CHM 204: PHYSICAL CHEMISTRY-II

EQILIBRIUM AND NON EQUILIBRIUM THERMODYNAMICS

TOPICS : Properties of non-ideal solutions, thermodynamic functions of mixing of non-ideal solutions & excess functions.

Reference books:

1. An Introduction to Chemical Thermodynamics: By R.P Rastogi & R.R Mishra

2. Principles of Physical Chemistry: By Puri, Sharma & Pathania

Non-Ideal Solutions

The solutions which do not obey Raoult's Law are called non-ideal solutions. In such solutions, the molecules of the constituents interact with each other and such solutions do not obey additivity rule.

In non-ideal solutions, inter-molecular ~~attractions~~ interactions of components in the solution are different, than that in pure components. Thus such solutions, show deviations from Raoults Law.

[If the unlike intéractions A–B are different from the like intéractions A–A, B–B, in a solution it is said to be a non ideal solution]

Characteristics of Non-ideal Solutions.

(1) Non ideal solutions show deviations from Raoult's Law.

(2) The activity of component in the solution is not equal to its mole fraction. That is

$$a_i \neq x_i$$

(3) They show volume-change after mixing, that is, there may be compression or expansion in dissolution. Hence the volume-change of mixing is not zero.

$$\Delta V_{mixing} \neq 0 \qquad (40ml + 25ml \neq 60ml)$$

(4) During the mixing of components, heat effects are observed. Heat may be evolved or absorbed. Hence enthalpy change of mixture is not zero.

$$\Delta H_{mixing} \neq 0.$$

Deviations from Ideal Behaviour (or Raoult's Law)

For Non-ideal solutions

$$a \propto c \qquad (a = \text{activity}, C = \text{concentration})$$

or $$a = \gamma C$$

where γ is called activity coefficient. The concentration can be expressed in terms of mole fraction (X), molality (m), molarity (M) etc. Hence we can write for a component i

$$a_i = \gamma_i x_i \qquad \text{—(1)}$$

Therefore, the chemical potential of a component i in a non-ideal solution is given by:

$$\mu_i = \mu_i^0 + RT \ln a_i$$

or $$\mu_i = \mu_i^0 + RT \ln (\gamma_i x_i) \qquad \text{——(2)}$$

Negative Deviations from Raoult's Law in case of Non-ideal solutions

Causes:

The negative deviations from Raoult's Law in case of non-ideal solutions are due to various factors,

causes:

(i) If the different kinds of molecules (A-B) in the solutions are mutually attracted with a greater force (due to solvation, formation of hydrogen bond, formation of a chemical compound) than molecules of same kind (A-A or B-B), then this hinders the transition of the molecules from the liquid phase to the gaseous phase (in comparision with the pure liquids), and negative deviations from Raoult's Law will be observed. As a result of stronger interactions (forces) of different kinds of molecules, the heat of mixing of the components will be negative. That is

$$\Delta H_{mixing} = -ve \quad \text{or} \quad \Delta H_{mixing} < 0$$

Also, the volume change of mixing is negative.

$$\Delta V_{mixing} = -ve \quad \text{or} \quad \Delta V_{mixing} < 0$$

Thus the sign of deviation (ie, negative sign) from Raoult's Law and the signs of heat of mixing and volume of mixing coincide in general case. Such a coincidence is observed, as a rule.

(ii) Examples: The liquid pairs showing such behaviour are.

(a) water + nitric acid.

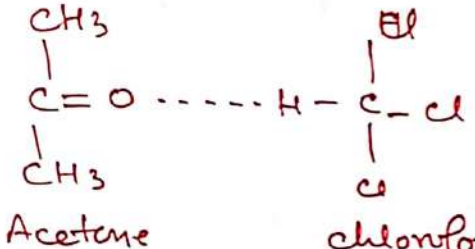
(b) toluene + acetic acid

(c) acetone + chloroform

(d) pyridine + acetic acid, etc.

(e) chloroform + benzene → specific interaction is weak hydrogen bond between the H atom of chloroform and the π-electrons of benzene.

(f) chloroform + methyl ether



Acetone chloroform

(iii) **Pressure - Composition Diagram:** The total and partial vapour pressures are plotted against composition. The dotted lines represent the ideal behaviour, in accordance with Raoult's Law, whereas solid lines are result of experimental measurements.

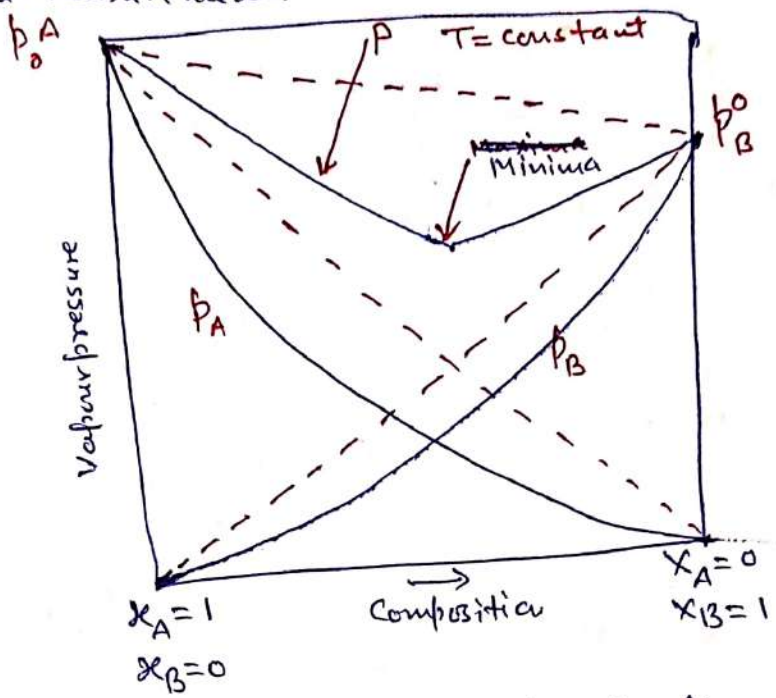


Fig: vapour pressure - composition diagram for non-ideal solution, showing negative deviation from Raoult's Law.

From the above Diagram the following conclusions may be drawn.

(a) The vapour pressures of individual components in solution are lower than the ideal vapour pressure. That is:

(i) For ideal behaviour $p_A = p_A^0 x_A$ and $p_B = p_B^0 x_B$ (represented by dotted lines)

(ii) but the experimental results in non-ideal solution (negative deviation) show that

$p_A < p_A^0 x_A$ and $p_B < p_B^0 x_B$ (represented by Solid lines)

(b) The total vapour pressure of the solution (P) is lower than the sum p_A and p_B. That is

$P < (p_A + p_B)$

or $P < (p_A^0 x_A + p_B^0 x_B)$

} while in case of ideal solution $P = p_A + p_B = p_A^0 x_A + p_B^0 x_B$

(c) Vapour pressure of the solution (P) at the minimum point is less than vapour pressure of either constituent in pure state, That is, at minimum point

$P < p_A^0$ and $P < p_B^0$.

Positive Deviations from Raoult's Law:

(I) **Causes:** The positive deviations of non-ideal solutions from Raoult's Law are due to various factors.

"If the different kinds of molecules (A–B) in the solution are mutually attracted with a smaller force than molecules of the same kind (A–A and B–B), then it facilitates the transition of molecules from the liquid phase to gaseous phase (in comparision with pure liquids) and positive deviations from Raoult's Law will be observed.

The process of the mutual removal of homogeneous molecules (A–A or B–B) in the formation of a solution (containing only A–B) is accompanied by absorption of heat, and therefore the heat of mixing of pure components will be positive and volume change of mixing will also be positive. That is

$\Delta H_{mixing} = +ve$ $\quad \Delta H_{mixing} > 0$

$\Delta V_{mixing} = +ve$ $\quad \Delta V_{mixing} > 0.$

The liquid pairs showing positive deviations from Raoult's Law must differ in:

(a) polarity

(b) length of the hydrogen chain

(c) internal pressure, or

(d) when either of the components happens to be associated in liquid state.

The magnitude of positive deviations depends on the difference between the liquids, in the above characteristics. Thus in some cases the deviations are small but in many cases the deviations are appreciable.

(II) **Examples:** The liquid pairs showing positive deviations from Raoult's Law are:

(a) acetone + carbondisulphide ($CH_3COCH_3 + CS_2$)

(b) acetone + ethylalcohol ($CH_3COCH_3 + CH_3CH_2OH$)

(c) benzene + acetone ($C_6H_6 + CH_3COCH_3$)

(d) benzene + CCl_4 ($C_6H_6 + CCl_4$)

(e) $CCl_4 + CHCl_3$ ($CCl_4 + CHCl_3$)

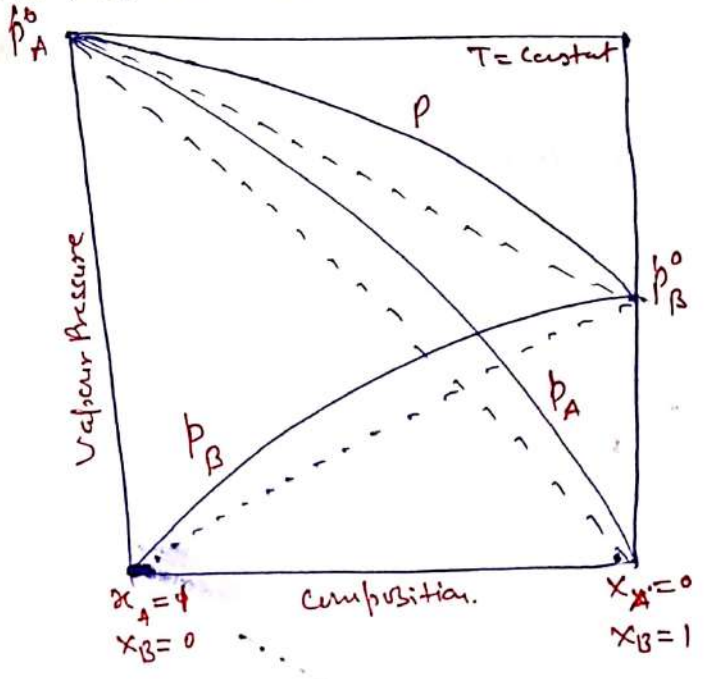
(f) $CCl_4 + C_6H_5CH_3$ ($CCl_4 + C_6H_5CH_3$)

(g) $C_2H_5OH + (C_2H_5)_2O$, ($C_2H_5OH + (C_2H_5)_2O$)

(iii) Vapour Pressure - Composition Diagram: Positive deviations are of two types:

(a) Small positive Deviations

At any composition of the solution, the total vapour pressure is somewhat higher than the value obtained by applying Raoult's Law. The vapour pressure composition diagram in this case is shown below



Ideal solutions showing small positive Deviations from Raoult's Law.

From this diagram, the following conclusions may be drawn.

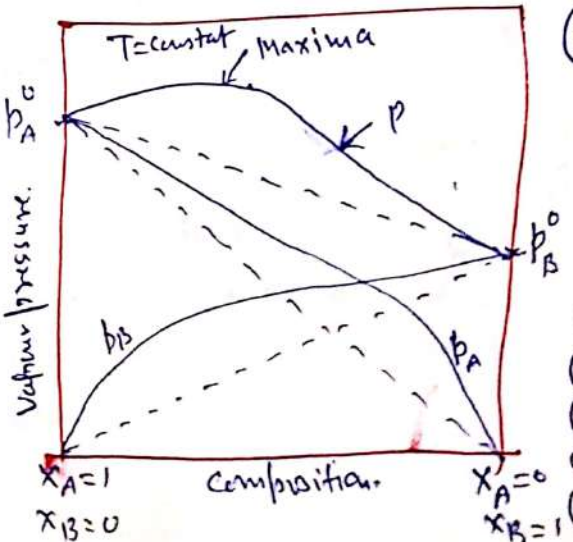
(1) The total vapour pressure (P) of the solution is somewhat higher than the additive vapour pressures $(p^0_A x_A + p^0_B x_B)$ ~~but at no point does it exceed the vapour pressure of either of the components~~.

(2) The partial vapour pressures of individual components (p_A or p_B) also show positive deviations.

(3) The examples are $H_2O + CH_3OH$; $C_6H_6 + C_6H_5CH_3$ etc.

(b) Appreciable Positive Deviation showing a Maximum:

The variation of vapour pressure with composition is shown in fig.



The following conclusion can be drawn regarding the solutions showing positive deviations with a maximum point.

(1) The individual vapour pressure p_A or p_B is higher than the ideal value. That is $p_A > p^0_A x_A$, $p_B > p^0_B x_B$.

(2) Total vapour pressure $P > (p_A + p_B)$ or $P > (p^0_A x_A + p^0_B x_B)$

(3) The total vapour pressure (P) shows a maxima. That is at certain composition, the total vapour pressure (P) of the system is higher than both p^0_A and p^0_B.

Examples

(1) C_6H_6 + cyclohexane
(2) $H_2O + C_2H_5OH$
(3) $C_6H_6 + C_2H_5OH$
(4) $CH_3COCH_3 + CS_2$

Ideal and Non-ideal Solutions

Criterion	Ideal Solution	Non-ideal solutia	
		Negative Deviatia	Positive deviatia
(1) Interactions	A–A, B–B, A–B are identical	A–B interaction is stronger than A–A and B–B interactions	A–B interaction is weaker than A–A and B–B interactions
(2) Vapour pressure	P(observed) = P(calculated)	P(observed) < P(calculated)	P(observed) > P(calculated)
(3) ΔH_{mixing}	~0	<0 (exothermic)	>0 (endothermic)
(4) ΔV_{mixing}	~0	≠0 (-ve) <0	≠0 >0
Examples.	n-Hexane + n-heptane	Acetone + $CHCl_3$	CCl_4 + acetone.

Thermodynamics of Vapour Pressure of Liquid Mixtures:

Vapour Pressure of Liquid or mixtures from thermodynamic consideration

1. Duhem–Margules Equation:

* This equation is indeed a correlation between the composition of constituents in liquid phase and their partial vapour pressures in the liquid phase.
** This equation gives variation of partial vapour pressures of the constituents of a liquid mixture with the variation of the composition in the liquid phase.

It is mathematically given by:

$$\frac{d\ln p_1}{d\ln x_1} = \frac{d\ln p_2}{d\ln x_2} \quad \text{—(1)}$$

Let us apply this equation to ideal and real solutions.

For Ideal solutions: According to Raoult's law:

$$p_1 = p_1^0 x_1 \quad \text{—(2)}$$

Taking logarithm both sides:

$$\ln p_1 = \ln p_1^0 + \ln x_1$$

On differentiation: $d\ln p_1 = d\ln p_1^0 + d\ln x_1$

Since p_1^0 = constant, hence $d\ln p_1^0 = 0$, therefore

$$d\ln p_1 = d\ln x_1$$

or $$\frac{d\ln p_1}{d\ln x_1} = 1 \quad \text{—(3)}$$

→ From Duhem-Margules equation (1) we get

$$\frac{d\ln p_1}{d\ln x_1} = \frac{d\ln p_2}{d\ln x_2} = 1$$

or $$\frac{d\ln p_2}{d\ln x_2} = 1 \quad \text{—(4)}$$

From equations (3) and (4) it is concluded that for a solution in which component 1 obeys Raoult's law at all compositions, the other component 2 will also obey Raoult's law. That is

$$p_2 = p_2^0 x_2 \quad \text{—(5)}$$