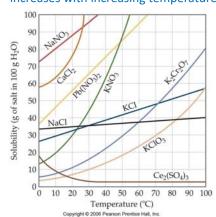
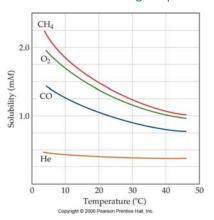
Temperature and Solubility

Solubility of most solid solutes in water increases with increasing temperature



In contrast, solubility of gases in water decreases with increasing temperature

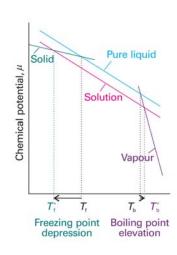


Effect of solute on boiling and melting points of solvent

$$\mu_A = \mu_A^* + RT \ln x_A$$

$$\mu_A = \mu_A^* + RT \ln a_A$$

$$\mu_A = \mu_A^* + RT \ln a_A$$



Raoult's law: solvent + non-volatile solute



Solvent + Solute

(Non-volatile)

The decrease in vapor pressure is directly proportional to the mole fraction of solute in an ideal solution:

$$P=P_A^0x_A$$
,

 x_A = mole fraction of solvent (A)

$$\Delta P = P_A^0 - P = P_A^0 (1 - x_A) = P_A^0 x_B$$

Number of solvent molecules on the surface is less than that was in case of pure solvent therefore, the vapor pressure of the final solution is lower than that of the pure solvent.

Because of solute-solvent intermolecular attractions, higher concentrations of nonvolatile solutes make it harder for solvent to escape to the vapour phase.





(b)

Henry's Law

The vapour pressure of a solute, P_2 , in a solution in which the solute has a mole fraction of x_2 is given by:

$$P_2 = x_2 P_2 *$$

where P_2^* is the vapour pressure of the solute in a pure liquefied state.

> It is also found that at the limits of infinite dilution, the vapour pressure of the solute obeys Henry's law.

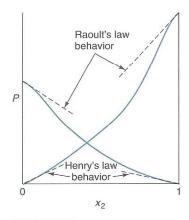


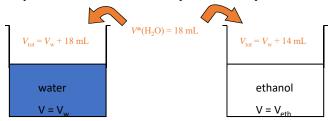
FIGURE 5.11
A hypothetical binary liquid mixture exhibiting negative deviation from Raoult's law, showing regions where Henry's and Raoult's laws are obeyed.

Partial Molar Quantities

- > The method using partial molar quantities enables us to treat nonideal solutions. In this method we consider the changes in the properties of the system as its compositions change by adding or subtracting.
- ➤ The thermodynamic quantities, such as U, H, and G, are extensive functions and they depend on the P and T. For example, $G = G(P, T, n_1, n_2, n_3, ...)$.

Partial Molar Volume

➤In this treatment, the volume is used as starting point to lead to the thermodynamic functions in terms of partial molar quantities.



The volume occupied by H₂O molecules added is dependent on the nature of surrounding molecules.

5

Thermodynamics of Simple Mixtures

Partial Molar Volume

1 mol of water added to a huge volume of water increases the volume by 18 cm³. V_m =18 cm³/mol

1 mol of water added to a huge volume of *ethanol* increases the volume by 14 cm^3 . $V_m = 14 \text{ cm}^3/\text{mol}$

$$\begin{split} V_i = & \left(\frac{\partial V}{\partial n_i}\right)_{p,\,T,\,n_{j \neq i}} \quad \textit{Partial Molar Volume} \qquad \textit{Can be +ve, -ve, or 0!} \\ dV = & \left(\frac{\partial V}{\partial n_i}\right)_{p,\,T,\,n_B} dn_A \ + \left(\frac{\partial V}{\partial n_i}\right)_{p,\,T,\,n_A} dn_B \ = V_A dn_A \ + V_B dn_B \\ V = & \int_0^{n_A} V_A dn_A \ + \int_0^{n_B} V_B dn_B \ = V_A n_A \ + V_B n_B \\ G_{p,T} = & n_1 \mu_1 + n_2 \mu_2 + \dots = \sum_i n_i \mu_i \end{split}$$

3

Gibbs-Duhem Equation

$$G_{p,T} = n_1 \mu_1 + n_2 \mu_2 + \dots = \sum_i n_i \mu_i$$

$$dG_{p,T} = \sum_i \mu_i dn_i + \sum_i n_i d\mu_i$$

$$dG_{p,T} = \sum_{i} \mu_{i} dn_{i}$$
 At thermal and mechanical equilibrium.

At constant p and T

$$\sum_i n_i d \mu_i = 0$$
 Gibbs-Duhem Equation

For a binary mixture, $n_1 d\mu_1 + n_2 d\mu_2 = 0$

Hence, $d\mu_1 = -(n_2/n_1) d\mu_2$

If $n_2 > n_1$, a small change in μ_2 causes a large change in μ_1

Chemical potential of one component of a mixture can not change independently of the chemical potentials of other components.

Phase transformations (phase separation) in the systems with a *single* type of particles. Consequences: the energy of intermolecular interactions is the same for all the molecules, and the entropy is reduced because of the indistinguishability of particles.

The behavior of a system becomes more complicated when the system contains two or more types of particles (mixtures). A mixture is homogeneous when its constituents are intermixed on the atomic scale (it is also called a solution).

A mixture is *heterogeneous* when its contains two or more distinct phases, such as oil and water that do not mix at normal T, each phase has different concentrations of intermixed atoms/molecules (phase separation).

Difference from chemical compounds: concentrations of components are not mutually fixed, they can vary over a wide range. However, interactions between molecules do play an important part in forming a mixture.

For example, forming a mixture usually leads to releasing or absorbing some heat (typically, this energy is only an order of magnitude less than the heat released in chemical reactions).

Also, the volume of a mixture may differ from the sum of volumes of starting compounds (e.g., mixture of water and ethanol has a smaller volume than the sum of starting volumes).

Our goal is to find out how the free energy minimum principle governs the behavior of mixtures.

The complexity of phase diagrams for multicomponent systems is limited by the "Gibbs' phase rule". This restriction on the form of the boundaries of phase stability applies also to single-component systems.

Consider a mixture of ${\it k}$ components, and assume that the mixture consists of ${\it k}$ different phases. For a multi-component system, the # of different phases might be > 3 (these phases might have different *concentrations* of components).

At equilibrium, $T_1 = T_2 = ... = T$ and $P_1 = P_2 = ... = P$ the values of chemical potential for **each** component must be the same in **all** phases:

$$\begin{array}{c} x_1^I + x_2^I + \ldots + x_k^I = 1 \\ x_1^N + x_2^N + \ldots + x_k^N = 1 \end{array} \} \quad \textbf{\textit{N}} \text{ equations} \qquad \begin{array}{c} \text{(in each phase, the sum of all } \\ \text{concentrations = 1)} \end{array}$$

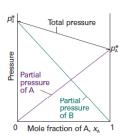
The lower index refers to a component, the upper index – to the phase. Each phase is specified by the concentrations of different components, $\mathbf{x_i^j}$. The total number of variables: Nk,+2 equations: k(N-1)+N In general, to have a solution, the # of equations should not exceed the # of variables. Thus: $N \leq k+2$

For a *single-component* system (k=1), either *two or three phases are allowed to be in equilibrium* (but not four). Coexistence of three phases – the triple point.

Raoult's Law

$$\frac{p_A}{p_A^*} = x_A$$
$$p_A = x_A p_A^*$$

The ratio of partial vapor pressure of each component to its vapor pressure as a pure liquid is equal to the mole fraction A in the liquid mixture (x_A) .



<u>Ideal solutions</u> obey Raoult's law for the entire range of mole fraction, from pure A to pure B

Fig. 5.11 The total vapour pressure and the two partial vapour pressures of an ideal binary mixture are proportional to the mole fractions of the components.

$$\mu_{A,l} = \mu_{A,l}^* + RT \ln x_A$$

$$\mu_{B,l} = \mu_{B,l}^* + RT \ln x_B$$

For ideal solution - solvent & solute both obey Raoult's law

$$p_A < p_A^*$$

$$\mu_{A,l} < \mu_{A,l}^*$$

The vapor pressure (and chemical potential) of the solvent in the solution is lower than that of the pure solvent

Total VP of an ideal solution

$$\mu_{A} = \mu_{A}^{*} + RT \ln \frac{P_{A}}{P_{A}^{*}}$$

$$P_{A} = x_{A}P_{A}^{*}$$
This serves to define an ideal solution if true for all values of x_{A}

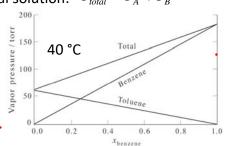
$$\mu_{A} = \mu_{A}^{*} + RT \ln x_{A}$$

The total vapor pressure of an ideal solution: $P_{total} = P_A + P_B$

$$P_{total} = x_A P_A^* + x_B P_B^*$$

$$P_{total} = P_A^* + x_B (P_B^* - P_A^*)$$

Liquids A and B form an ideal solution. At 45 $^{\circ}$ C, the vapour pressures of pure A and Pure B are 66 Torr and 88 Torr respectively. Calculate the composition of the vapour in equilibrium with a solution containing 36 mole percent of A at this temperature.



Sample Problem

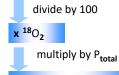
Applying Dalton's Law of Partial Pressures

PROBLEM:

In a study of O_2 uptake by muscle at high altitude, a physiologist prepares an atmosphere consisting of 79 mol% N_2 , 17 mol% $^{16}O_2$, and 4.0 mol% $^{18}O_2$. (The isotope ^{18}O will be measured to determine the O_2 uptake.) The pressure of the mixture is 0.75 atm to simulate high altitude. Calculate the mole fraction and partial pressure of $^{18}O_2$ in the mixture.

Find the $x_{18}_{O_2}$ and $P_{18}_{O_2}$ from P_{total} and mol% $^{18}O_2$.

mol% $^{18}O_2$ SOLUTION: $x_{18}_{O_2} = \frac{4.0 \text{ mol}\% \, ^{18}O_2}{100}$

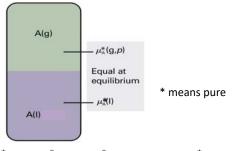


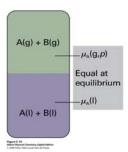
 $P_{18} = X_{18} = X_{18} = 0.040 \times 0.75 \text{ atm}$ = 0.030

= 0.040

partial pressure P

Chemical Potential of Liquids: Ideal Solutions





$$\mu_{A,l}^* = \mu_{A,g}^* = \mu_{A,g}^0 + RT \ln p_A^* \qquad \mu_{A,l} = \mu_{A,g}^0 + RT \ln p_A$$

$$\mu_{A,g}^0 = \mu_{A,l}^* - RT \ln p_A^* \qquad \mu_{A,l} = \mu_{A,l}^* - RT \ln p_A^* + RT \ln p_A$$

$$\mu_{A,l} = \mu_{A,l}^* - RT \ln p_A^* + RT \ln p_A$$

$$\mu_{A,l} = \mu_{A,l}^* + RT \ln \frac{p_A}{p_A^*}$$

 $\mu_{A,l} = \mu_{A,l}^* + RT \ln \frac{p_A}{p_A^*} \qquad p_A^* \text{ vapour pressure of Pure A(I)} \\ p_A \text{ vapour pressure of A(I) in a mixture}$

Relationship between ratio of vapor pressures and composition of liquid.

Ideal-Dilute Solutions

Henry's Law: In dilute solution, for solute, B

 $p_{\scriptscriptstyle B} \propto x_{\scriptscriptstyle B}$ but p

 $p_B = x_B K_B$

solute, b

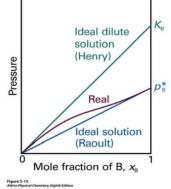
For practical applications $p_{\scriptscriptstyle B}=b_{\scriptscriptstyle B}K_{\scriptscriptstyle B}$ $b_{\scriptscriptstyle B}$ = molality of ${\scriptscriptstyle B}$

 K_B = Empirical constant (dimension of p) called Henry's law constant

Solutions in which solvent obeys Raoult's law and solute obeys Henry's law is an <u>Ideal-Dilute</u> solution

 $\mu_{B} = \mu_{B}^{*} + RT \ln(p_{B} / p_{B}^{*})$ $= \mu_{B}^{*} + RT \ln(x_{B}K_{B} / p_{B}^{*})$ $= \mu_{B}^{*} + RT \ln(K_{B} / p_{B}^{*}) + RT \ln x_{B}$ $= \mu_{B}^{0} + RT \ln x_{B}$

if $p_B^* = K_B \implies \mu_B^0 = \mu_B^*$



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Real Solutions: (Activity, the effective mole fraction)

The Solvent Activity

$$\mu_A = \mu_A^* + RT \ln \frac{p_A}{p_A}$$

For ideal solution (Raoult's law)

$$\mu_A = \mu_A^* + RT \ln x_A$$

$$\mu_A = \mu_A^* + RT \ln a_A$$

$$a_A = \frac{p_A}{p_A^*}$$

$$a_A = x_A$$
 as $x_A \to 1$

$$a_A = \gamma_A x_A \; ; \; \gamma_A \to 1 \quad \text{as} \quad x_A \to 1$$

 γ_A is activity coefficient

The Solute Activity:

$$\mu_B = \mu_B^* + RT \ln \frac{p_B}{p_B^*}$$

For Ideal Dilute Solution (Henry's law)

$$\mu_B = \mu_B^0 + RT \ln x_B$$

For real solutions,

$$\mu_B = \mu_B^0 + RT \ln a_B$$

$$a_B = \gamma_B x_B$$

$$a_B \to x_B$$
 and $\gamma_B \to 1$ as $x_B \to 0$

Ideal Solution

$$\mu_i(T) = \mu_i^*(T) + RT \ln x_i$$

* means pure

Ideal-Dilute Solutions

$$\mu_A(T) = \mu_A^*(T) + RT \ln x_A$$
A= Solvent,

$$\mu_B(T) = \mu_B^0(T) + RT \ln x_B$$

$$\mu_B(T) = \mu_B^0(T) + RT \ln b_B$$

⁰ means Standard

Real Solutions

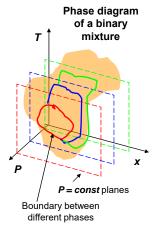
For solute

$$\begin{bmatrix} \mu_B = \mu_B^0 + RT \ln a_B \end{bmatrix} \begin{bmatrix} a_B = \gamma_B b_B ; & \gamma_B \to 1 \text{ as } b_B \to 0 \end{bmatrix}$$
$$\begin{bmatrix} \mu_A = \mu_A^* + RT \ln a_A \end{bmatrix} \begin{bmatrix} a_A = \gamma_A x_A ; & \gamma_A \to 1 \text{ as } x_A \to 1 \end{bmatrix}$$

$$\overline{\mu_A = \mu_A^* + RT \ln a_A} \boxed{a_A = \gamma_A x_A \; ; \; \gamma_A \to 1 \text{ as } x_A \to 1}$$

Binary Mixtures

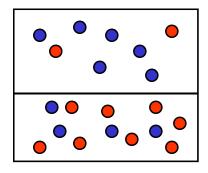
- (a) A binary mixture consists of two types of molecules, A and B, x is the fraction of B molecules (if the particles are atoms, and not molecules, the mixture is called an alloy.) The phase diagram for such a system (in comparison with the phase diagram for a single-component system) has an extra dimension x.
- **(b)** We assume that the process of mixing accurs at fixed **T,P** within a fixed volume **V**. In this case, it does not matter which free energy we minimize both **F** and **G** work equally well.



$$G = U + PV - TS$$
$$F = U - TS$$

$$\Delta F = \Delta U - T \Delta S$$

A miixture will seek the state of equilibrium by minimizing this combination of its *internal energy* and *entropy*.



Liquid contains

1 mol A () and

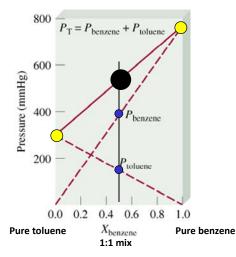
1 mol B ()

P_A° = 10kPa;P_B° = 30kPa

Composition of liquid: $X_A = 0.5$; $X_B = 0.5$

Composition of vapour?

Partial pressure of A = $10 \times 0.5 = 5$ kPa Partial pressure of B = $30 \times 0.5 = 15$ kPa Total vapour pressure = 5 + 15 = 20 kPa mole fraction of A in vapour = 5/20 = 0.25mole fraction of B in vapour = 15/20 = 0.75 If both components of the solution are volatile, the vapor pressure of the solution is the sum of the individual partial pressures.



$$P_{A} = X_{A} P_{A}^{0}$$

$$P_{B} = X_{B} P_{B}^{0}$$

$$P_{T} = P_{A} + P_{B}$$

$$P_{T} = X_{A} P_{A}^{0} + X_{B} P_{B}^{0}$$





Strength of Intermolecular attraction in pure A Strength of Intermolecular attraction in pure B Strength of Intermolecular attraction between particle A and particle B in mixture

Ideal solutions - existence only holds for <u>very dilute solutions</u>.

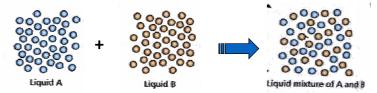
- the escape tendency of molecule A or B in mixture equals to their respective escape tendency in pure A and pure B
- ===> no enthalpy change upon mixing
- ===> no volume change upon mixing
- · Reasons: interaction doesn't change upon mixing
- more nearly alike the two substances are chemically, the more nearly they exhibit ideal behaviour
- non-ideal solutions
- mixtures of liquids having dissimilar structures
 - have marked deviations from the linear boiling point - composition relationship

Deviations from Raoult's Law

- Non-ideal Solution
 - How about those liquid mixtures do not obey Raoult's law??
 - ===> Non-ideal Solution
 - 1) Solution with positive deviation from Raoult's Law
 - 2) Solution with negative deviation from Raoult's Law

Positive Deviation from Raoult's Law

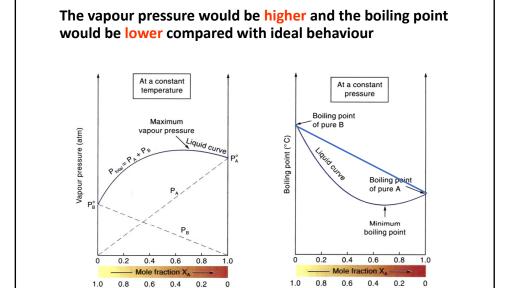
- Occurs when P_t > that is predicted by Raoult's law i.e. $P_A > x_A P_A^{\circ}$ & $P_B > x_B P_B^{\circ}$ ===> $P_t > x_A P_A^{\circ} + x_B P_B^{\circ}$
- Molecules A & B in the mixture escape from the liquid surface more easily than that expected for an ideal mixture.



Average

Mole fraction X

Strength of Intermolecular attraction in pure A Strength of Intermolecular attraction in pure B Strength of
Intermolecular
attraction between
particle A and
particle B in mixture

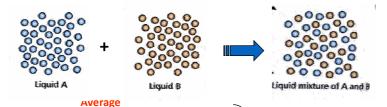


Example: Binary mixture of cyclohexane and ethanol

- the interaction is now weaker after mixing the solution
- ===> escape tendency of molecule is higher
- ===> P_t is greater than expected
- ===> enthalpy change is endothermic
 Energy(breaking interaction between molecules in pure solution) >
 Energy(formation of new interaction between 2 kinds of molecules in mixture)
- ===>Volume expansion
 weaker attraction between molecules in the mixture
 => intermolecular distance increase

Negative Deviation from Raoult's Law

- Occurs when P_t < that predicted by Raoult's law i.e. $P_A < X_A P_A{}^o$ & $P_B < X_B P_B{}^o$ ===> $P_t < X_A P_A{}^o + X_B P_B{}^o$
- Molecules A & B in the mixture has a lower escape tendency from the liquid surface compared with that of ideal mixture.



Strength of Intermolecular attraction in pure A

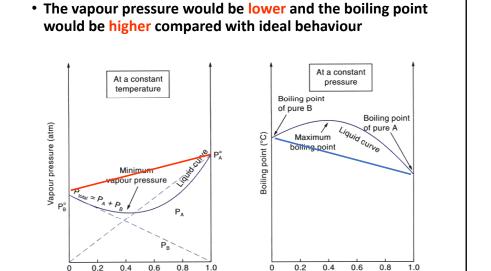
0.8

0.6

0.4

0.2

Strength of Intermolecular attraction in pure B Strength of
Intermolecular
attraction between
particle A and
particle B in mixture



0.8

0.6

0.2

0

0.4

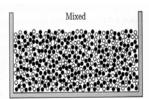
Example: mixture of ethyl ethanoate & trichloromethane

Strong hydrogen bonding in the mixture

- the interaction is now stronger after mixing the solution
- ===> escape tendency of molecule is lower
- ===> P_t is lower than expected
- ===> enthalpy change is exothermic
 Energy(breaking interaction between molecules in pure solution)
 Energy(formation of new interaction between 2 kinds of molecules in mixture)
- ===>Volume contraction stronger attraction between molecules in the mixture => intermolecular distance decrease

Interaction Energy in Binary Mixtures

Assume that the mixture is in a solid state, both species share the same lattice structure. Consider N_A atoms of species A and $N_B = N - N_A$ atoms of species B ($x = N_B/N$).



Each atom has **p** nearest neighbours

Let u_{AA} , u_{AB} , u_{BB} represent the bond energy between A-A, A-B, and B-B pairs, respectively.

On average, an A atom is involved in p(1-x) interactions of A-A type and px interactions of A-B type.

The average interaction energy per **A** atom:

$$u_A = p(1-x)u_{AA} + pxu_{AB}$$

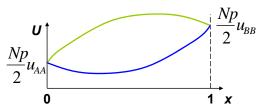
The average interaction energy per **B** atom:

$$u_B = p(1-x)u_{AB} + pxu_{BB}$$

The total interaction energy: $U = \frac{1}{2} \big[N_A u_A + N_B u_B \big]$ $= \frac{N}{2} \big[(1-x)u_A + xu_B \big]$ $= \frac{Np}{2} \big[(1-x)^2 u_{AA} + 2x(1-x)u_{AB} + x^2 u_{BB} \big]$

(the factor ½ corrects the fact that each bond has to be counted once)

The overall shape of U(x) depends on the interactions between different species:



Ideal and Non-Ideal Mixtures

Ideal mixtures – the molecules **A** and **B** are of the same size and interactions **A-A**, **A-B**, and **B-B** are identical

 $u_{AA} = u_{AB} = u_{BB} = u$

$$U = \frac{Np}{2} \left[(1-x)^2 u_{AA} + 2x(1-x)u_{AB} + x^2 u_{BB} \right]$$

$$U_{ideal} = \frac{Np}{2}u$$



does not depend on \boldsymbol{x}

In **real** (**non-ideal**) **mixtures** of liquids and solids, the interactions **A-A**, **A-B**, and **B-B** might be very different

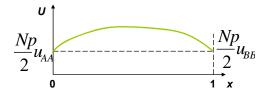
(e.g., the water and oil molecules: water molecules carry a large dipole moment that leads to a strong electrostatic attraction between water molecules; in oil molecules this dipole moment is lacking).

To be specific, consider the case of a non-ideal mixture when *unlike molecules are less attracted to each other* than are like molecules

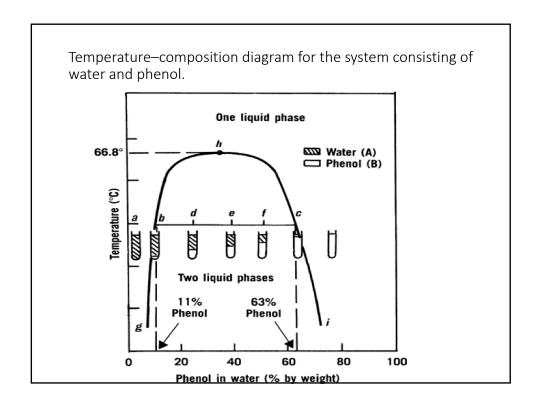
$$(u_{AB} > u_{AA} = u_{BB})$$

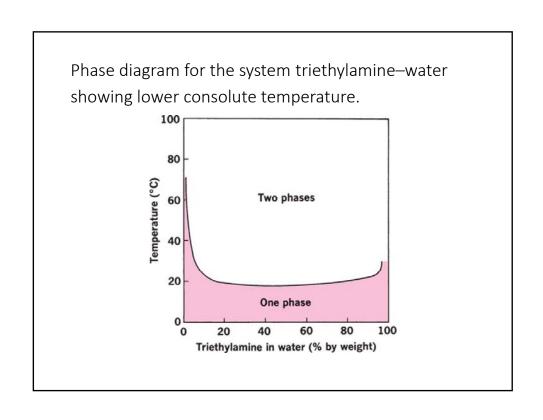
Mixing of the two substances *increases* the total energy. (Note the sign of *u:* it's negative for attraction)

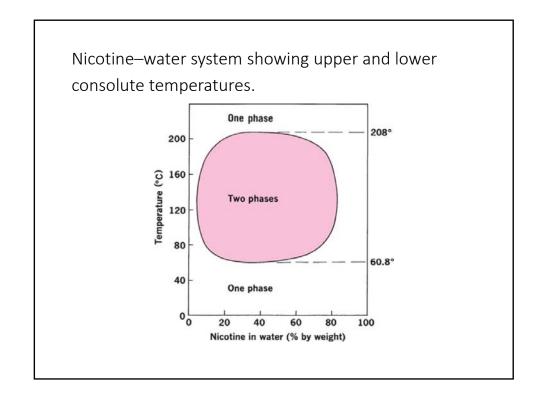
$$U = \frac{Np}{2} \left[(1 - x)^2 u_{AA} + 2x(1 - x) u_{AB} + x^2 u_{BB} \right]$$

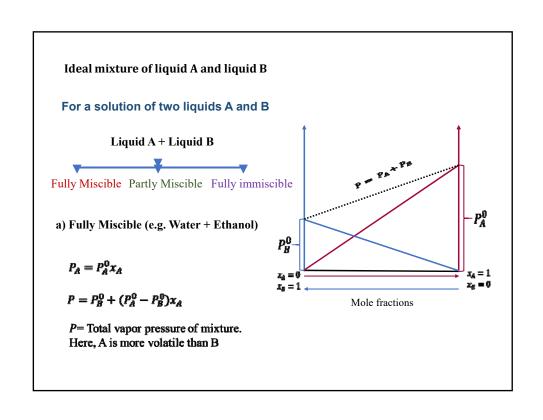


The fact that *U* has an upward bulge will have important consequences for phase separation in this mixture.



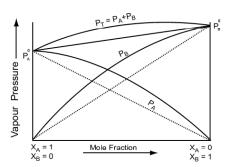






a) Positive deviation from Raoult's law

Here total vapor pressure for any mole fraction is more than what is expected according to Raoult's law.



This happens when the new interactions are weaker than the interaction in the pure component i.e. A-A or B-B interactions are much stronger than A-B interactions.

 $\Delta H = + ve$, $\Delta V = + ve$

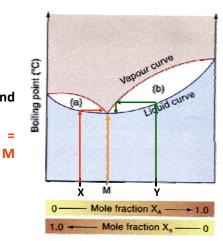
Example: Ethanol + Water; Acetone + Ethanol

Positive Deviation from Raoult's Law

Liquid mixtures which deviate positively from Raoult's law show a minimum in the boiling point-composition curve

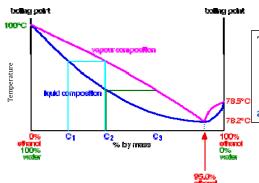
- Start from X, distillate and residue?
- Distillate =
 Azeotropic mixture M

 Residue = pure B
- Start from Y, distillate and residue?
- Distillate
 Azeotropic mixture
 Residue = pure A
- start from M, distillate and residue?
- Azeotropic mixture M



Boiling point vs composition diagram

A high vapour pressure means a low boiling point



The liquid curve and the vapour curve meet at constant boiling point where the vapour composition is exactly the same as the liquid. It is known as a constant boiling mixture or an

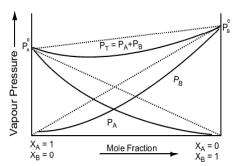
azeotropic mixture or an azeotrope.

- \triangleright At composition C_1 , mixture will boil at a temperature given by the liquid curve and produce a vapour with composition C_2 which is richer in water.
- After condensation at C2 if we reboil the mixture it will produce a vapour with composition C₃ which is richer in ethanol.

This is very useful to separate pure solvent from a mixture of binary liquids by distillation process.

b) Negative deviation from Raoult's law

Here total vapor pressure for any mole fraction is less than what is expected according to Raoult's law.

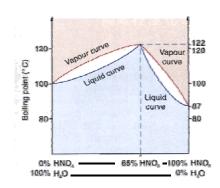


This happens when the new interactions are Stronger than the interaction in the pure component i.e. A-A or B-B interactions are much weaker than A-B interactions.

 $\Delta H = -ve$, $\Delta V = -ve$

Example: Nitric acid + Water; Chloroform + benzene

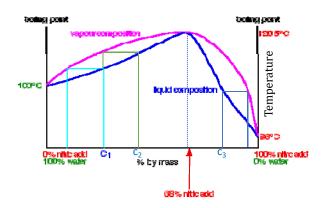
- a) A constant boiling mixture (azeotropic mixture) is a mixture of liquids with a fixed composition and it cannot be separated by fractional distillation since the vapour composition is the same as the liquid composition.
- b) b.p. composition diagram for HNO₃ water mixture



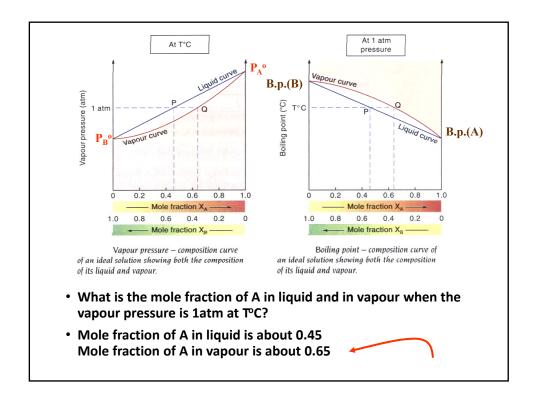
- c)According to the diagram, it is known that the mixture deviates negatively from Raoult's Law. There will be a stronger attraction between molecules in the mixture. When nitric acid is added to water, there is an evolution of heat. That means the reaction is exothermic. Moreover, there is a reduction is volume when nitric acid and water are mixed.
- d) Raoult's Law states that the partial vapour pressure of a component in a mixture is directly proportional to its mole fraction, and is equal to the product of its mole fraction and the vapour pressure of the pure component at that temperature.

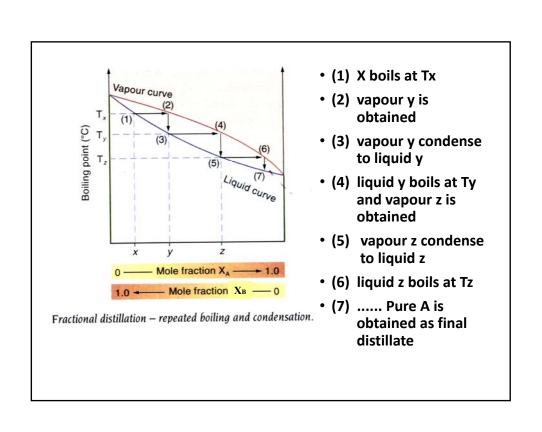
- e) The total vapour pressure above the nitric acid water mixture is less than the predicted value based on the ideal behaviour. It shows a negative deviation from Raoult's law meaning that there is less tendency for the molecules to escape from the solution than from the pure liquids.
- f) The temperature of the mixture would rise gradually until it reaches 122°C. The residual mixture is more concentrated in nitric acid as water is distilled off until its composition is 65% by mass of nitric acid.

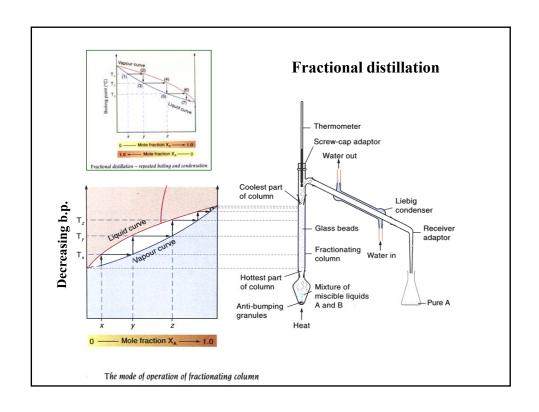
Low vapor pressure implies a high boiling point.

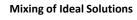


- At composition C₁ The vapor produced is richer in water than the original acid. If you condense the vapor and reboil it, the new vapor is even richer in water.
- At C₃, The vapor formed is richer in nitric acid. If we continue to do the condensation and reboil this all the way up the fractionating column, we can get pure nitric acid









$$G_{\rm i}=n_A\mu_A^*+n_B\mu_B^*$$

$$\Delta G_{mix} = nRT \sum_{i} x_{i} \ln x_{i}$$

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$$\Delta S_{mix} = -nR \sum_{i} x_{i} \ln x_{i}$$

$$\Delta H_{mix} = 0$$

$$\Delta H_{\text{min}} = 0$$

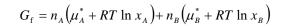
$$\Delta V_{mix} = \left(\frac{\partial \Delta G_{mix}}{\partial p}\right)_{T} = 0$$

Mixing of Real Solutions (excess functions)

$$S^{E} = \Delta S_{mix} - \Delta S_{mix} (ideal)$$

Excess entropy

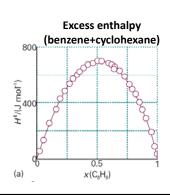
 $Interaction_{AB} < Interaction_{AA}$ $Interaction_{AB} < Interaction_{BB}$



Ideal solution - Raoult's law

Leading to ideal solution, similar to mixing of ideal gases.

 $Interaction_{AB} = Interaction_{AA} = Interaction_{BB}$

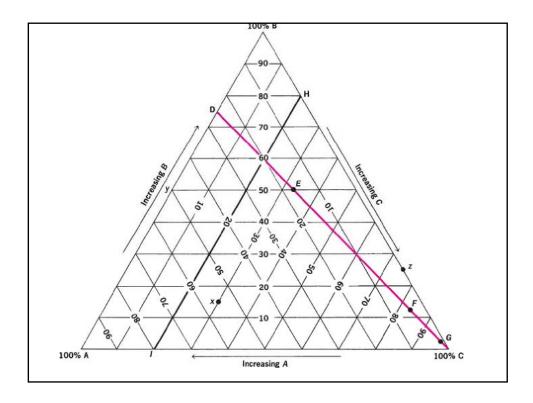


Three-Component Systems

- In systems containing three components but only one phase, F = 3 - 1 + 2 = 4 for a noncondensed system.
- The four degrees of freedom are temperature, pressure, and the concentrations of two of the three components.
- Only two concentration terms are required because the sum of these subtracted from the total will give the concentration of the third component.

Rules Relating to Triangular Diagrams

- The concentrations in ternary systems are expressed on a weight basis.
- Each of the three corners of the triangle represent 100% by weight of one component (A, B, or C).
- that same apex will represent 0% of the other two components.



Ternary Systems with One Pair of Partially Miscible Liquids

- Water and benzene are miscible only to a slight extent, a mixture of the two usually produces a twophase system.
- The heavier of the two phases consists of water saturated with benzene, while the lighter phase is benzene saturated with water.
- On the other hand, alcohol is completely miscible with both benzene and water.
- the addition of sufficient alcohol to a two-phase system of benzene and water would produce a single liquid phase in which all three components are miscible.

