Nonelectrolytes

Lecturer Ghaidaa S. Hameed

Introduction

A true solution is defined as a mixture of two or more components that form a homogenous molecular dispersion, in other words, a one-phase system, the composition of which can vary over a wide range.

Pharmaceutical dispersion

- Two component may be forming a true solution (completely dispersed).
- Two component:
- **Colloidal dispersion** (size between 1-500 nm).

Such as blood, liposome and zinc oxide paste.

- **Coarse dispersion** (>500nm).

Such as emulsion and suspension.

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

Types of Solutions

- The solutes (whether gases, liquids, or solids) are divided into two main classes: nonelectrolytes and electroytes.

- Nonelectrolytes are substances that do not yield ions when dissolved in water and therefore do not conduct an electric current through the solution.

- Examples of noneletrolytes are sucrose, glycerin, naphthalene, and urea.

Types of Solutions

- Electrolytes are substances that form ions in solutions, conduct the electric current.
- Examples of electrolytes are hydrochloric acid, sodium sulfate, ephedrine, and phenobarbital.
- Electrolytes may be subdivided further into strong electroytes (hydrochloric acid, sodium sulphate) and weak electrolytes (ephedrine, phenobarbital).

Concentration Expressions

Expression	**Symbol**	**Definition**
Molarity	**M**	**Moles (gram molecular weights) of solute in 1 liter of solution**
Normality	**N**	**Gram equivalent weights of solute in 1 liter of solution**
Molality	**m**	**Moles of solute in 1000g of solvent**
Mole fraction	**X, N**	**Ratio of the moles of one constituent (e.g. the solute) of a solution to the total moles of all constituents (solute and solvent)**
Mole percent		**Moles of one constituent in 100 moles of the solution. Mole percent is obtained by multiplying the mole fraction by 100**
Percent by weight	**% w/w**	**Grams of solute in 100g of solution**
Percent by volume	**% v/v**	**Milliliters of solute in 100mL of solution**
Percent weight-in-volume	**% w/v**	**Grams of solute in 100mL of solution**
Milligram percent	**-**	**Milligrams of solute in 100mL of solution**

Equivalent Weights

- Equivalent weights are known as the quantities of an atom or molecule that combines with 1.008 g (gram atomic weight) of hydrogen.

$$\text{Equivalent weight (g/Eq)} = \frac{\text{Atomic weight}}{\text{Number of equivalents per atomeic weight (valence)}}$$

Example: Equivalent weight for
Fluorine = 19/1= 19 g/ Eq
Oxygen = 16/ 2= 8 g/ Eq
Magnesium= 24/2= 12 g/ Eq

Equivalent Weights

- Similarly for molecules:

$$\text{Equivalent weight } (g/Eq) = \frac{\text{molecular weight } (\frac{g}{mol})}{\text{number of equivalent per mol}}$$

Example: Equivalent weight for:
NaCl= 58.5 (g/mol)/1 (Eq/mol)= 58.5 g/Eq.
Na_2CO_3= 106/2= 53 g/Eq.
K_3PO_4= 212/3= 70.7 g/Eq.
KNO_3= 101/1= 101 g/Eq.
$Ca_3(PO_4)_2$= 310/6= 51.7 g/Eq.

- Example:

An aqueous solution of ferrous sulfate was prepared by adding 41.5 g of $FeSO_4$ to enough water to make 1000 ml of solution at 18°C. The density of the solution is 1.0375 and the molecular weight of $FeSO_4$ is 151.9. Calculate:

a) The molarity.
b) The normality.
c) The molality.
d) The mole fraction and mole percent for both solute and solvent.
e) The percentage by weight of $FeSO_4$.

Answer:

a) Molarity = moles of $FeSO_4$/Liters of solution
= (41.5/151.9)/ 1 L = 0.2732 M.

b) Normality = (41.5/ 75.95)/ 1L= 0.5464 N

Equivalent weight= 151.9/2= 75.95 g/Eq

c) Molality = moles of $FeSO_4$/ kg of solvent
= 0.2732/ 0.996= 0.2743 m

Grams of solution = volume * density
= 1000 * 1.0375= 1037.5 g
Grams of solvent = 1037.5- 41.5= 996 g

- Example…….cont.:

d) Mole fraction and mole percent:

Moles of water = n_1= 996/18.02= 55.27 moles.

Moles of FeSO4 = n_2 = 0.2732 moles.

Mole fraction of water = X_1 = 55.27/ (55.27 + 0.2732) = 0.9951

Mole percent of water = 0.9951 * 100%= 99.51%.

Mole fraction of $FeSO_4$= X_2= 0.2732/ (55.27 + 0.2732) = 0.0049

Mole percent of $FeSO_4$= 0.49%

e) Percentage by weight of $FeSO_4$= (g of $FeSO_4$/ g of solution) *100

= (41.5/ 1037.5) *100 = 4 %

Solution properties

- Solution properties may be classified as extensive properties , depending on the quantity of the matter in the system (e.g. mass and volume) and intensive properties, which are independent of the amount of substances in the system (e.g. temperature, pressure, density, surface tension, and viscosity of pure liquids).
- Solution properties can also be classified as additive, constitutive and colligative.
- Additive properties are derived from the sum of the properties of the individual atoms or functional groups within the molecule e.g. mass
- Constitutive properties are dependent on the structural arrangement of the atoms within the molecule e.g. optical rotation.
- Colligative properties will be discussed soon later.

Ideal solutions

- Ideal solutions are formed by mixing substances with similar properties.

- Ideality in solution means complete uniformity of attractive forces (i.e. cohesive forces between A molecules are similar to cohesive forces between B molecules; both of which are similar to the adhesive forces between A and B molecules).

- Ideal solution is the solution in which there is no change in the properties of the components, other than dilution, when they are mixed to form the solution.

- In ideal solution, no heat is evolved or absorbed during the mixing process, and the final volume of the solution represents an additive property of the individual constituents. No shrinkage or expansion occurs when substances are mixed together (e.g. a solution of methanol and ethanol).

Escaping Tendency

- When two bodies are in contact with each other and one is heated to a higher temperature than the other, heat will flow from the hotter to the colder body until the bodies are in thermal equilibrium. This process is termed the escaping tendency.

- The hotter body has a greater escaping tendency until the temperature of both bodies is the same.

- Temperature is a quantitative measure of escaping tendency of heat.

Escaping Tendency

- Free energy is a quantitative measure of escaping tendencies of substances undergoing physical and chemical transformations – for a pure substance, it is the molar free energy, for a solution, it is the partial molar free energy.
- Free energy of a mole of ice is greater than that of a liquid water at 1 atm above 0ºC.

$$\Delta G = G_{liq} - G_{ice} < 0$$

- Above 0ºC, The escaping tendency of ice is greater than that of liquid water, so ice is converted to water.
- At 0ºC, the escaping tendencies of ice and water are the same, $\Delta G = 0$.

Raoult’s Law

- Raoult’s Law applies for solvents while Henry’s law applies for solutes.

- Activity, “effective concentration”, is a term used to describe departure of the behavior of a solution from ideality. In an ideal solution or in a real solution at infinite dilution there is no interactions between components and the activity equals the concentration (activity = concentration).

Raoult’s Law

- The activity, in general, is less than the actual or stoichiometric concentration of the solute as interactions occur between the components which reduce the effective concentration of the solute.

- Non-ideality in real solutions at high concentrations causes a divergence between the values of activity and concentration. The ratio of the activity to the concentration is called the activity coefficient, γ.

$$\gamma = \frac{activity}{concentration}$$

Raoult’s Law

- Depending on the units used to express the concentration we can have either a molal activity coefficient, γ_m, a molar activity coefficient, γ_c, or if mole fractions are used, a rational activity coefficient, γ_x.

$$a = \gamma_m m \qquad a = \gamma_c c \qquad a = \gamma_X X$$

where m is the molality, c is the molar concentration, x is the mole fraction.

Raoult's Law

- The activity coefficient is a proportionality constant relating activity to concentration.

- The activity coefficient usually decreases and assumes different values as the concentration increases.

- Differences among the three activity coefficients may be disregarded in dilute solutions in which $c \cong m < 0.01$.

- The concept of activity and activity coefficient may be applied to nonelectrolytes, weak as well as strong electrolytes.

Raoult’s Law- Ideal solutions

- The vapor pressure of a solution is a quantitative expression of escaping tendency.
- Raoult’s law: In an ideal solution, 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 solution.

$$P_t = P_1^o X_1 + P_2^o X_2$$

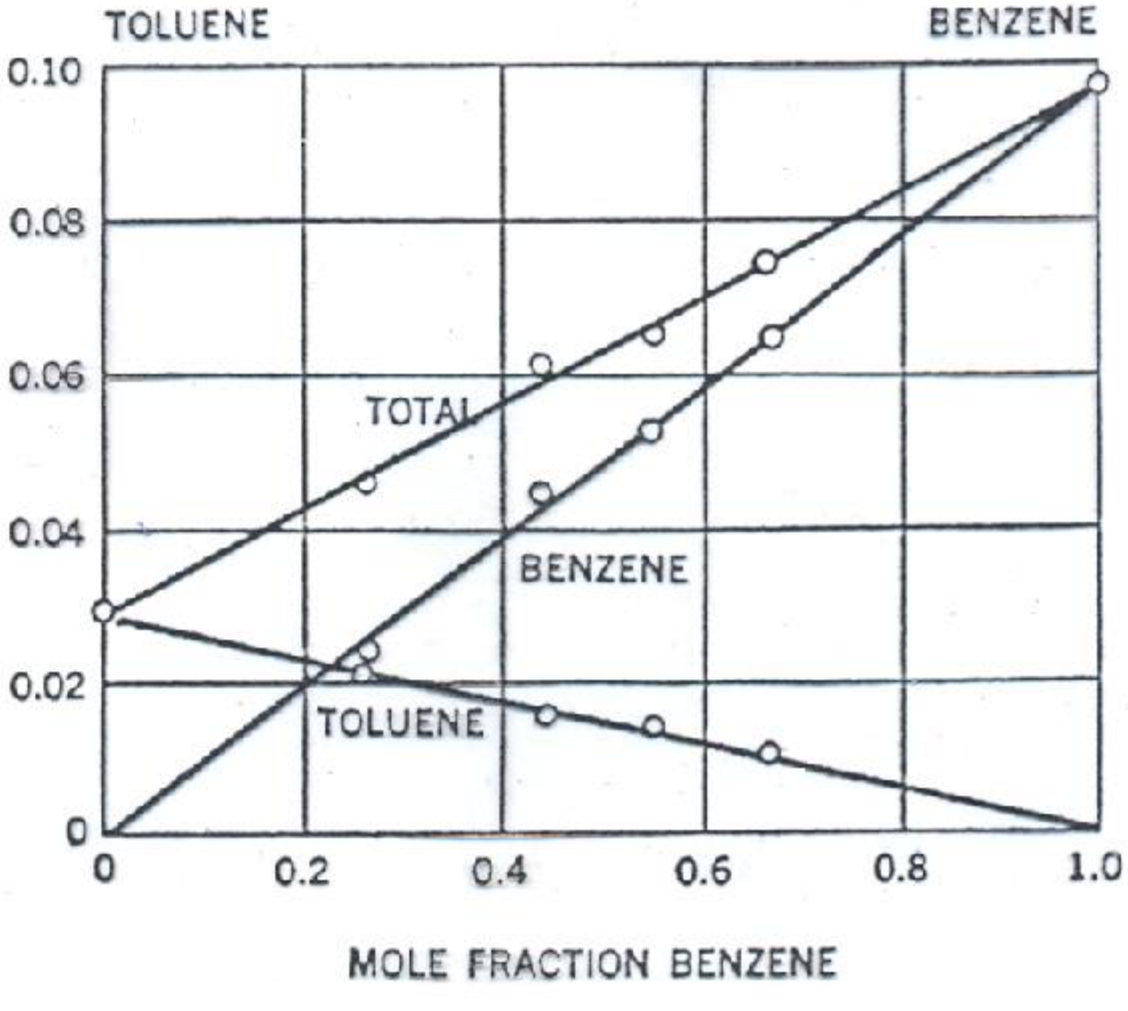
where $P_1^oX_1$ and $P_2^oX_2$ are the partial vapor pressures of the pure components when the mole fractions are X_1 and X_2. P_1^o and P_2^o are the vapor pressure of the pure components.

Raoult’s Law- Ideal solutions

- So in ideal solutions, 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 solution. This will diminish 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.

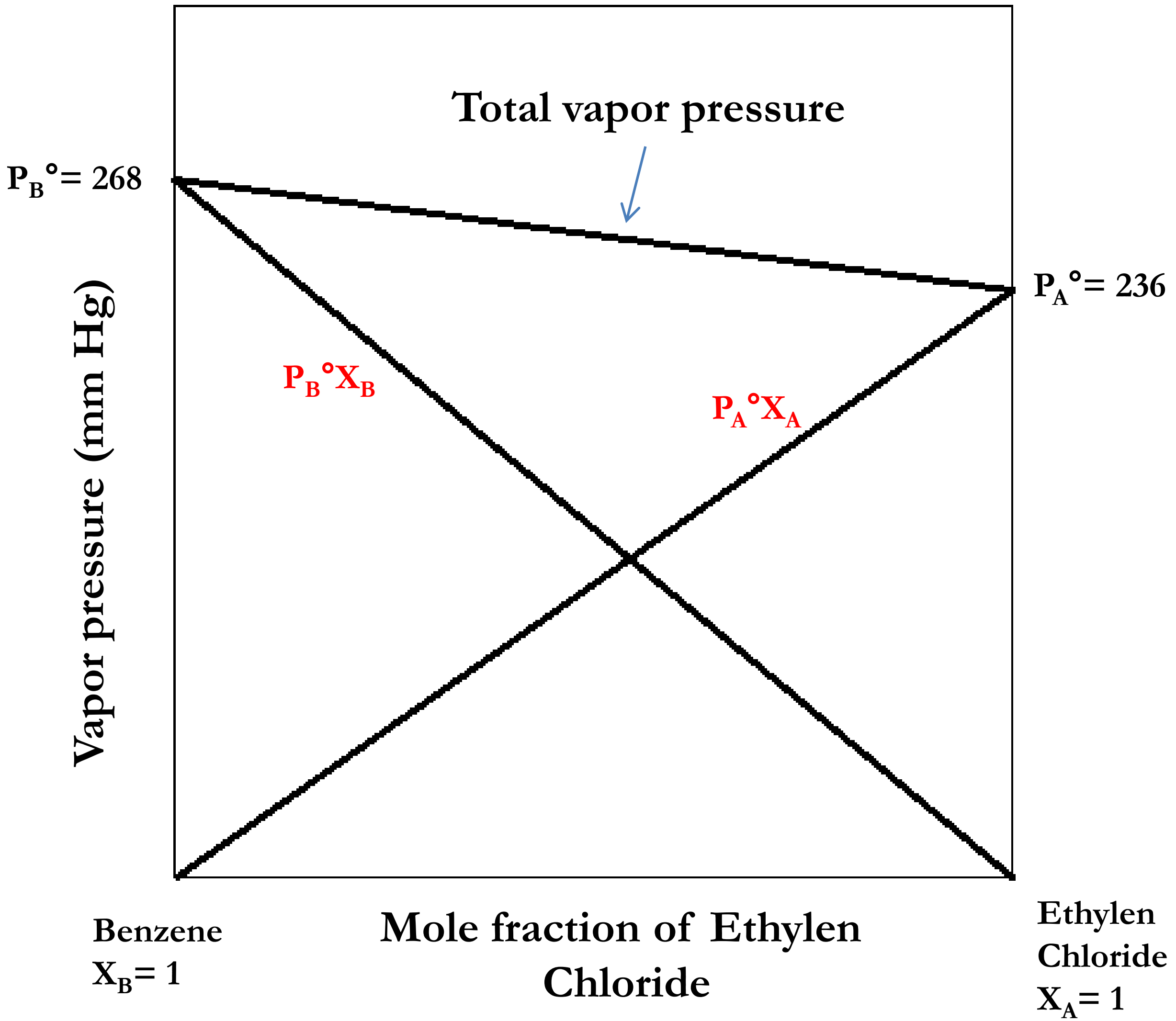
The activities and activity coefficients of solvents on the assumption of ideal-gas behavior of the vapor

Solvent benzene (solute toluene, 20°C)			Solvent toluene (solute benzene, 20°C)		
Mole fraction X	Activity a	Act.coeff γ	Mole fraction X	Activity a	Act.coeff γ
1.00	1.00	1.00	1.00	1.00	1.00
0.67	0.65	0.97	0.77	0.78	1.01
0.55	0.54	0.98	0.57	0.55	1.07
0.43	0.46	1.07	0.45	0.47	1.04



The vapor pressures of the components and the total vapor pressures for the nearly ideal solution benzene-toluene at 20ºC

Raoult’s Law- Ideal solutions



Real (nonideal) solutions

- Many examples of solution pairs are known in which the “cohesive” attraction of A for A exceeds the “adhesive” attraction existing between A and B. Similarly, the attractive forces between A and B may be greater than those between A and A or B and B. This may occur even though the liquids are miscible in all proportions. Such mixtures are <u>real or nonideal.</u>

Real (nonideal) solutions

Negative deviation:

When "adhesive" attractions between molecules of different species exceed the "cohesive" attractions between like molecules, the vapor pressure of the solution is less than expected from Raoult's ideal solution law, and negative deviation occurs.

$P_t < P_1^oX_1 + P_2^oX_2 \rightarrow$

$a_1 < X_1\ ,\ \ a_2 < X_2 \rightarrow P_t = P_1^oa_1 + P_2^oa_2$

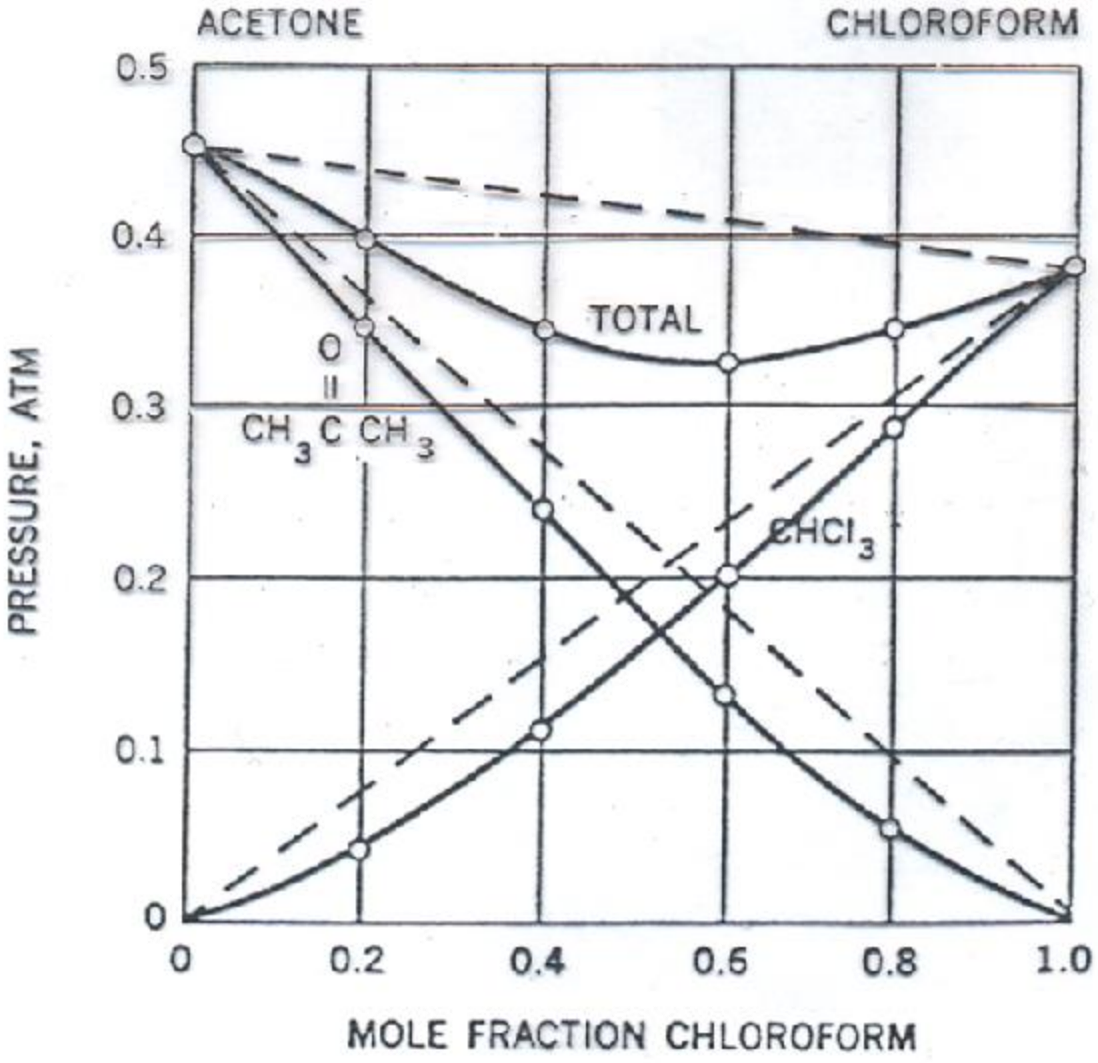
Example: chlorofrom and acetone – due to formation of hydrogen bonds thus reducing the escaping tendency of each other.

$Cl_3C\text{-}H\cdots\cdots O{=}C(CH_3)_2$

The activities and activity coefficients of solvents showing negative deviation from Raoult's law

Solvent acetone (solute $CHCl_3$, 35°C)			Solvent chloroform ($CHCl_3$) (solute acetone, 35°C)		
X	a	γ	X	a	γ
1.00	1.00	1.00	1.00	1.00	1.00
0.94	0.94	1.00	0.92	0.91	0.99
0.88	0.87	0.99	0.81	0.76	0.94
0.73	0.70	0.96	0.66	0.55	0.83
0.63	0.57	0.90	0.58	0.48	0.83
0.51	0.42	0.82	0.49	0.38	0.78

Note: with dilution, $a \rightarrow c$, $\gamma \rightarrow 1$



Vapor pressure diagram for the system chloroform-acetone at 35°C

Real (nonideal) solutions

Positive deviation:

When interaction between A and B molecules is less than that of the pure constituents, the presence of B molecules reduce the interaction of A molecules, and A molecules reduce B-B interaction → greater escaping tendency of A and B molecules → partial vapor pressure of the constituents is greater than that expected from Raoult's law.

$$P_t > P_1^o X_1 + P_2^o X_2 \rightarrow a_1 > X_1 \, , a_2 > X_2 \rightarrow$$

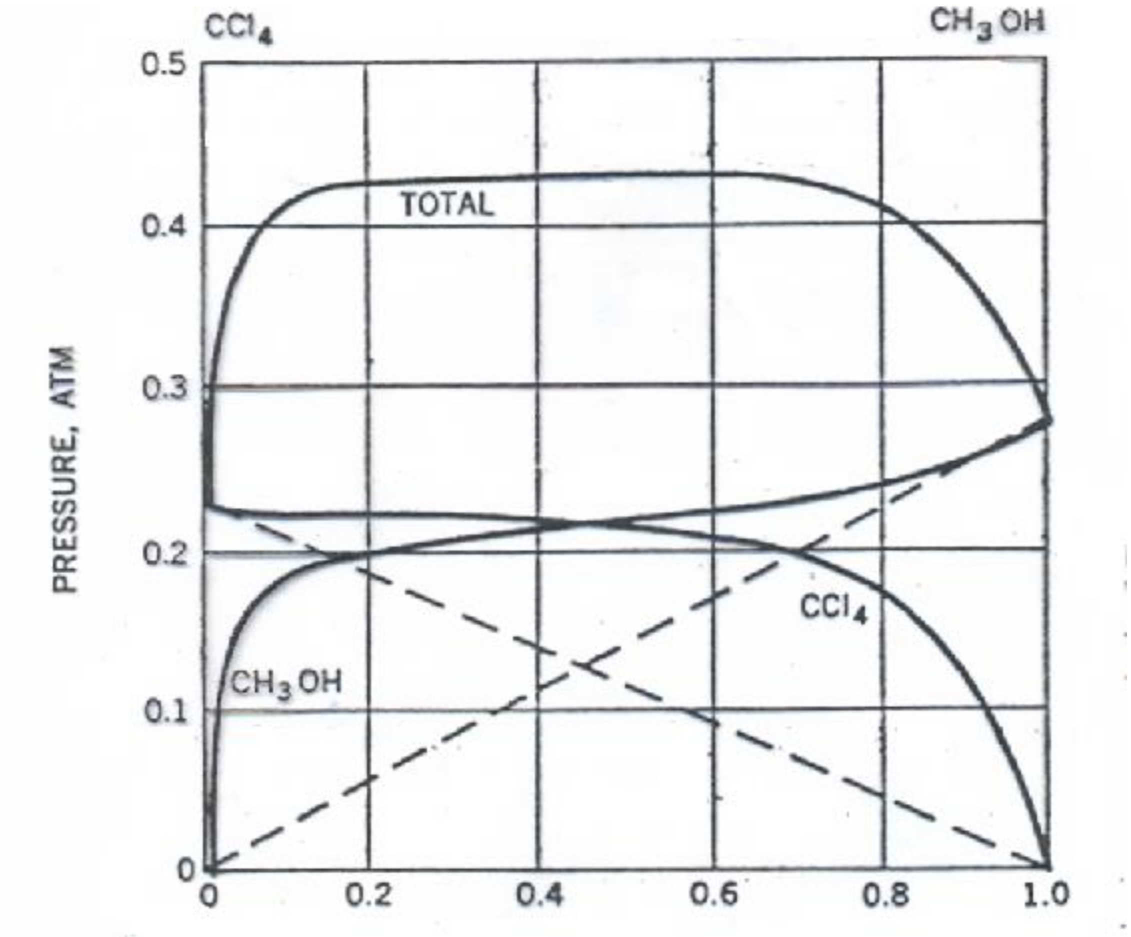
$$P_t = P_1^o a_1 + P_2^o a_2$$

Examples: benzene and ethyl alcohol, carbon disulfide and acetone, chloroform and ethyl alcohol, carbon tetrachloride and methyl alcohol

The activities and activity coefficients of solvents showing positive deviation from Raoult's law

Solvent methyl alcohol (CH_3OH) (solute CCl_4, 35°C)			Solvent carbon tetrachloride (CCl_4) (solute CH_3OH, 35°C)		
X	a	γ	X	a	γ
1.00	1.00	1.00	1.00	1.00	1.00
0.91	0.95	1.04	0.98	0.99	1.01
0.79	0.88	1.11	0.87	0.97	1.11
0.66	0.84	1.27	0.64	0.94	1.47
0.49	0.80	1.63	0.51	0.92	1.80
0.36	0.78	2.16	0.34	0.87	2.56

Note: dilution of the dimer structure in alcohol → increases the vapor pressure of the alcohol



Vapor pressure diagram for the system carbon tetrachloride (CCl_4) – methyl alcohol (CH_3OH) at 35°C

Real (nonideal) solutions

- **In real solutions, Raoult’s law does NOT apply over the entire concentration range. It can only be applicable for a substance with high concentration (i.e. solvents in real solutions). For the previous figures (slides 18 and 20), you can observe that the actual vapor pressure curve of subtances approach the ideal curve defined by Raoult’s law at high concentrations (being solvent).**

Raoult’s Law

- If you have the fourth edition of the book, solve problems 5-9 and 5-10 page 122, and problems 6-27 and 6-28 page 142.

- If you have the fifth edition of the book, solve problems 5-9 and 510 page 693, and problems 6-27 page 697 and 6-28 page 698.

Colligative properties

- Colligative properties depend mainly on the number of particles in a solution.

- The value of the colligative properties are approximately the same for equal concentrations of different nonelectrolytes in solution regardless of the species or chemical nature of the constituents.

- The colligative properties of solutions are: osmotic pressure, vapor pressure lowering, freezing point depression, and boiling point elevation.

- In considering the colligative properties of solid-in-liquid solutions, it is assumed that the solute is nonvolatile and that the pressure of the vapor above the solution is provided entirely by the solvent.

Colligative properties

- The colligative properties of solutions of nonelectrolytes are fairly regular. A 0.1 M solution of a nonelectroyte produces approximately the same colligative properties as any other nonelectrolyte solution of equal concentrations.

- Solutions of electrolytes show apparent “anomalous” colligative properties, that is, they produce a considerably greater freezing point depression and boiling point elevation than do nonelectrolytes of the same concentration.

Lowering of Vapor Pressure, ΔP

- **When a nonvolatile 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 is lowered proportional to the relative number (rather than the weight concentration) of the solute molecules.**

- **Since the solute is nonvolatile, the vapor pressure of the solvent P_1 is identical to the total pressure of the solution P.**

- **It is more convenient to express the vapor pressure of the solution in terms of the solvent.**

Lowering of Vapor Pressure, ΔP

- X_1 is the solvent mole fraction and X_2 is the solute mole fraction

  $X_1 + X_2 = 1$ i.e. $X_1 = 1 - X_2$

  so $P = P_1^\circ (1 - X_2) \rightarrow P_1^\circ - P = P_1^\circ X_2$

thus

$$\frac{P_1^\circ - P}{P_1^\circ} = \frac{\Delta P}{P_1^\circ} = X_2 = \frac{n_2}{n_2 + n_1}$$

Where ΔP is the lowering of the vapor pressure and $\Delta P/P_1^\circ$ is the relative vapor pressure lowering.

- As $\Delta P/P_1^\circ$ depends only on the number of solute molecules, it is considered as a colligative property.

Lowering of Vapor Pressure, ΔP

- For dilute solutions ($n_2 << n_1$) so

$$\frac{\Delta P}{P_1^{\circ}} = X_2 = \frac{n_2}{n_1} = \frac{w_2 / M_2}{w_1 / M_1}$$

- When water is the solvent, 1000g = 1L

$$\frac{\Delta P}{P_1^{\circ}} = X_2 = \frac{w_2 / M_2}{1000 / 18.02} = \frac{n_2}{55.5}$$

Thus

$$\frac{\Delta P}{P_1^{\circ}} = X_2 = 0.018\ m$$

where m is the solute molatity
(Why in molality, not in molarity or normality?)

Lowering of Vapor Pressure, ΔP

Q) Calculate the relative vapor pressure lowering at 20°C for a solution containing 171.2 g of sucrose in 1000g of water. The molecular weight of sucrose is 342.3 and the molecular weight of water is 18.02.

Moles of sucrose (n2) = 171.2/342.3= 0.5 mol

Moles of water (n1)= 1000/18.02= 55.5 mol

$\Delta P/P_1° = X2 = 0.5/ (0.5+55.5) = 0.0089.$

Q) For the above question, providing that the vapor pressure of water at 20°C is 17.54 mm Hg. Calculate the vapor pressure when added 171.2 g of sucrose (0.5 mol).

$\Delta P/P_1° = (P_1° - P)/ P_1° = (17.54-P)/17.54=0.0089$

P= 17.38 mmHg