

Quiz 4

10.213

Solution

① a) using modified Raoult's law

$$P_A = x_A \gamma_A P_A^{\text{sat}}$$

For components 1 & 2:

$$P = x_1 \gamma_1 P_1^{\text{sat}} + x_2 \gamma_2 P_2^{\text{sat}}$$

$$x_1 = x_2 = 0.5$$

Since G^E is symmetric with respect to x_1 and x_2 . Therefore, for equimolar quantities of two liquids $\gamma_1 = \gamma_2$

$$55 = 0.5 \gamma_1 \cdot 50 + 0.5 \gamma_1 \cdot 60$$

$$\text{That means that } \gamma_1 = \gamma_2 = 1$$

Therefore the solution is ideal and $B=0$.

Method 2

We can also prove this by getting the equation for γ from G^E

$$\ln \gamma_1 = \left[\frac{\partial \left(\frac{nG^E}{RT} \right)}{\partial n_1} \right]_{n_2, T, P}$$

$$\frac{nG^E}{RT} = \frac{nB}{RT} \frac{n_1}{n} \frac{n_2}{n} = \frac{B}{RT} \frac{n_1 n_2}{n}$$

$$\left[\frac{\partial \left(\frac{nG^E}{RT} \right)}{\partial n_1} \right]_{n_2, T, P} = \frac{B n_2}{RT} \left[\frac{\partial (n_1/n)}{\partial n_1} \right]_{n_2, T, P} = \frac{B n_2}{RT} \left[\frac{-n_1}{n^2} + \frac{1}{n} \right]$$

$$= \frac{B n_2}{RT} \left[\frac{-n_1 + n}{n^2} \right] = \frac{B n_2 n_2}{RT n^2} = \frac{B}{RT} x_2^2$$

Similarly for γ_2 , $\ln \gamma_2 = \frac{B}{RT} x_1^2$

Substituting in the total pressure equation

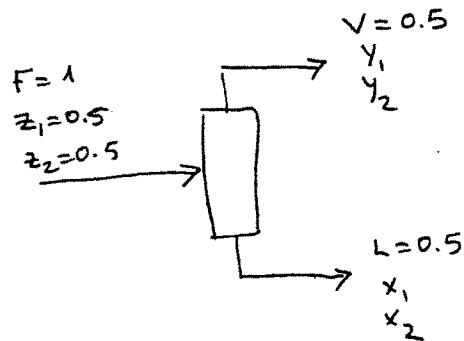
$$55 = 0.5 \exp[B(0.5)^2] 50 + 0.5 \exp[B(0.5)^2] 60$$

$$55 = 55 \exp[B(0.5)^2] \rightarrow B(0.5)^2 = 0 \rightarrow \boxed{B = 0}$$

b) Using Raoult's law (since $\gamma_i = 1$)

$$y_1 = \frac{x_1 P_i^{\text{sat}}}{P} = \frac{0.5 \times 50}{55} = 0.455$$

c) The 50% - composition liquid is allowed to evaporate to equal amounts of liquid and vapor. This is a flash problem as follows:



Raoult's law

$$x_1 P_i^{\text{sat}} = y_1 P$$

$$50 x_1 = y_1 P \quad \text{--- (1)}$$

$$(1-x_1) P_2^{\text{sat}} = (1-y_1) P$$

$$60(1-x) = (1-y_1) P \quad \text{--- (2)}$$

MB

$$F z_1 = V y_1 + L x_1$$

$$0.5 = 0.5 y_1 + 0.5 x_1$$

$$x_1 + y_1 = 1 \quad \text{--- (3)}$$

Three equations in three unknowns (x_1, y_1, P)

Using (3) in (1) & (2)

$$50 x_1 = (1-x_1) P$$

$$60(1-x_1) = x_1 P$$

dividing

$$\frac{50 x_1}{60(1-x_1)} = \frac{(1-x_1)}{x_1}$$

$$50 x_1^2 = 60(1-x_1)^2$$

$$5 x_1^2 = 6(1-2x_1+x_1^2)$$

$$x_1^2 - 12x_1 + 6 = 0$$

$$x_1 = \frac{12 - \sqrt{12^2 - 4 \times 6}}{2} = 0.523$$

$$x_2 = 0.477$$

$$y_1 = 0.477$$

$$y_2 = 0.523$$

$$P = \frac{50 \times 0.523}{0.477} = 54.8 \text{ kPa}$$

② a) At equilibrium

$$f^L = f^V$$

For a pure component, $f^V = \phi P$

Using the generalized correlation

$$\phi = \phi^0 (\phi')^w$$

For water $T_c = 647.1 \text{ K}$ $P_c = 220.55 \text{ bar}$ $w = 0.345$

$$T_r = \frac{T}{T_c} = \frac{300 + 273}{647.1} = 0.885 \sim 0.9$$

$$P_r = \frac{P}{P_c} = \frac{8592.7}{22055} = 0.39 \sim 0.4$$

From the table $\phi^0 = 0.8204$ $\phi' = 0.9141$

$$\phi = 0.8204 \times (0.9141)^{0.345} = 0.795$$

$$f^V = f^L = 0.795 \times 8592.7 = 6834 \text{ kPa}$$

b) For the mixture $\hat{f}_i^L = x_i \gamma_i f_i^L$

$\gamma_w \sim 1$ because $x \sim 1$

$$\therefore \hat{f}_i^L = 0.99 \times 6834 = 6766 \text{ kPa}$$

c) $\hat{f}_i^V = \hat{f}_i^L = 6766 \text{ kPa}$

$$\hat{f}_i^V = \phi P$$

$\phi \sim 0.795$ [not exact because P is diff. than for part a]

$$P = \frac{6766}{0.795} = 8510 \text{ kPa}$$

Another method

$$P = x_A P_A^{\text{sat}} = 0.99 \times 8592.7 = 8507 \text{ kPa}$$

↳ this comes from

$$\hat{f}_A^V = \hat{f}_A^L$$

$$\phi_A P = x_A \gamma_A P_A^{\text{sat}} \hat{\phi}_A$$

$\therefore P_A^{\text{sat}} \sim P \therefore \phi_A \sim \hat{\phi}_A$ and can be cancelled out

pointing factor $\Rightarrow P = x_A P_A^{\text{sat}}$