Relative Volatility

- Relative volatility, α, is the ratio of concentration of A & B in one phase to that in the other. Relative volatility is the measure of separability.

$$\alpha = \frac{y^*/(1-y^*)}{x/(1-x)}$$

; The larger the value of 'α' (>1), the greater the degree of separability.

- For ideal binary solution,

$$y_i P = x_i P_i^{vap} \Rightarrow \frac{y_A P}{(P_A^*)} = x_A P_A^{vap} \ \& \ \frac{y_B P}{(P_B^*)} = x_B P_B^{vap}$$

$$\Rightarrow \alpha = \frac{(P_A^*/P)/(P_B^*/P)}{(P_A^*/P_A^{vap})/(P_B^*/P_B^{vap})} = \frac{P_A^{vap}}{P_B^{vap}} = \text{Ratio of vapor pressures of A \& B}$$

- In a multicomponent mixture; $\alpha_{ij} = (y_i^*/y_j^*)/(x_i/x_j)$

  α_{ij} is the degree of enrichment of component 'i' in the vapor phase compared to component 'j'

- Equilibrium in a multicomponent system: we will assume that the system forms an ideal multicomponent system, therefore Raoult's law is applicable. In this section, bubble point & dew point calculations will be discussed.

[Note: For hydrocarbons, equilibrium vaporization ratio is often used in VLE calculations.

$$\boxed{K_i = y_i/x_i}$$
]

At a given temperature & liquid composition, the vapor composition is calculated as shown below:

$$y_j^* = (P_j^*/P) \quad ; \text{ From Raoult's law: } P_j^* = x_j P_j^v$$

$$\Rightarrow y_j^* = \frac{x_j P_j^v}{\sum_{i=1}^{n} x_i P_i^v}$$

$$\Rightarrow y_j^* = \frac{x_j}{\sum_{i=1}^{n} x_i (P_i^v/P_j^v)} = \frac{x_j}{\sum_{i=1}^{n} \alpha_{ij} x_i}$$

As discussed, $K_i = \dfrac{y_i}{x_i} = \dfrac{P_i^v}{P}$

$$\Rightarrow \alpha_{ir} = \frac{y_i/y_r}{x_i/x_r} = \frac{(y_i/x_i)}{(y_r/x_r)} = \frac{K_i}{K_r}$$

$$\Rightarrow \boxed{K_i = K_r \alpha_{ir}}$$

& therefore, $y_i = K_i x_i$

$$\Rightarrow y_i = K_r \alpha_{ir} x_i \Rightarrow \sum_{i=1}^{n} y_i = \sum_{i=1}^{n} K_r \alpha_{ir} x_i$$

$$\Rightarrow K_r \sum \alpha_{ir} x_i = 1$$

<u>Bubble point calculations:</u> In bubble point calculations, the liquid composition is known and the total pressure is given.

- we start by assuming the temperature & calculate P_i^v or K_i.
- Then, we compare: $\sum_{i=1}^{n} y_i = \underline{\sum_{i=1}^{n} K_i x_i = 1}$

If the above equation holds, then the guess of temperature is correct, else we perform a few iterations.

Dew point calculations: In this case, the composition of vapor phase is known. We assume a value of dew point & obtain vapor pressure or K-values at this temperature & iterate till the following is satisfied.

$$\sum_{i=1}^{n} x_i = \sum_{i=1}^{n} y_i/K_i = \frac{1}{K_r} \sum \frac{y_i}{\alpha_{ir}} = 1$$

(BK Dutta)
Example 7.3: Calculate the dew point of a vapor containing 15 mol % n-butane(1), 15 mol % n-pentane(2), 20 mol % cyclohexane(3), 20 mol % n-hexane(4), & 30 mol % n-heptane(5) at 1.5 bar total pressure. Raoult's law applies. Use Table 7.2 to obtain vapor pressure of pure components.

Solution: $M_1 = 58$ g/mol ; $M_2 = 72$ g/mol ; $M_3 = 84$ g/mol ; $M_4 = 86$ g/mol
$M_5 = 100$ g/mol

$$M_{av} = (0.15 \times 58) + (0.15 \times 72) + (0.2 \times 84) + (0.2 \times 86) + (0.3 \times 100) = 83.6 \text{ g/mol}$$

As an approximation of the dew point, ~~let~~ let us take the boiling point of component 3 as the initial guess because the average molecular mass of the mixture is close to component 3.

At boiling point of n-cyclohexane (component 3) @ 1.5 bar, its vapor pressure = total pressure

$$\Rightarrow P_3^v = 1.5 \text{ bar} = 1125 \text{ mm Hg}$$

Using Antoine's equation for component 3:

$$\ln(1125) = A' + B'/(T + C') \; ; \; A', B', C' \text{ are given in Table 2}$$

$$\Rightarrow T = 367.5 \text{ K (initial guess)}.$$

At this temperature;

$P_1^v = 13.31$ bar ; $P_4^v = 2.122$ bar

$P_2^v = 5.211$ bar ; $P_5^v = 0.8978$ bar

$\Rightarrow$

$$\Rightarrow \alpha_{13} = P_1^u / P_3^u = 8.873 \; ; \; \alpha_{43} = P_4^u / P_3^u = 1.415$$

$$\alpha_{23} = P_2^u / P_3^u = 3.474 \; ; \; \alpha_{53} = P_5^u / P_3^u = 0.5985$$

$$\Rightarrow \text{Using } \sum_{i=1}^{n} x_i = \sum_{i=1}^{n} y_i / k_i = \frac{1}{k} \sum_{i=1}^{n} \frac{y_i}{K_r \alpha_{ir}}$$

$$\Rightarrow \frac{1}{K_3} \sum_{i=1}^{n} \frac{y_i}{\alpha_{i3}} = 1 \Rightarrow \frac{1}{K_3}\left(\frac{0.15}{8.873} + \frac{0.15}{3.474} + \frac{0.20}{1.0} + \frac{0.2}{1.415} + \frac{0.3}{0.5925}\right) = 1$$

$$\Rightarrow K_3 = 0.9027$$

Now, $K_3 = P^u_{(3)} / P \Rightarrow P^u_{(3)} = 1.354 \text{ bar} = 1016 \text{ mm Hg}$ [~~Higher~~ Lower than our initial guess]

Note: $k_3 = y_i / x_i$ & from Raoult's law: ~~$y_i P_i = P$~~ $y_i P = P_i^v x_i$ $\Rightarrow y_i / x_i = \frac{P_i^v}{P}$

~~From,~~ Since, $P^u_{(3)}$ obtained differ from our initial guess, we will iterate by choosing a new temperature from the vapor pressure obtained above.

$$\Rightarrow \ln(1016) = A' + B' / (T + C')$$

$$\Rightarrow T_{new} = 363.8\,K$$

Repeat the steps shown above till $\underline{\sum_{i=1}^{n} y_i / k_i \approx 1}$

—x— —x—