Lecture 24: Vapor - Liquid Equilibrium

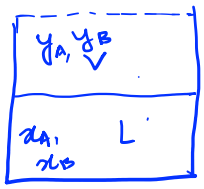
- P - X - Y
- T - X - Y
- we will limit our discussion to binary mixtures

2 component & 2 phase

$F = 2$

P - fixed

T - fixed



Find x_A & y_A ?
at equilibrium

Phases & components

L - V A & B

L

V

- At equilibrium:

$$\underline{f}_i^L(T, P, \underline{x}) = \underline{f}_i^V(T, P, \underline{y})$$

For ideal mixtures at low pressure, one can write the above equation as:

$$x_i P_i^{vap} = y_i P \quad \text{(using Raoult's law)} \quad -(1)$$

(P ← Total pressure)

(P_i^{vap} ↑ Vapor pressure of pure component 'i' at temperature T)

$$\sum_{i=1}^{n} x_i = 1 \quad ; \quad \sum_{i=1}^{n} y_i = 1$$

How do you obtain the vapor pressure of pure component 'i' at any temperature T?

(i) Antoine Equation:

$$\ln P^{vap} = A' - \frac{B'}{T + C'}$$

(ii) Clausius-Clapeyron Equation:

$$\ln\left(\frac{P^{vap}(T_2)}{P^{vap}(T_1)}\right) = -\frac{\Delta_{vap}H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

This equation is valid for small ΔT (assuming $\Delta_{vap}H$ remains constant in this temperature range)

Case 1: x, T are known. Find P, y?

(i) Since T is known, P_A^{vap} & P_B^{vap} are known

(ii) From Raoult's law:

$$P_A = x_A P_A^{vap}$$
$$P_B = x_B P_B^{vap}$$
$$\Rightarrow \boxed{P = P_A + P_B}$$

$$y_A = P_A/P \; ; \; y_B = P_B/P$$

Case 2: x, P are known. Find y & T?

(1) Assume temperature T

(2) Find P_A^{vap} & P_B^{vap} at T

(3) Find partial pressures of A & B in the vapor phase from Raoult's law

$$P_A = P_A^{vap} x_A$$
$$P_B = P_B^{vap} x_B$$

(4) $P_{guess} = P_A + P_B$ = Total pressure

(5) If $P_{guess} = P_{actual}$, then the temperature guess is correct & therefore T & y are correct. If $P_{guess} \neq P_{actual}$, then you choose a new guess for temperature & repeat previous steps.

- Solved Example problem 7.1 of Bk Dutta