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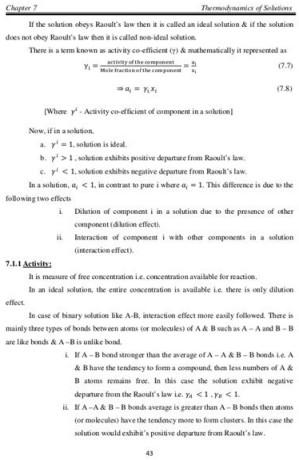

Chapter 7 *Thermodynamics of Solutions*

If the solution obeys Raoult's law then it is called an ideal solution & if the solution does not obey Raoult's law then it is called non-ideal solution.

There is a term known as activity co-efficient (γ) & mathematically it represented as

$$\gamma_i = \frac{\text{activity of the component}}{\text{Mole fraction of the component}} = \frac{a_i}{x_i} \quad (7.7)$$

$$\Rightarrow a_i = \gamma_i x_i \quad (7.8)$$

[Where γ^i - Activity co-efficient of component in a solution]

Now, if in a solution,

a. $\gamma^i = 1$, solution is ideal.
b. $\gamma^i > 1$, solution exhibits positive departure from Raoult's law.
c. $\gamma^i < 1$, solution exhibits negative departure from Raoult's law.

In a solution, $a_i < 1$, in contrast to pure i where $a_i = 1$. This difference is due to the following two effects

i. Dilution of component i in a solution due to the presence of other component (dilution effect).
ii. Interaction of component i with other components in a solution (interaction effect).

7.1.1 Activity:

It is measure of free concentration i.e. concentration available for reaction.

In an ideal solution, the entire concentration is available i.e. there is only dilution effect.

In case of binary solution like A-B, interaction effect more easily followed. There is mainly three types of bonds between atoms (or molecules) of A & B such as A – A and B – B are like bonds & A –B is unlike bond.

i. If A – B bond stronger than the average of A – A & B – B bonds i.e. A & B have the tendency to form a compound, then less numbers of A & B atoms remains free. In this case the solution exhibit negative departure from the Raoult's law i.e. $\gamma_A < 1$, $\gamma_B < 1$.
ii. If A –A & B – B bonds average is greater than A – B bonds then atoms (or molecules) have the tendency more to form clusters. In this case the solution would exhibit's positive departure from Raoult's law.

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