Solutions CC2/GE2 (CU, Chemistry Gen)

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Ideal solution/mixture

- No such thing as an ideal solution
- However, some liquid pairs, when mixed, behave as *nearly ideal*, e.g.,
 - i. benzene & toluene
 - ii. hexane & heptane
- For ideal solution: $\Delta H=0$, $\Delta V=0$ on mixing
- The partial vapor pressure of each component of an ideal solution obeys Raoult's law

Vapour pressure



In equilibrium, number of particles leaving the surface is the same as the number rejoining

The pressure exerted by the fixed no. of particles above the surface on the inner walls of the container is called the saturated vapour pressure(SVP)

- Liq → vapor, ∆H>0 (endothermic)
- Rise in temperature leads to rise in SVP

SVP and boiling point

- A liquid boils when its SVP becomes equal to the external pressure exerted on the liquid
- In an open container at sea level, the external pressure on the liquid is 1 atm
- For water, its SVP becomes equal to 1 atm at 100°C under normal condition
- Variation of external pressure changes boiling point
- SVP of solids are normally very low

Raoult's Law

The partial vapour pressure of a component in a solution at a given temperature is equal to the vapour pressure of the pure component at that temperature multiplied by the mole fraction of the component in the solution.

$$p_i = x_i p_i^0, \sum x_i = 1.$$

The above law holds exactly only for ideal solutions Total vapour pressure $p = \sum p_i$ This is the general case with all the components being volatile

Raoult's Law (simplified form)

• For a two-component solution with non-volatile solute (1-solvent, 2-solute)



• Relative lowering of vapour pressure of solvent is equal to the mole fraction of solute

Vapour pressure-composition diagrams: Ideal solutions



Source: internet

Example



Boiling point-composition curves: Ideal solution

Between two liquids, one with the higher vapour pressure has the lower boiling point



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Source: internet

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Source: internet

Non-ideal solutions

- In ideal solutions, the interaction among the particles is the same as in the respective pure components, *i.e.,* solute-solvent interaction is the same as solute-solute and solvent-solvent interactions
- Thus, the tendency to escape to the vapour phase is the same for the solution and for the pure components
- Non-ideal solutions do not show this kind of behavior, *i.e.*, *show deviations from Raoult's law*

Positive deviation from Raoult's law



Example: Ethyl alcohol-water mixture; maximum vapour pressure at composition with 95.6% ethanol by mass

Negative deviation from Raoult's law



Example: mixture of nitric acid-water

 $H_2O(I) + HNO_3(I) - H_3O^+(aq) + NO_3^-(aq)$

Fractional distillation of an ideal solution



Temperature(B.P.)-composition diagram for non-ideal solutions(min B.P.)



Point 'a' on the diagram corresponds to what is known as an azeotrope or Azeotropic mixture or constant-boiling mixture

Such a mixture can not be separated to the pure components by using Fractional distillation

Temperature(B.P.)-composition diagram for non-ideal solutions(max B.P.)



Source: internet

Fractional distillation: Set up



Immiscible liquids: steam distillation



Total vapour pressure can be taken as the summation of vapour pressures of individual pure components

The 'mixture' boils at a temperature lower than that of either component

For example, a mixture of phenylamine(184°C)+ water(100°C)boils at ~98°C

Problems and...

1. Suggest a method to measure the SVP of water at room temperature ?

2. How does SVP vary with temperature? Explain.

3. Liquids A and B form an ideal solution. If there are 2 moles of A and 8 moles of B and the respective vapour pressures of pure A and B are 10 kPa and 50 kPa, calculate the following:
(i) partial vapour pressures of A and B in the solution
(ii) Total vapour pressure.

4. Which of the following pairs is expected to form an ideal mixture(a) 1-butanol, 2-butanol (b) Ethanol, hexane

5. A non-ideal solution shows a large positive deviation from ideal behavior. Predict whether the mixing process is endo or exothermic.

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6. Diethyl ether (M.W. 74) has a vapour pressure of 442 mm at 20°C. When 6.0 g benzoic acid is dissolved in 50 g of ether the vapour pressure becomes 410 mm at 20°C. Calculate the molecular weight of benzoic acid.

7. 1% solution (w/w) of aniline in ether (M.W. = 74) shows a relative lowering of vapour pressure of 0.0075. Calculate the Molecular Weight of aniline.

8. Determine the vapour pressure of a 5% solution of water in glycerol at 100°C. Neglect vapour pressure of glycerol (M.W. 92.1).

Nernst Distribution/Partition Law

A solute distributes itself between two liquid phases in such a manner that the ratio of its concentrations is constant irrespective of the absolute amount of the solute or the solvents.

If C_1 and C_2 are the concentrations of the solute in the two phases, then, according to Nernst distribution law: $C_1/C_2 = K$, where K is denoted as the distribution or partition coefficient. Example: Iodine in water and chloroform, oxalic acid in water+ether.

When the solute is associated in one of the liquid phases, then the law is modified as follows: C_1

$$\frac{C_1}{\sqrt[n]{C_2}} = K$$

E.g., benzoic acid in water-benzene system gets dimerized to a small extent in the benzene layer.

Solvent extraction

Given that partition coefficient of iodine between water and carbon disulphide is 62.5. If 1 L of an aqueous solution containing 1g of I_2 is shaken with 50 ml of CS_2 , find the residual amount of I_2 in water.

Ans: Let, after shaking with CS_2 , w g of iodine goes to CS_2 layer. Then, according to Nernst distribution law,

$$\frac{[I_{2,CS_2}]}{[I_{2,water}]} = 62.5, \ i.e., \ \frac{w/50}{(1-w)/1000} = 62.5$$

Then, w = 0.7576g. So, (1-w) = 0.2424 g.

Phases, Components and Degrees of Freedom

- Phase: physically distinct portion of matter which is homogeneous and uniform in composition and is separable from other parts of the system by disticnt boundary surfaces.
 - a. There can be only one gaseous phase.
 - b. Immiscible liquids form separate phases.
 - c. All the different kinds of solids form different phases(except solid solutions).
- Component: smallest number of independently variable constituents starting from which the composition of each phase can be expressed directly or in the form of a chemical equation.
- Degrees of Freedom(DOF): minimum number of the intensive properties of a system, such as temperature, pressure and concentration, which can completely define the equilibrium of a system.

Phase Rule

 The sum of the number of phases(P) and the DOF(F) of any system exceeds the number of components(C) by two, provided that the only significant external factors acting are T & P.

P+F = C+2 or, F = C-P+2.

• Example: $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$

No. of phases : P = 3; 1 constraint due to chemical equilibrium, so no. of components C = 2. Then F = 2-3+2 = 1. Univariant.