Quadrant II – Transcript and Related Materials
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Paper Title: Physical Chemistry and Organic Chemistry

Unit : 1

Module Name:Non ideal solutions, deviations from Raoult's law.

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Solutions : Non- ideal solutions, deviations from Raoult's Law

A solution formed by two components i.e. by mixing of two liquids G and H is said to be non- ideal if it does not obey Raoult's law .

or if the interaction of molecues of liquids G and H in the solution are not similar to those of pure liquid G and pure liquid H.

or if the change in volume of mixing ΔV mix $\neq 0$ [greater or lesser]

or change in enthalpy of mixing ΔH mix $\neq 0$[greater or lesser].

Raoult's law states that the vapour pressure of each component in a solution is equal to the mole fraction of that component multiplied by vapour pressure of that component in a pure state at the same temperature.

$p_G = x_G . p^o_G$

At a particular temperature the values of pressure of the solutions can be determined experimentally for different mole fractions. Values of p^o_G and p^o_H can be measured at the same temperature. Hence p_G and p_H can be calculated for any particular mole fraction.

Deviations of non ideal solutions from Raoult's law :
When Vapour pressure of the solution versus composition (mole fraction) is plotted,

three types of curves are obtained.

Type I: This curve shows a small positive deviation

Type II: This curve shows a large positive deviation

Type III: This curve shows a negative deviation.

The dotted straight line indicates ideal solutions.

There are three types:

Type I : Plot of vapour pressure versus Composition showing a small positive deviation.

- Vapour pressure of these solutions is slightly more than the ideal solutions.
- Examples: Benzene -Toluene,Water-methyl alcohol Carbon tetrachloride- cyclohexane

Type II :Plot of vapour pressure vs composition showing a large positive deviation.

- Vapour pressure of the solutions is more than ideal solutions.
- Tendency of the molecules to escape from the solution is **more** than that of pure liquids.
- Due to intermolecular forces of attraction the molecules of solution have a **weaker** force than that of pure component
- Heat is absorbed and volume increases.

Examples: water- ethanol,ethanol - chloroform

Type III: Plot of vapour pressure versus composition showing a negative deviation.

- Vapour pressure of solutions is less than ideal solutions.
- Tendency of the molecules to escape from the solution is **less** than that of pure liquids.
- Intermolecular forces of attraction of solution are **stronger** than pure components.
- Evolution of heat and contraction in volume.

Examples: water-nitric acid, water -sulphuric acid.

Conclusion:

Raoult's Law: $P_G = x_G.P^o_G$

Hence it can be concluded that for non – ideal solutions
Type: I and Type: II which show a positive deviation

$P_G > x_G P^o_G$

Type: III which shows negative deviation

$P_G < x_G.P^o_G$