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SOLUTIONS OF NON-ELECTROLYTES:

- Materials may be mixed together to form true soln, colloidal soln, or coarse dispersion.
- **A true soln** is defined as a mixture of two or more components that form a homogeneous molecular dispersion. i.e. one phase system
- The term **phase** defined as a distinct homogeneous part of a system separated by definite boundaries from other parts of the system.
- **Coarse dispersions** it may be distributed as small particles throughout the system, such as oil droplets in an emulsion or solid particles in suspension.
- the diameter of the particles in emulsions and suspensions for the most part being larger than 0.1 μm. (1000A or 10^{-5}cm)

- **A colloidal dispersion** represents a system having a particle size intermediate between that of a true soln and a coarse dispersion, roughly 10 to 5000 A.
- A colloidal dispersion may be considered as a two phase system (heterogeneous) under certain conditions and as a one phase system (homogeneous) in others.
- A colloidal dispersion of silver proteinate in water is heterogeneous since it consists of distinct particles constituting a separate phase.
- A colloidal dispersion of acacia or sodium carboxymethylcellulose in water, on the other hand, is homogeneous.
- A soln composed of only two substances is known as a **binary solution**, and the components or constituents are the **solvent** and the **solute**.

- The constituent present in the **greater** amount in a binary soln is the **solvent** and the constituent in the **lesser** amount as the **solute**.
- When a solid is dissolved in a liquid the liquid is usually taken as the solvent and the solid as the solute.
- When water is one of the constituents of a liquid mixture, it is usually considered the solvent.
- Mixtures of liquids that are miscible in all proportions, such as alcohol and water, it is less meaningful to classify the constituents as solute and solvent.

Properties of solutions:

- The physical properties of substances may be classified as: 1-colligative, 2- additive, and 3- constitutive.
- **Colligative properties** depend mainly on the number of particles in a soln.
- It includes: **osmotic pressure, vapor pressure lowering, freezing point depression, and boiling point elevation**.
- The values of the colligative properties are approximately the same for equal concs., of different non-electrolytes regardless of chemical nature of the constituents.

- **Additive properties** depend on the total contribution of the atoms in the molecules or on the sum of the properties of the constituents in a solution.
- An example of an additive property of compound is the **molecular weight**, i.e., the sum of the masses of the constituent atoms.
- **Constitutive properties** depend on the arrangement and to a lesser extent on the number and kind of atoms within a molecule.
- Many physical properties may be partly additive and partly constitutive.
- The refraction of light, electric properties, surface and interfacial characteristics, and the solubility of drugs are at least in part constitutive and in part additive properties.

Types of Solutions:

- A solution may be classified according to:
- **1- The states in which the solute and solvent occur,** and since three states of matter (gas, liquid, and solid) exist, nine types of homogeneous mixtures of solute and solvent are possible.
- These types, together with some examples, are included in Table (1)

- **2- The degree of ionization: (two main classes)**
- The solutes (gases, liquids or solids) are divided into two main classes, **non-electrolytes** and **electrolytes**

Table(1): Types of solutions

Solute	Solvent	Example
Gas	Gas	Air
Liquid	Gas	Water in oxygen
Solid	Gas	Iodine vapor in air
Gas	Liquid	Carbonated water
Liquid	Liquid	Alcohol in water
Solid	Liquid	Aqueous sodium chloride solution
Gas	Solid	Hydrogen in palladium
Liquid	Solid	Mineral oil in paraffin
Solid	Solid	Gold-silver mixture, mixture of alums

Non-electrolytes:

- **Non-electrolytes** are substances that do not yield ions when dissolved in water and do not conduct an electric current through the soln.
- Examples of non-electrolytes are sucrose, glycerin, naphthalene, and urea.
- The colligative properties of solns of non-electrolytes are fairly regular.
- A 0.1 molar soln of a non-electrolyte produces approximately the same colligative effect as any other non-electrolytic soln of equal conc.
- **Electrolytes** are substances that form ions in soln, conduct the electric current, and show apparent anomalous (different) colligative properties.
- Examples of electrolytes are hydrochloric acid, sodium sulfate, ephedrine, and Phenobarbital.

SOLUTIONS OF NON-ELECTROLYTES: IDEAL AND REAL SOLUTIONS:

- **Ideal soln** is **defined** as one in which there is no change in the properties of the components, other than dilution, when they are mixed to form the solution.
- **Properties:** 1- No heat is evolved or absorbed during the mixing process.

2- Final volume of the soln represents an additive property of the individual constituents. i.e., there is no shrinkage or expansion when the substances are mixed.

3-The constitutive properties, e.g., the vapor pressure, refractive index, surface tension, and viscosity of the soln, are the weighted averages of the properties of the pure individual constituents.

- Ideal solns are **formed** by mixing substances with similar properties.
- **For example**, when 100 ml of methanol are mixed with 100 ml of ethanol, the final volume of the solution is 200 ml, and **no** heat is evolved or absorbed. The soln is nearly ideal.
- Any constitutive property is an average between the 2 solns.
- **Real or non-ideal solns** When 100 ml of sulfuric acid are combined with 100 ml of water,
  a- The volume of the soln is about 180 ml at room temp, and **b-** mixing is attended by evolution of heat.
- Some solns are quite ideal in moderate conc. while others approach ideality only under extreme dilution.

- To summarize, **ideality in gas** means <u>complete absence of attractive forces</u>.

- **Ideality in solution** means <u>complete uniformity of attractive forces.</u>

- If a mixture soln of A and B molecules, is considered ideal when the forces between A and A, B and B, and A and B are all of the same order.

- **Cohesive forces = adhesive forces**

Escaping Tendency:

- If one body is heated to a higher temp. than the other, heat will flow "downhill" from the hotter to the colder body until both bodies regain in thermal equilibrium.
- This process is called **escaping tendency,** and saying that the hotter body has a greater escaping tendency than in the colder one.
- **1- Temp** is a quantitative measure of the escaping tendency of heat. and
- **At thermal equilibrium**, when both bodies finally have the same temp, the escaping tendency of each constituent is the same in all parts of the system.
- **2- Free energy** is a quantitative measure of the escaping tendencies of substances undergoing physical and chemical transformations.
- For a pure substance, the **free energy per mole** or **molar free energy** provides a measure of escaping tendency.

- **<u>Example</u>**

- The free energy of a mole of ice is **greater** than that of liquid water at 1 atm above 0°C and is spontaneously converted into water,
- Since $\Delta F = F\ liq - F\ ice < 0$
- At 0°C, at which temp the system is in equilibrium, the molar free energies of ice and water are identical and $\Delta F = 0$.

- In terms of escaping tendencies, we can say that above 0°C, escaping tendency of ice is greater than escaping tendency of liquid water, at equilibrium, the escaping tendencies of water in both phases are identical.

Ideal Solutions and Raoult's Law:

- 3- **Vapor pressure** of a soln is important property as it serves as a quantitative expression of escaping tendency.
- **Raoult's Law:** for an ideal soln, **the partial vapor pressure of each volatile constituent is equal to the vapor pressure of the pure constituent multiplied by its mole fraction in the soln.**
- Thus, for two constituents **A** and **B**:

$$P_A = p_A°X_A \qquad\qquad P_B = p_B°x_B$$

in which P_A and P_B are the partial vapor pressures of the constituents over the soln when the mole fraction concentrations are X_A and X_B respectively.

$p_A°$ and $p_B°$ are the vapor pressures of the pure components.

- **For example**, if the vapor pressure of ethylene chloride in the pure state is 236 mmHg at 50°C, then in a soln consisting of a mole fraction of 0.4 ethylene chloride and 0.6 benzene, the partial vapor pressure of ethylene chloride is 40% of 236 or 94.4 mm.
- Thus, in an ideal soln, when liquid **A** is mixed with liquid **B**, the vapor pressure of **A** is reduced by dilution with **B** in a manner depending on the mole fractions of **A** and **B** present in the final soln.
- This will decrease the escaping tendency of each constituent, leading to a reduction in the rate of escape of the molecules of **A** and **B** from the surface of the liquid.

- **Example 1 :**
  What is the partial vapor pressure of benzene and of ethylene chloride in a soln at a mole fraction of benzene of 0.6? The vapor pressure of pure benzene at 50°C is 268 mm, and the corresponding pa° for ethylene chloride is 236mm.

 $P_B = 268 \times 0.6 = 160.8$ mm
  $P_A = 236 \times 0.4 = 94.4$ mm

- The total pressure is the sum of the partial pressures of all the constituents.
- In **Example 1**, the total vapor pressure P is calculated as follows:
  $P = P_A + P_B = 160.8 + 94,4 = 255.2$ mm.

The vapor pressure-composition curve for the binary system benzene and ethylene chloride at 50°C is shown in **Fig. (1).**

The three curves represent the partial pressures of ethylene chloride, the partial pressure of benzene, and the total pressure of the soln as a function of the mole fraction of the constituents.
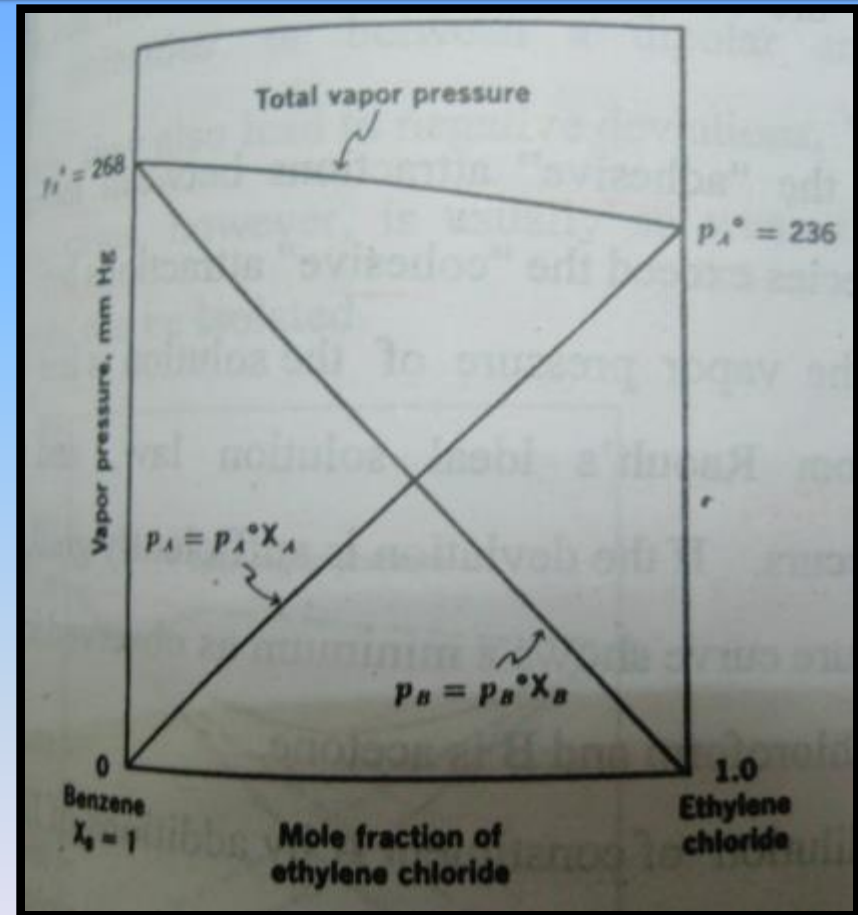

Fig.(1): Vapor pressure-composition curve for an ideal binary system.

Real Solutions:

- Ideality in solns means complete uniformity of attractive forces.
- **A-A** or **B-B** "cohesive forces", **A-B** "adhesive forces"
- If cohesive force = adhesive forces **ideal soln**.
- If cohesive forces ≠ adhesive **Real or true soln.**

- **Real or non-ideal solns:**
- Have different attractive forces.
- Adhesive attraction may exceed cohesive attraction.
- Cohesive attraction may exceed adhesive attraction.
- These solutions don't adhere to Raoult's law throughout the entire range of composition.
- Two types of deviation from Raout's law are recognized: **negative deviation** and **positive deviation**.

Negative deviation:

- When the "adhesive" attractions between different molecules exceed the "cohesive" attractions between like molecules,
- The vapor pressure of the soln is less than that expected from Raoult's ideal soln law, and **negative deviation occurs**.
- If the deviation is sufficiently great, the total vapor pressure curve shows a **minimum** as observed in **(Fig. 2)** where A is **chloroform** and B is **acetone.**
- The dilution of constituent A by additions of B normally would be expected to reduce the partial vapor pressure of A; this is the simple dilution effect in Raoult's law.
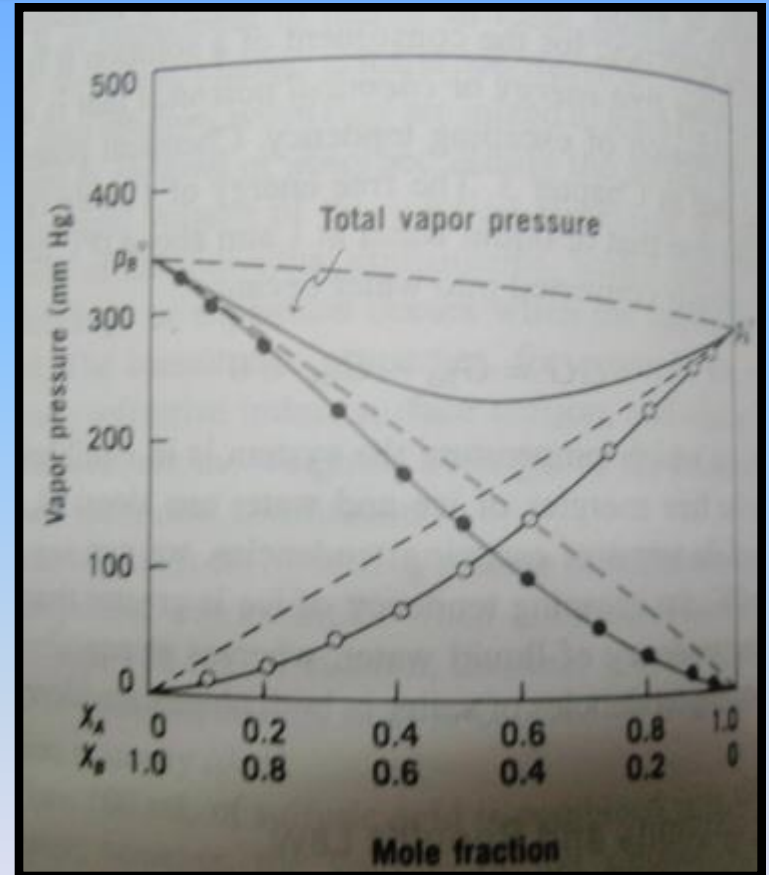
Fig.(2): Vapor pressure of a system showing negative deviation from Raoult`s law

- In the case of liquid pairs that show negative deviation from the law the addition of B to A tends to reduce the vapor pressure of A to a greater extent than can be accounted for by the simple dilution effect.
- Chloroform and acetone manifest such an attraction for one another through the formation of a hydrogen bond, thus further reducing the escaping tendency of each constituent.
- This pair forms a weak compound, which may be isolated and identified.

$$Cl_3C - H \ldots O = C (CH_3)_2$$

- Reactions between **dipolar molecules**, or between **a dipolar and a non-polar** molecule, may also lead to negative deviations.
- The interaction in these cases, is usually so weak that no definite compound can be isolated.

Positive deviation:

- When the interaction between **A** and **B** molecules is less than between molecules of the pure constituents,

- The presence of **B** molecules reduces the interaction of the **A-A** and **A** molecules correspondingly reduce the **B-B** interaction.

- Accordingly, the dissimilarity of polarities or internal pressures of the constituents results in a greater escaping tendency of both the **A** and the **B** molecules.

- The partial vapor pressure of the constituents is greater than that expected from Raoult's law, and the system is said to exhibit **positive deviation.**

■ The total vapor pressure often shows a **maximum** at one particular composition if the deviation is sufficiently large.

■ An example of positive deviation is shown in **(Fig. 3).** Liquid pairs that demonstrate positive deviation are:

1- Benzene & ethyl alcohol,
2-Carbon disulfide & acetone,
3- Chloroform & ethyl alcohol.
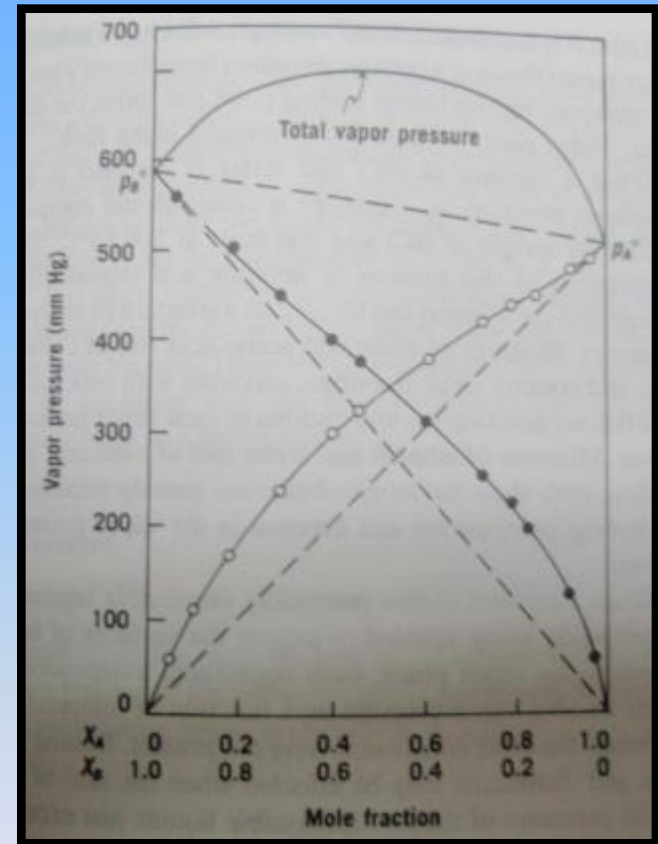
Fig.(3): Vapor pressure of a system showing positive deviation from Raoult`s law.

Notes:

- Raoult's law does not apply over the entire conc range in a non-ideal soln.
- It describes the behavior of either component of a real liquid pair only when that substance is present in high conc and thus is considered to be the solvent.
- Raoult's law may be expressed as:

$$P_{solvent} = P^{\circ}_{solvents} \cdot X_{solvent}$$

in such a situation, and it is valid only for the solvent of a **non-ideal** soln that is sufficiently dilute with respect to the solute.
- It cannot hold for the component in low conc, i.e., the solute, in a dilute non-ideal soln.
- Raoult's law also applies over the entire conc range (to both solvent and solute) when the constituents are sufficiently similar to form an ideal soln.

Henry's Law:

- Raoult's law can apply to the solvent:

$$P_{solvent} = P°_{solvents} \cdot X_{solvent}$$

- **<u>Raoult's law can not be applied to the solute because:</u>**
  1- The molecules of solute, are relatively small in number,
  2- They are completely surrounded by molecules of solvent and so reside in a uniform environment.
- The vapor pressure of the solute cannot be expressed by Raoult's law, but instead by an equation known as **Henry's law:**

$$P_{solute} = K_{solute} \cdot X_{solute}$$

 in which k for (solute) is less than p°.
- **<u>Henry's law applies to the solute and Raoult's applies to the solvent in dilute solutions of real liquid pairs.</u>**

Distillation of Binary Mixtures:

- The relationship between vapor pressure & boiling point & composition of binary liquid phases is the underlying principle in distillation.
- In the case of **1- miscible liquids, exhibit ideal behavior** instead of plotting vapor pressure versus composition, it is more useful to plot the boiling points of the various mixtures, against composition.
- The higher the vapor pressure of a liquid, i.e., the more volatile it is, the lower the boiling point.
- Since the vapor of a binary mixture is always richer in the more volatile constituent, **So**, the process of distillation can be used to separate the more volatile from the less volatile constituent.

- For binary mixture **2- [Non-ideal (real) behavior]:**
- As vapor pressure curves can show maxima (+ve deviation) and minima (–ve deviation) it follows that boiling point curves will show corresponding minima and maxima respectively.
- With these mixtures, distillation produces either pure **A** or pure **B** plus a mixture of constant composition and constant boiling point.
- This latter is known as an **azeotrope** or **axeotropic** mixture.
- It is not possible to separate such a mixture completely into two pure components by simple fractionation.

- **There is two cases**
- 1- If the vapor pressure curves show a minimum (i.e., -ve deviation from Raoult's law), then the **azeotrope has the highest boiling point** of all the mixtures possible, it is therefore **least volatile** and **remains in the flask**, while either pure **A** or pure **B** is distilled off.
- 2- If the vapor pressure curve exhibits a maximum (showing a +ve deviation from Raoult's law), the azeotrope has the **lowest boiling point and mix is volatile** and **forms the distillate**. Either pure **A** or pure B then remains in the flask.

- **Importance of Azerotrope mixture:**

- The composition of Azerotrope mixture is **accurate** and **reproducible** that the soln can be **used as a standard in analytical chemistry.**

- **Examples:**
1- Mixture of Hcl and water is distilled at atmospheric pressure, an azeotrope is obtained that contains 20.22% by weight of Hcl and that boils at 108.58°C.

2- Mixtures of water & acetic acid and of chloroform & acetone both yield azeotropic mixtures with maxima in their boiling point curves and minima in their vapor pressure curves. Mixtures has the highest boiling point become least volatile &remain in flask.

3- Mixtures of ethanol & water and of methanol & benzene both yield azeotropic mixtures with minima in the boiling point curves and maxima in the vapor pressure curves. Mixtures has lowest boiling point become more volatile and form the distillate.

- **3- In case of immiscible liquids:**
- When a mixture of two practically immiscible liquids is heated, while being agitated to expose the surfaces of both liquids to the vapor phase,
- The total vapor pressure is the sum of individual vapor pressure.
- The combined vapor pressure will reach the external pressure (atmospheric pressure) **before** the vapor pressure of **either of the individual components.**
- So agitating of immiscible liquids allows boiling at a temperature lower than the boiling point of **either** of individual components.

- This principle is applied in steam distillation, whereby many organic compounds insoluble in water can be purified at a temp well below the point at which decomposition occurs.
- **Examples**:
- 1- Bromobenzene alone boils at 156.2°C, water boils at 100°C at a pressure of 760 mm Hg.
- A mixture of the two, in any proportion, boils at 95°C.
- Bromobenzene may thus be distilled at a temp 61°C below its normal boiling point.
- Steam distillation is **useful** for obtaining volatile oils from plant tissues without decomposing the oils.

COLLIGATIVE PROPERTIES

- Colligative properties of solutions **depend chiefly on the number of solute particles rather than on the nature of the constituents.** (define)

- **1- Lowering of the Vapor Pressure:**

- When a non-volatile solute is combined with a volatile solvent, the vapor above the solution is provided solely by the solvent.

- The solute **reduces the escaping tendency of the solvent**, and, on the basis of Raoult's law,

- The vapor pressure of a soln containing a non volatile solute is **lowered** proportional to the relative number (rather than the weight conc) of the solute molecules.

- **According to Raoult's Law, and Henry's law:**
- the vapor pressure, P_1 of a solvent over a dilute soln is equal to the vapor pressure of the pure solvent, $P_1°$, times the mole fraction of solvent in the soln, X_1.

$$P_{solvent} = P°_{solvent.} \cdot X_{solvent}$$
$$P_{solute} = P°_{solutet.} \cdot X_{solute}$$
$$P_{solution} = P_{1\ solvent} + P_{2\ solute}$$

- Since the solute under discussion here is considered to be non-volatile, the vapor pressure of the solvent P_1 is identical with the total pressure of the soln P.

$$P = P_1°, X_1$$

- The sum of the mole fractions of the constituents in a soln is unity:

$$X_1 + X_2 = 1 \qquad\qquad X_1 = 1 - X_2$$

in which X_1 is the mole fraction of the solvent and X_2 is the mole fraction of the solute.
Raoult's equation may be modified by substituting equation

$$P = P_1°, X_1$$

for X_1 to give

$$P = P_1°(1 - X_2) \qquad P = P_1° - P_1°X_2 \qquad P - P_1° = - P_1°X_2$$

by multiplying in -1 is equal to $\qquad P_1° - P = P_1° X_2$

$$P_1° - P / P_1° = \Delta P / P_1° = X_2 \qquad\qquad X_2 = n_2 / n_1 + n_2$$

- $\Delta P = P_1° - P$ is the lowering of the vapor pressure &
- $\Delta P/P_1°$ is the relative vapor pressure lowering.
- According to this equation, the relative vapor pressure lowering depends only on the mole fraction of the solute X_2, i.e., on the number of solute particles in a definite volume of soln.
- So, the relative vapor pressure lowering is a colligative property.

- **Example 2 :**
- Calculate the relative vapor pressure lowering at 20°C for a soln containing 171.2 g of sucrose (w_2) in 1000 grams (w_1) of water. The molecular weight of sucrose (M_2) is 342.3 and the molecular weight of water (M_1) is 18.02.

  Moles of sucrose = n2 = w_2/M_2 = 171.2/342.3 = 0.5

  Moles of water = w_1/M_1 = 1000/18.02 = 55.5

  $\Delta p/p_1° = X_2 = n_2/n_1 + n_2$

  $\Delta p/p_1° = 0.5/55.5 + 0.5 = 0.0089$

- Notice that in this example , the relative vapor pressure lowering is a dimensionless number, as would be expected from its definition.
- The result may also the stated as a percentage, the vapor pressure of the soln has been lowered 0.89% by the 0.5 mole of sucrose.

- In very dilute soln, The mole fraction, n_2 is very small and $n_2/(n_1 + n_2)$, is nearly equal to, and may be replaced by, the mole ratio n_2/n_1.

$$\Delta P/P_1^\circ = X_2 = n_2/(n_1 + n_2) = n_2/n_1$$

Number of moles= wt/ M.wt

$$X_2 = \Delta p/p_1^\circ \approx n_2/n_1 = w_2/M_2/w_1/M_1$$

So it can be written, $n_2/n_1 = w_2 . M_1/M_2 . w1$

- Then, the relative vapor pressure lowering can be expressed in terms of molal conc of the solute by setting the weight of solvent w_1 equal to 1000 grams. For an aqueous soln, So, M_1 (M.wt for water) =18
  the number of moles of solute is the molal conc
  (no. of moles in 1000g soln)

 $X_2 = \Delta P/P_1° \approx n_2/n_1 = w_2/M_2/1000/M_1 =$
  $X_2 = \Delta P/P_1° \approx n_2/n_1 = w_2/M_2 . M_1/1000 = m.18/1000 = 0.018\ m$

  m= no. of solute moles in 1000 g solvent

Elevation of the Boiling Point:

- As stated previously the normal boiling point is the temp at which the vapor pressure of the liquid becomes equal to an external pressure of 760 mm Hg.
- The boiling point of a soln of a non-volatile solute is **higher** than that of the pure solvent, owing to the fact that the solute lowers the vapor pressure of the solvent.
- The vapor pressure curve for the soln lies below that of the pure solvent, and the temp of the soln must be elevated to a value above that of the solvent in order to reach the normal boiling point.
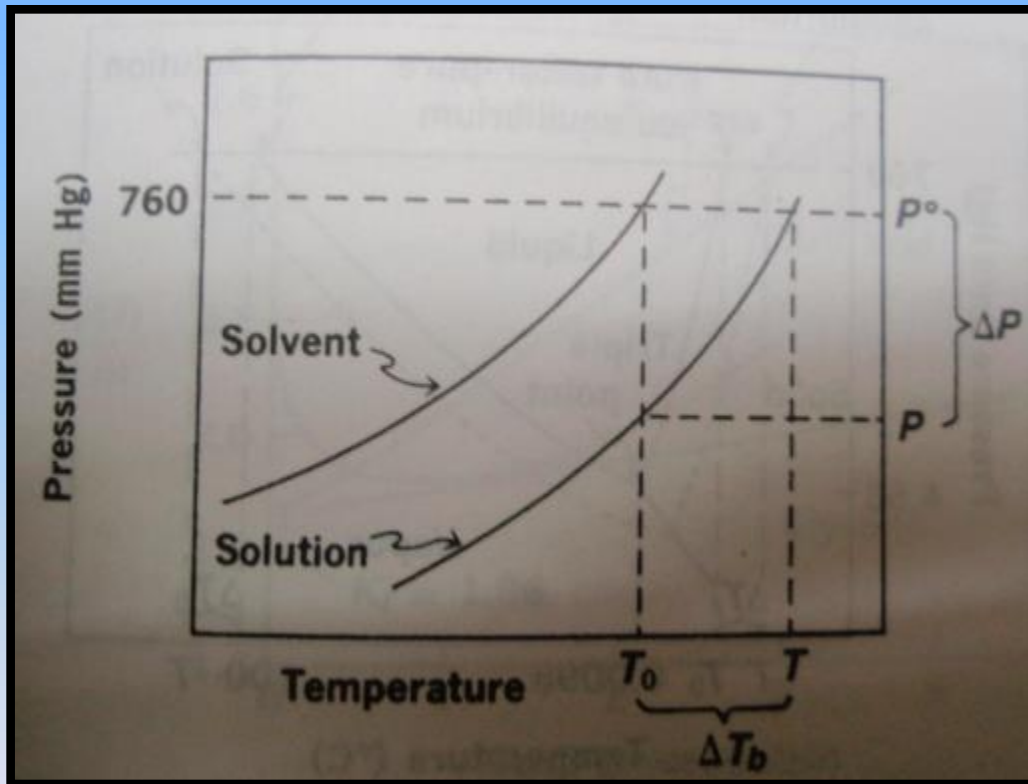
Fig.(6): Boiling point elevation of the solvent due to addition of a solute

- The elevation of the boiling point is shown in the figure as $T - T_0 = \Delta T_b$.

- The ratio of the elevation of the boiling point, ΔT_b, to the vapor pressure lowering, $\Delta p = p° - p$, at 100°C is approximately a constant at this temp; it is written as

$$\Delta T_b / \Delta p = k^1 \quad \text{or} \quad \Delta T_b = k^1 \Delta p$$

- Moreover, since $p°$ is a constant, the boiling point elevation may be considered proportional to $\Delta p/p°$, the relative lowering of vapor pressure. $\Delta T_b \; ά \; \Delta p/p°$,

$$\Delta p/p° = X_2 \qquad\qquad \Delta T_b = kX_2$$

- Since the boiling point elevation depends alone on the mole fraction of the solute, it is a colligative property.

- In dilute solns, X_2 is equal approximately to $m/(1000/M_1)$ and equation may be written as
  $$\Delta T_b = kM_1/1000 \; m \qquad \text{or} \qquad \Delta T_b = K_b m$$

- in which ΔT_b is known as the boiling point elevation & K_b is called the molal elevation constant or the **ebullioscopic** constant.

- K_b has a characteristic value for each solvent, as seen in (Table 2).

- **It may be considered as the boiling point elevation for an ideal 1 molal soln.**

- **Stated another way, K_b is the ratio of the boiling point elevation to the molal conc in an extremely dilute soln in which the system is approximately ideal. (2 definitions for K_b)**

Table (2): Ebullioscopic and Cryoscopic constants for various solvents

Substance	Boiling Point (°C)	K_b	Freezing Point (°C)	K_f
Acetic acid	118.0	2.93	16.7	3.9
Acetone	56.0	1.71	94.82*	2.40*
Benzene	80.1	2.53	5.5	5.12
Camphor	208.3	5.95	178.4	37.7
Chloroform	61.2	3.63	-63.5	-
Ethyl alcohol	78.4	1.22	-114.49*	3*
Ethyl ether	34.6	2.02	-116.3	1.79*
Phenol	181.4	3.56	42.0	7.27
Water	100.0	0.51	0.00	1.86

- **Example 4 :**

A 0.200 m aqueous soln of a drug gave a boiling point elevation of 0.103°C. Calculate the approximate molal elevation constant for the solvent, water. Substituting into this equation yields

$$k_b = \Delta T_b / m = 0.103/0.200 = 0.515 \text{ deg Kg/ mole}$$

The proportionality between ΔT_b and the molality is exact only at infinite dilution, at which the properties of real and ideal solns coincide.

Depression of the Freezing Point:

- The normal freezing point or melting point of a pure compound is the temp, at which the solid and the liquid phases are in equilibrium under a pressure of 1 atm.
- Equilibrium here means that the tendency for the solid to pass into the liquid state is the same as the tendency for the reverse process to occur, since both the liquid and the solid have the same escaping tendency.
- The value T_0, observed in (Fig. 8), for water saturated with air at this pressure is 0°C.

- The triple point of air free water, at which solid, liquid, and vapor are in equilibrium, **lies at a pressure of 4.58 mm Hg and a temp of 0.0098°C.**
- It is not identical with the ordinary freezing point of water at atmospheric pressure, but is rather the freezing point of water under the pressure of its own vapor.
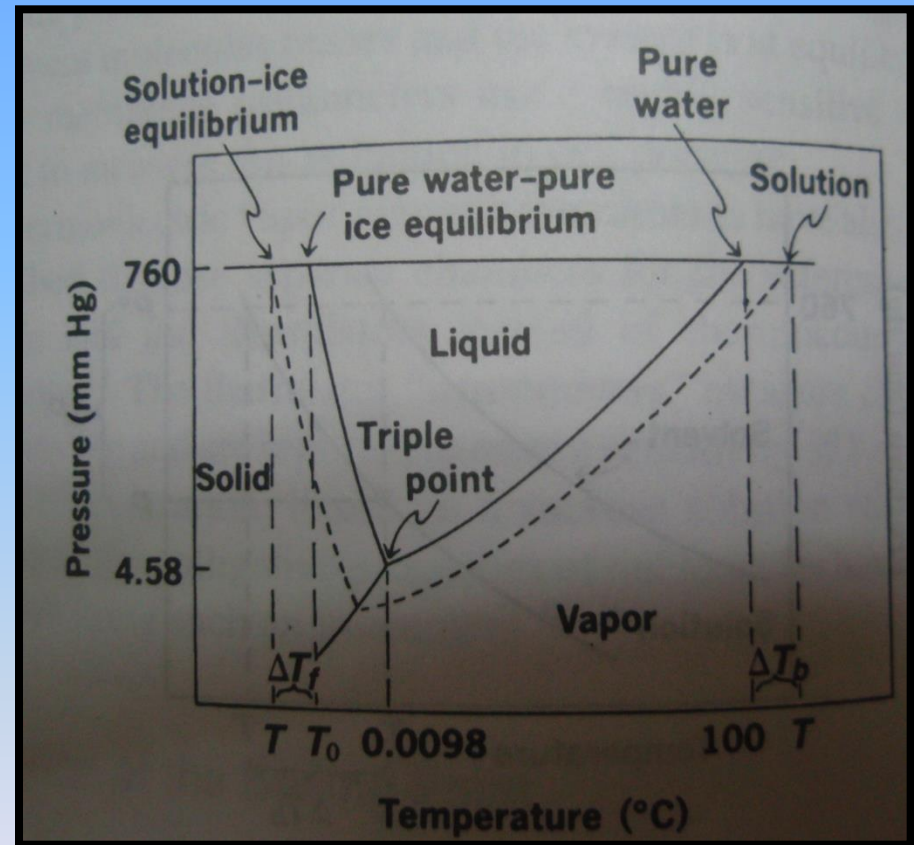
Fig.(8): Depression of the freezing point of the solvent by a solute

- Now if a solute is dissolved in the liquid at the triple point, the escaping tendency or vapor pressure of the liquid solvent is lowered below that of the pure solid solvent.
- The temp, must drop in order to re-establish equilibrium between the liquid and the solid.
- Because of this fact, the freezing point of a solution is always lower than that of the pure solvent.
- **The more concentrated the soln, the greater is the freezing point depression.**
- The depression of the freezing point, like the boiling point elevation, is a direct result of the lowering of the vapor pressure of the solvent.

- The freezing point depression is proportional to the molal conc of the solute.
- The equation is

$$\Delta T_f = K_f m \quad \text{or} \quad \Delta T_f = K_f 1000 \cdot w_2 / w_1 M_2$$

- ΔT_f is the freezing point depression,
- K_f is the molal depression constant or the **cryoscopic constant**, which depends on the physical and chemical properties of the solvent.
- The freezing point depression of a solvent is a function only of the number of particles in the soln, and for this reason it is referred to as a **colligative property.**
- **It may be considered as the freezing point depression for an ideal 1 molal soln.**
- **Stated another way, is the ratio of the freezing point depression to the molal conc in an extremely dilute soln in which the system is approximately ideal. (2 definitions for K_f)**

- The value of K_f for water is 1.86.
- It may be determined experimentally by measuring $\Delta T_f/m$ at several molal concs and extrapolating to zero conc.
- As seen in this fig. K_f approaches the value of 1.86 for water solns of sucrose and glycerin as the concs tend toward zero, only in very dilute solns where concs are usually lower than 0.1M.
- The value K_f for the solvent in a soln of citric acid is observed not to approach 1.86.
- This abnormal behavior is to be dealing with solns of electrolytes.
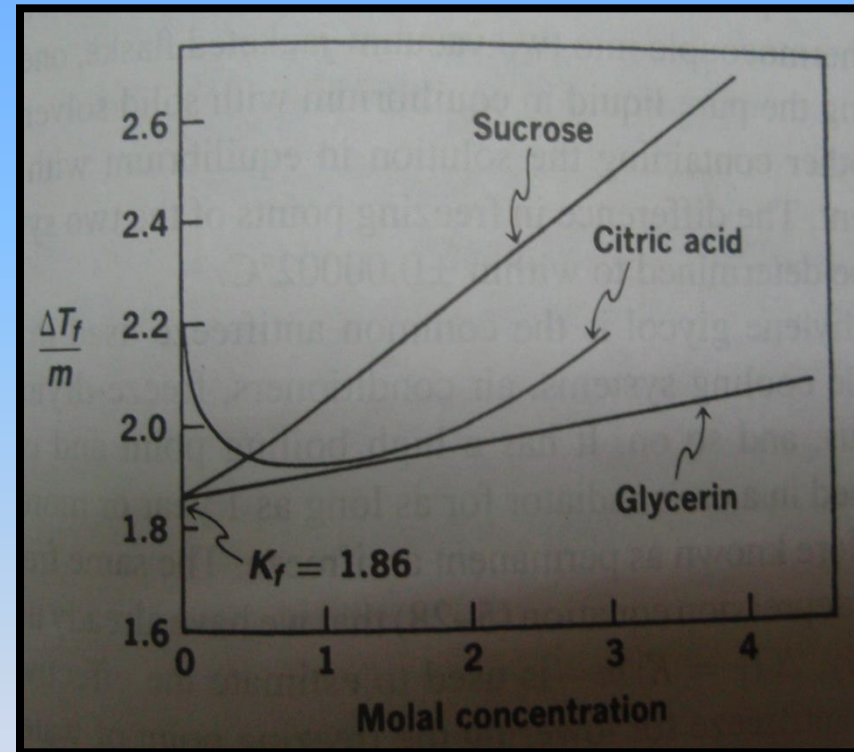
Fig. (9): The influence of concentration on the cryoscopic constant.

- **Example :**
  What is the freezing point of a soln containing 3.42 g of sucrose in 500 g of water? The molecular weight of sucrose is 342. In this relatively dilute solution, K_f is approximately equal to 1.86.
  $\Delta T_f = K_f m = K_f 1000 w_2 / w_1 m_2$
  $\Delta T_f = 1.86 \times 1000 \times 3.42 / 500 \times 342$
  $\Delta T_f = 0.037°C$
  Therefore, the freezing point of the aqueous soln is -0.037°C.

- **Example :**
  What is the freezing point depression of a 1.3 m soln of sucrose in water?
  From the graph (Fig. 9) one observes that the cryoscopic constant at this conc is about 2.1 rather than 1.86. Thus, the calculation becomes
  $\Delta T_f = K_f \times m = 2.1 \times 1.3 = 2.73°C$

- **Example :**

 The freezing point of water on the scale of the Bekmann thermometer was 1.112°C and the value for an aqueous soln of the solute was 0.120°C. What is the apparent K_f value if the conc of the soln is 0.50 m?

 $K_f = \Delta Tf/m = (1.112-0.120)/0.50 = 0.992/0.50 = 1.98.$

Osmotic Pressure:

- If cobalt chloride is placed in a parchment sac and suspended in a beaker of water, the water gradually becomes red as the solute diffuses throughout the vessel.
- In this process of diffusion, both the solvent and the solute molecules migrate freely.
- On the other hand, if the soln is confined in a membrane permeable only to the solvent molecules, the phenomenon known as **osmosis** occurs,
- and the barrier that permits only the molecules of one of the components (usually water) to pass through is known as a **semipermeable membrane.**

- A thistle tube, over the wide opening of which is stretched a piece of untreated cellophane, can be used to demonstrate the principle, as shown in next fig.
- The tube is partly filled with a concentrated soln of sucrose and the apparatus is lowered into a beaker of water.
- The passage of water through the semipermeable membrane and into the soln eventually creates enough pressure to drive the sugar soln up the tube until the hydrostatic pressure of the column of liquid equals the pressure causing the water to pass through the membrane and enter the thistle tube.
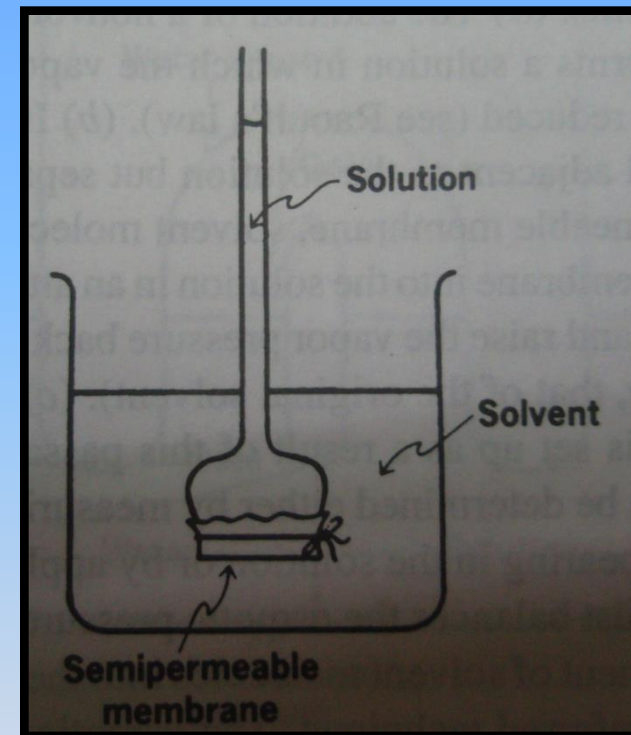
Fig. (10): Apparatus for demonstrating osmosis

- When this occurs, the soln ceases to rise in the tube.
- **Osmosis** is defined as **the passage of the solvent into a soln through a semipermeable membrane**.
- This process tends to equalize the escaping tendency of the solvent on both sides of the membrane.
- Escaping tendency can be measured in terms of vapor pressure or the closely related colligative property, osmotic pressure.
- It should be evident that osmosis can also take place when a concentrated soln is separated from a less concentrated soln by a semipermeable membrane.

- The phenomenon of osmosis depends on the fact that the chemical potential (a thermodynamic expression of escaping tendency) of a solvent molecule in soln is less than exists in the pure solvent.
- Solvent therefore passes spontaneously into the soln until the chemical potentials of solvent and soln are equal. The system is then at equilibrium.

- **You consider osmosis in terms of the following sequence of events:**
  (1): The addition of a non-volatile solute to the solvent forms a soln in which the vapor pressure of the solvent is reduced (see Raoult's law).

(2) If pure solvent is now placed adjacent to the soln but separated from it by a semipermeable membrane, solvent molecules will pass through the membrane into the soln in an attempt to dilute out the solute and raise the vapor pressure back to its original value (namely, that of the original solvent).

(3) The osmotic pressure that is set up as a result of this passage of solvent molecules may be determined either by: a- **measuring the hydrostatic head appearing in the soln** or b- **applying a known pressure that just balances the osmotic pressure and prevents any net movement of solvent molecules into the soln**.

The latter is the preferred technique.

- The osmotic pressure thus obtained is proportional to the reduction in vapor pressure brought about by the conc of solute present.
- Since this is a function of the molecular weight of the solute, osmotic pressure is a **colligative property** and may be used to determine molecular weights.

- **Van't Hoff and Morse Equations for Osmotic Pressure:**
- Van't Hoff concluded that there was an apparent analogy between solns and gases and that the osmotic pressure in a dilute soln was equal to the pressure that the solute would exert if it were a gas occupying the same volume.

- The equation is $\pi V = nRT$

  in which π is the osmotic pressure in atm, V is the volume of the soln in liters, n is the no. of moles of solute, R is the gas constant equal to 0.082 liter atm/mole deg, and T is the absolute temp.

- **Example :**

  One gram of sucrose, molecular weight 342, is dissolved in 100 ml of soln at 25°C. What is the osmotic pressure of the soln?

  Moles of sucrose = 1/342 = 0.0029

 π x 0.10 = 0.0029 x 0.082 x 298

  π = 0.71 atm

- The previous equation can be expressed as

$$\pi = n/V \; RT = cRT$$

in which **c** is the conc of the solute in moles per liter (molarity).

- **Morse and others** have shown that when the conc is expressed in molality rather than molarity, the results compare more nearly with the experimental findings.

- The Morse equation is $\pi = RTm$

- **(Fig. 4)** shows a mixture of a high boiling liquid **A** and a low boiling liquid **B**.
- A mixture of these substances having the composition **a** is distilled at the boiling point **b**.
- The composition of the vapor **V1** in equilibrium with the liquid at this temperature is **c**; this is also the composition of the distillate when it is condensed.
- The vapor is therefore richer in **B** than the liquid from which it was distilled.
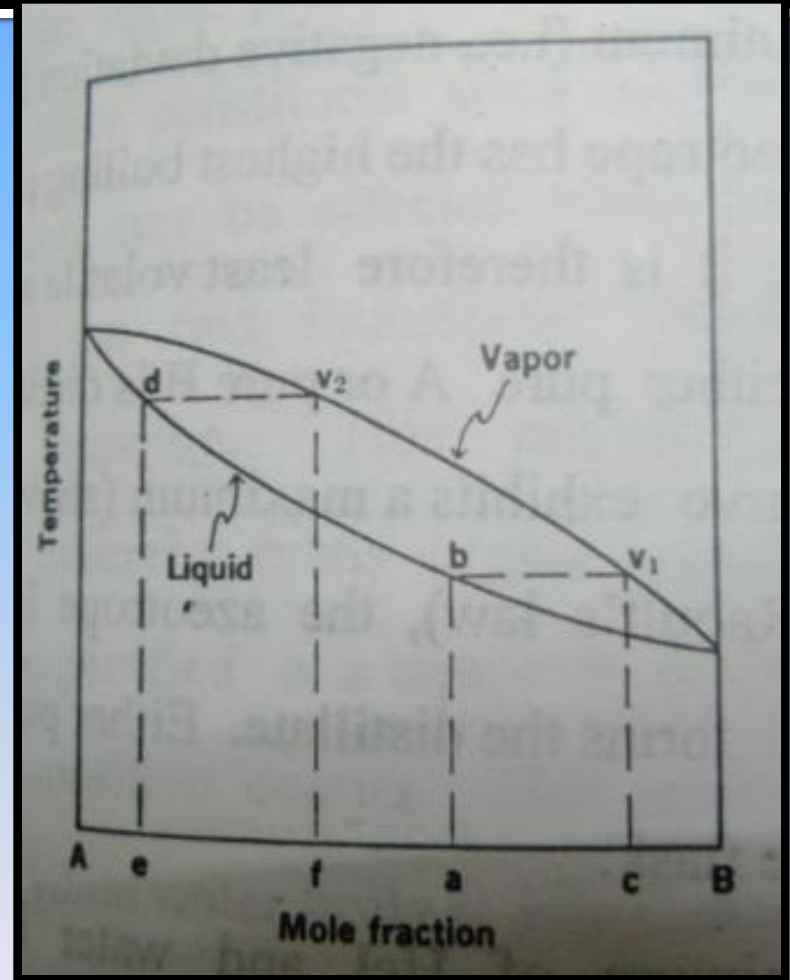
Fig.(4): Boiling point diagram of an ideal binary mixture

- As the rising vapor is cooled by contact with the liquid, some of the lower boiling fraction condenses, and the vapor contains more of the volatile component than it did when it left the retort.
- As the vapor proceeds up the fractionating column, it becomes progressively richer in the more volatile component **B**, and the liquid returning to the distilling retort becomes richer in the less volatile component **A**.

Example3:

Calculate the vapor pressure when 0.5 mole of sucrose is added to 1000 g of water at 20°C. The vapor pressure of water at 20°C is 17.54 mm Hg. The vapor pressure lowering of the soln is

$\Delta p = p_1° X_2 = p_1° \times 0.018 \times m = 17.54 \times 0.018 \times 0.5$

$= 0.158 \text{ mm} \approx 0.16 \text{ mm}$

The final vapor pressure is $\Delta p = P_1° - P$

$P = P_1° - \Delta p$

$17.54 - 0.16 = 17.38 \text{ mm}$