2 /(n_1 + n_2)$ ___________(4)

Where n_2 = number of moles of the solute

n_1 = number of moles of the solvent

$n_2 = W_2/M_2 \quad n_1 = W_1/M_1$

where W_2 = weight of the solute of the molecular weight M_2

W_1 = weight of the solvent of the molecular weight M_1

From equation (3) and (4),

$$(p^o - p)/p^o = n_2 /(n_1 + n_2)$$

$$(p^o - p)/p^o = (W_2/M_2) / (W_1/M_1 + W_2/M_2) \text{\_\_\_\_\_\_\_\_\_\_(5)}$$

Since the solution is very dilute , therefore

$n_2 << n_1$ and $n_1 + n_2 = n_1$

$$(p^o - p)/p^o = W_2M_1 / W_1M_2$$

$M_2 = (W_2/W_1) . (p^o / (p^o - p)) . M_1$ __________ (6)

Henry’s Law

- Henry’s Law : The most commonly used form of Henry’s law states “the partial pressure (p) of the gas in vapour phase is proportional to the mole fraction (x) of the gas in the solution” and is expressed as

  $p = k_H . x$

  where k_H is proportionality constant known as Henry law constant

- Greater the value of k_H, higher the solubility of the gas. The value of k_H decreases with increase in the temperature. Thus, aquatic species are more comfortable in cold water [more dissolved O_2] rather than Warm water.

Applications OF Henry's Law

1. In manufacture of soft drinks and soda water, CO_2 is passed at high pressure to increase its solubility.
2. For deep divers, O_2 diluted with less soluble Helium gas is used as breathing gas and it minimizes the painful effect due to higher solubility of nitrogen gas in blood.
3. At high altitudes, the partial pressure of O_2 is less then that at the ground level. This leads to low concentrations of O_2 in the blood of climbers which causes Hypoxia.

Measurement of lowering of vapor pressure

1. Barometric Method : This method was neither practical nor accurate as the lowering of vapor pressure is almost negligible.

2. Manometric Method : The vapor pressure of a liquid or solution can be fairly measured with the help of a manometer.

   Let us assume a bulb is charged with the liquid or solution. The air in the connecting tube of the instrument is then removed with a vacuum pump. With the stopcock being closed, the pressure is only due to vapor evaporating from the solution or liquid. This method can be applied to aqueous solutions. The manometric liquid used can be either mercury or n-butyl phthalate which has low density and low volatility.

3. Ostwald and Walker’s Dynamic Method (Gas Saturation Method)

Ostwald and Walker’s Dynamic Method (Gas Saturation Method)

The apparatus used consist of two sets of bulbs:

(a) Set A contains the solution

(b) Set B contains the solvent

The weight of each set is calculated separately. A slow stream of dry air is then removed by a suction pump through the two sets of bulbs. At the end of the operation, the weight of these sets is measured. From the weight loss in each of the two sets, the lowering of vapor pressure is measured. Here the temperature of the air, the solution, and the solvent must be kept constant all throughout.

As the air bubbles through set A reaches saturation up to the vapor pressure p_s of the solution and then up to vapor pressure p of the solvent in set B, the amount of solvent taken up in set A becomes proportional to p_s and the amount taken up in set B becomes proportional to $(p- p_s)$.

Ostwald and Walker's Dynamic Method (Gas Saturation Method) (contd.)

If w1 and w2 be the loss of weight in set A and set B respectively,

$w1 \propto p_s$ ________(1)

$w2 \propto (p - p_s)$ ______(2)

Adding these, we have

$w1 + w2 \propto (p_s + p - p_s)$

$w1 + w2 \propto p$ _______(3)

Dividing (2) by (3), we can write

$(p - p_s)/p = w2/(w1+w2)$

Knowing the loss of mass in set B (w2) and the net loss of mass in the two sets (w1+w2), we can find the relative lowering of vapor pressure.

Ostwald and Walker’s Dynamic Method (Gas Saturation Method) (contd.)

Example:

If we use water as the solvent, a set of Calcium chloride tubes (or a set of bulbs containing conc. H_2SO_4) is linked to the end of the apparatus to capture the escaping water vapor. Therefore, the gain in mass of $caCl_2$ tubes will be equal to (w_1+w_2), the total loss of mass in sets A and B.