LECTURE-22

Raoult’s law of Ideal Solution:

Raoult's Law states that for an ideal solution the partial vapor pressure of a component in solution is equal to the mole fraction of that component times its vapor pressure when pure:

$$a_i = \frac{P_A}{P_A^0} = x_i \text{ (where } \gamma_i = 1 \text{ i. e. activity coefficient } (\gamma) \text{ is 1)} \qquad (222)$$

Properties of Ideal Solution:

- ☐ The enthalpy of solution (or "enthalpy of mixing") is zero as is the volume change on mixing; the closer to zero the enthalpy of solution is, the more "ideal" the behavior of the solution becomes.
- ☐ The vapor pressure of the solution obeys Raoult’s law
- ☐ The activity coefficient of each component (which measures deviation from ideality) is equal to one.

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ACTIVITY VS MOLE FRACTION (HENRY'S LAW):

Henry's Law: Henry's law stated as, if $x_B \to 0$, then $\gamma_B \to a$ constant γ_B^0. In other words, in Henry's law region for B.

$$a_B = \gamma_B^0 x_B \qquad (223)$$

[Where B is solute & A is solvent]

Similarly, to equation (223), we will also have

$$a_A = \gamma_A^0 x_A \qquad (224)$$

Where for

- $\gamma^i > 1$, solution exhibits positive departure from Raoult's law.
- $\gamma^i < 1$, solution exhibits negative departure from Raoult's law.

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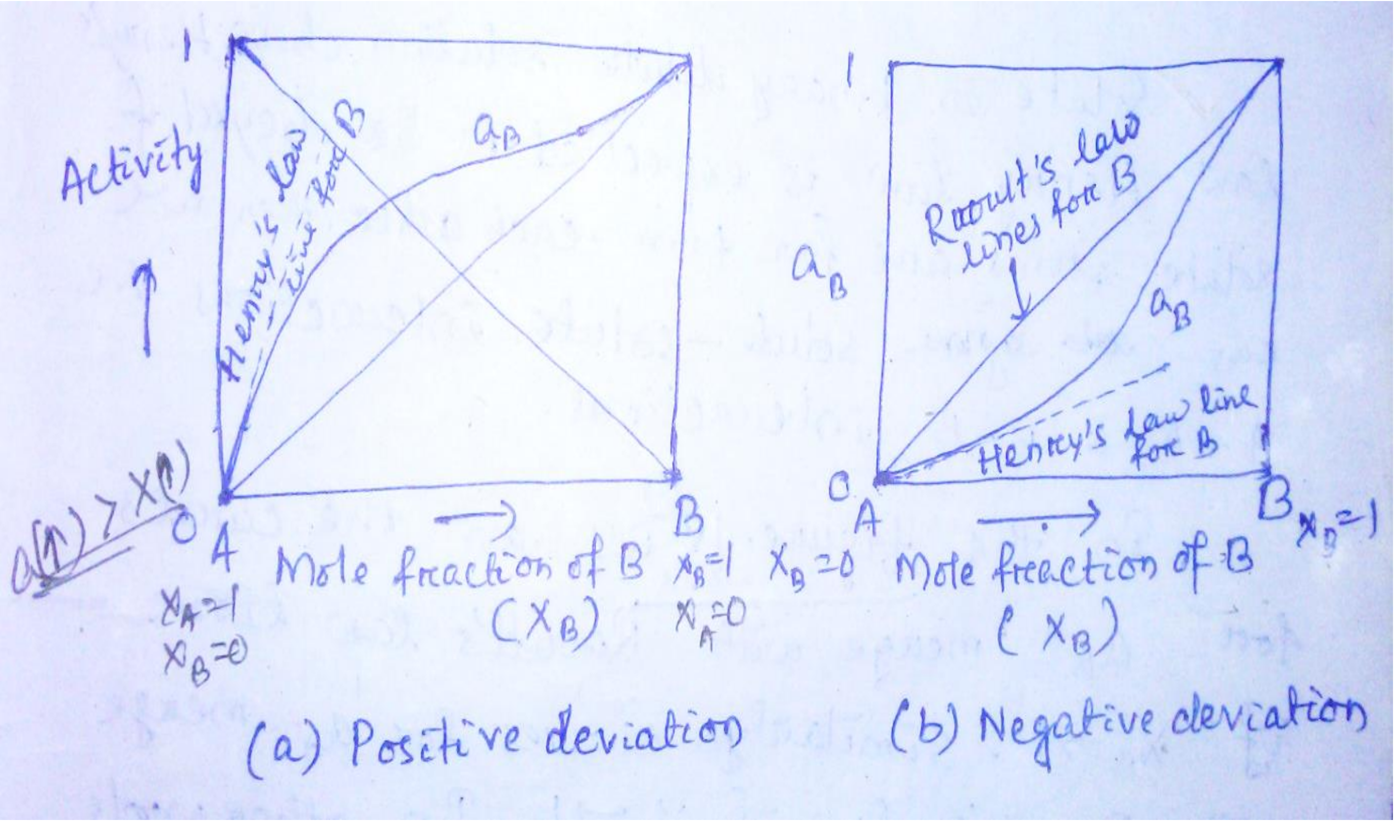

Fig (a) Positive & (b) Negative deviations from the Raoult's law for component B in the binary A-B solution; Henry's law lines for B are also shown.

- The above Fig represents activity vs mole fraction curves for binary A-B solutions at constant temperature.
- It shows Raoult's law line component A & B. Positive & negative departures from Raoult's law are illustrated for a_B with X_B is leaner. This is basis for Henry's law for binary solution.

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- Solute in binary dilute solution obeys Henry's Law. Henry's law is expected to be obeyed if solute atoms are far from each other then we can ignore solute-solute interaction i.e. A-A & B-B interactions.
- In the previous Fig (a) & (b), we have the curves for a_B merge with Raoult's law line if $x_B \rightarrow 1$. In other words, in the region where B obeys Henry's law, A tends to obey Raoult's law & Vice versa.

Proof of the Above Statement:

From the Gibb's-Duhem equation, we have

$$x_A \overline{dG_A^m} + x_B dG_B^m = 0 \tag{225}$$

$$\Rightarrow RT[x_A d(lna_A) + x_B d(lna_B)] = 0 \tag{226}$$

$$\Rightarrow RT\, x_A\, d\, lna_A + RT\, x_B\, d\, lna_B = 0 \tag{227}$$

$$\Rightarrow x_A\, d\, lna_A = -\, x_B\, d\, lna_B \tag{228}$$

Continued…

$$\Rightarrow\ d\ ln a_A = -\ \frac{x_B}{x_A} d\ ln a_B \tag{229}$$

If B obeys Henry's law, then

$$d\ (ln a_B) =\ d[\ln(\gamma_B^0 x_B) =\ d\ [\ln \gamma_B^0 + ln x_B] \tag{230}$$

[$a_B =\ \gamma_B^0 x_B$ From equation (223)]

$$\Rightarrow d(\ln a_B) = d \ln \gamma_B^0 +\ d \ln x_B \tag{231}$$

$$\Rightarrow d \ln a_B =\ d \ln x_B \tag{232}$$

[Since $d \ln \gamma_B^0 = 0$ as γ_B^0 is constant]

Now from equation (229), we have

$$d\ ln a_A = -\ \frac{x_B}{x_A} d\ ln x_B \tag{233}$$

Continued…

$$\Rightarrow d(\ln a_A) = -\frac{x_B}{x_A}\frac{dx_B}{x_B} \tag{234}$$

$$\Rightarrow \mathrm{d}(\ln \mathrm{a_A}) = -\frac{dx_B}{x_A} \tag{235}$$

[Since $\frac{d \ln x}{dx} = \frac{1}{x} \Rightarrow dlnx = \frac{dx}{x}$]

Again we know,

$$dx_A + dx_B = 0 \;\; (Since\ x_A + x_B = 1) \tag{236}$$

$$\Rightarrow dx_B = -dx_A \tag{237}$$

So, using equation (237) in equation (235), we will get

$$d(lna_A) = \frac{dx_A}{x_A} = d \ln x_A \tag{238}$$

Taking integration of equation (238), we have

$$\ln a_A = \ln x_A + Constant \tag{239}$$

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Let’s consider I as a constant, then $\ln I$ will also a constant. Therefore, we can write equation (239) as

$$\ln a_A = \ln X_A + \ln I \tag{240}$$

$$\Rightarrow \ln a_A = \ln(I x_A) \tag{241}$$

$$\Rightarrow \; a_A = I x_A \tag{242}$$

At $x_A \to 1, a_A \to 1$. Hence $I = 1$

Hence, equation (242) will become

$$a_A = x_A \tag{243}$$

i.e. A obeys Raoult’s law when B obeys Henry’s law.

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REGULAR SOLUTIONS:

- Since most of the solutions are non-ideal so there is a great need to express the thermodynamic quantity in these solutions in the form of analytical equations i.e. function of temperature & composition.
- Regular solution model first proposed by Hildebrand, on approximation the model is not much more consistent.
- Hildebrand defined a regular solution as one in which

$$\overline{\mathrm{S_i}}^{\mathrm{m}} = \overline{\mathrm{S_i}}^{\mathrm{m,id}} \text{ But } \overline{H_i^m} \neq 0 \qquad (244)$$

$$\text{i.e. } \Delta s^m = \Delta s^{m,id} \text{ But } \Delta H^m \neq 0 \qquad (245)$$

[Where “id” subscript refers to ideal solution]

- In other words, a regular solution has the same entropy as an ideal solution of same composition, but entropy is different from ideal solution.

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Excess Function: For dealing with non-ideal solutions, a function known as excess function (or molar excess property) used. It is only for extensive properties & defined as

$$Q^{xs} = Q - Q^{id} \tag{246}$$

Similarly, for partial molar excess properties the equation (246) will become

$$\overline{Q_i^{xs}} = \overline{Q_i} - \overline{Q_i^{id}} \tag{247}$$

[Here,

Q – Some extensive property (G, H, S……..) of the actual solution.

Q^{id} - Value of Q for ideal solution at same composition & temperature.

Q^{xs} - Value of Q in excess of that of ideal solution.]

For standard state, we can write equation (246) and (247) as

$$Q^{xs} = (Q - Q^0) \tag{248}$$

$$\Rightarrow Q^{XS} = \Delta Q^m - \Delta Q^{m,id} \tag{249}$$

Continued…

$$\overline{Q^{xs}} = \left(\overline{Q_i} - Q_i^0\right) - (\overline{Q_i^{id}} - Q_i^0) \qquad (250)$$

$$\overline{Q_i^{XS}} = \overline{Q_i^m} - \overline{Q_i^{m,id}} \qquad (251)$$

[Since, Q^0 is added & Q^0 subtracted. So, equation (249) & (251) are same as equation (246) & (247) respectively.

Hence, for a regular solution

$$\overline{G_i^{xs}} = \overline{H_i^{xs}} - T\overline{S_i^{xs}} = \overline{H_i^{xs}} = \overline{H_i^m} \qquad (252)$$

$$G^{xs} = \Delta H^m \qquad (253)$$

[Since for a regular solution no excess entropy, i.e., $\overline{S_i^{xs}} = 0$, $S^{xs} = 0$ and also $\overline{H_i^{xs}} = \overline{H_i^m}$, $H^{xs} = \Delta H^m$]

Again, $G^{xs} = \Delta G^m - \Delta G^{m,id} = RT \sum_i x_i \, ln a_i - RT \sum_i x_i \ln x_i = RT \sum_i x_i \, ln \gamma_i$ (254)

[Since, for ideal solution ($a_i = x_i$)]