

Dring 1

1 Phase rule

Consider the binary system butanol-water. Calculate the number of degrees of freedom and specify which variables can be fixed for the following cases:

- Vapor phase only
- Two liquid phases,
- Vapor phase and two liquid phases

a) 2 components, 1 phase

$$\Rightarrow N = 2 - 1 + 2 = 3$$

The system has 3 degrees of freedom, we can choose temperature (T), pressure (P) and composition of the gas ($y_{\text{H}_2\text{O}}$ or y_{butanol})

b) 2 components, 2 phases

$$\Rightarrow N = 2 - 2 + 2 = 2$$

2 degrees of freedom, we can choose two variables, for example T and P, and the rest will be given

c) 2 components, 3 phases

$$\Rightarrow N = 2 - 3 + 2 = 1$$

1 degree of freedom, we can choose one variable, and the others will be given. Example, choose T, then P and composition will be given

2 Raoult's law and flash for benzene-toluene

- How do you think the two last columns in the Table below were obtained? (Hint: compare with Raoult's law).

TABLE 11.1-1. Vapor-Pressure and Equilibrium-Mole-Fraction Data for Benzene-Toluene System

Vapor Pressure						Mole Fraction Benzene at 101.325 kPa	
Temperature		Benzene		Toluene		x_A	y_A
K	°C	kPa	mm Hg	kPa	mm Hg		
353.3	80.1	101.32	760			1.000	1.000
358.2	85	116.9	877	46.0	345	0.780	0.900
363.2	90	135.5	1016	54.0	405	0.581	0.777
368.2	95	155.7	1168	63.3	475	0.411	0.632
373.2	100	179.2	1344	74.3	557	0.258	0.456
378.2	105	204.2	1532	86.0	645	0.130	0.261
383.8	110.6	240.0	1800	101.32	760	0	0

- Compute the relative volatility for the six last compositions given in the Table. Is it approximately constant?
- If a liquid mixture at 358.2 K and 1 bar has $x_A = 0.411$, will it boil? If not, at what temperature will it boil, and what will be the composition of the vapor first coming off? What is this point called?
- What are the saturation pressure (bubble point pressure) and vapor composition for a liquid mixture at 100°C (373.2K) with 50 mol-% benzene and 50 mol-% toluene?
- Explain what a dew point is. Consider a gas mixture at 911 mmHg (1.21 bar) with 50 mol-% benzene and 50 mol-% toluene. What is the dew point temperature, and what is the composition of the first liquid drop?

a) The last columns were obtained by calculations, using Raoult's law.

Raoult's law: $P_A = X_A P_A^{sat}$

$$P_B = X_B P_B^{sat} = (1 - X_A) P_B^{sat}$$

$$P = P_A + P_B = X_A P_A^{sat} + (1 - X_A) P_B^{sat}$$

$$P = X_A P_A^{sat} + P_B^{sat} - X_A P_B^{sat}$$

$$P = P_B^{sat} + X_A (P_A^{sat} - P_B^{sat})$$

$$\Rightarrow X_A = \frac{P - P_B^{sat}}{P_A^{sat} - P_B^{sat}}$$

Partial pressure: $P_A = y_A P$

$$y_A = \frac{P_A}{P} = \frac{X_A P_A^{sat}}{P} = \frac{(P - P_B^{sat}) P_A^{sat}}{P(P_A^{sat} - P_B^{sat})}$$

$$\Rightarrow y_A = \frac{1 - \frac{P_B^{sat}}{P}}{1 - \frac{P_B^{sat}}{P_A^{sat}}}$$

Example: $T = 358,2 \text{ K}$

$$X_A = \frac{101,32 - 46,0}{116,9 - 46,0} = 0,760$$

$$y_A = \frac{1 - \frac{46,0}{101,32}}{1 - \frac{46,0}{116,9}} = 0,900$$

$\Rightarrow$ This matches the table, they were calculated.

b) $\alpha = \frac{y_A / X_A}{y_B / X_B} = \frac{P_A^{sat}}{P_B^{sat}}$

T	α
358,2	2,54
363,2	2,51
368,2	2,46
373,2	2,41
378,2	2,37
383,8	2,37

There is not much variation. $\Rightarrow$ It is approximately constant

c) • No, it won't boil

• At $X_A = 0,411$ it will boil at $T = 368,2 \text{ K}$

• The composition of the vapor will be 63,2% Benzene and 36,8% Toluene

• The point is called the bubble point.

$$d) P = P_A + P_B = X_A P_A^{sat} + X_B P_B^{sat}$$

$$P = 0,5 \cdot 179,2 + 0,5 \cdot 74,3$$

$$\underline{P = 126,75 \text{ kPa}}$$

$$\text{Composition: } y_A = \frac{P_A}{P} = \frac{X_A P_A^{sat}}{P} = \frac{0,5 \cdot 179,2}{126,75} = 0,710$$

$$\Rightarrow \underline{y_A = 0,710, y_B = 0,290}$$

e) • The dew point is where the vapour starts condensing into liquid.

• We have $P = 911 \text{ mmHg}$, $y_A = y_B = 0,5$

For the condensing liquid: $X_A + X_B = 1$

Combining $P_A = X_A P_A^{sat}$ and $P_A = y_A P$

$$\Rightarrow X_A P_A^{sat} = y_A \cdot P$$

$$X_A = \frac{y_A \cdot P}{P_A^{sat}}, \text{ or, likewise for B}$$

$$\Rightarrow \frac{y_A \cdot P}{P_A^{sat}} + \frac{y_B \cdot P}{P_B^{sat}} = 1$$

$$\frac{0,5 \cdot 911}{P_A^{sat}} + \frac{0,5 \cdot 911}{P_B^{sat}} = 1$$

$$\frac{455,5}{P_A^{sat}} + \frac{455,5}{P_B^{sat}} = 1$$

Need to find T , where this is correct

By interpolation of the data in the table, we get $T = 377,7 \text{ K}$

$$P_A^{sat} = 1543,1 \text{ mmHg}, P_B^{sat} = 646,3 \text{ mmHg}$$

$$\Rightarrow 0,2952 + 0,7048 = 1,$$

$\Rightarrow$ The dew point temperature is $377,7 \text{ K}$, $X_A = 0,2952$ and $X_B = 0,7048$

3

Single-stage flash

Assume that the relative volatility between components propane (1) and n-butane (2) is 6 (constant). The following two streams are mixed:

Stream Fa: 80 mol/s. Saturated vapour at 1 atm. 50% propane, 50% n-butane.

Stream Fb: 70 mol/s. Saturated liquid at 1 atm. 50% propane, 50% n-butane.

The mixed stream is separated in an adiabatic flash unit operating at 1 atm into a liquid product L and vapor product V (in equilibrium).

- Rank the temperatures of the streams Fa, Fb, L, and V (justify your answer).
- Find the amount and compositions of the streams L and V.

* For the energy balance, you can assume constant molar flows (which in this case means that $V = F_a$, $L = F_b$).

a) $T_{F_a} > T_V = T_L > T_{F_b}$

We know that the boiling temperature of n-butane is higher than the boiling temperature of propane. $\Rightarrow$ n-butane will accumulate in the liquid, propane in the vapor.

In F_a , both components are in vapor-phase

In F_b , both components are liquids

V and L are in equilibrium $\Rightarrow T_V = T_L$, also, there are both liquid and vapor in the equilibrium $\Rightarrow$ V and L are colder than F_a (all liquid has evaporated) and warmer than F_b (only liquid)

b) Feed: $F = F_a + F_b = 80 + 70 = 150 \text{ mol/s}$

$$x_F^1 = 0,5, \quad x_F^2 = 0,5$$

Mass balance:

$$x_F^i \cdot F = x_i \cdot L + y_i \cdot V$$

From assumption $V = F_a = 80 \text{ mol/s}$, $L = F_b = 70 \text{ mol/s}$

$\Rightarrow$ Propane I: $75 = x_1 \cdot 70 + y_1 \cdot 80$

Constant relative volatility (VLE)

$$\Rightarrow \text{III: } y_1 = \frac{\alpha x_1}{1 + (\alpha - 1)x_1} = \frac{6x_1}{1 + 5x_1}$$

$$\Rightarrow \text{Propane (I): } 70x_1 + \frac{6x_1}{1+5x_1} \cdot 80 = 75$$

$$70x_1 + 350x_1^2 + 480x_1 = 75 + 375x_1$$

$$350x_1^2 + 175x_1 - 75 = 0$$

$$\Rightarrow x_1 = 0.2761, \text{ insert into III:}$$

$$\Rightarrow y_1 = 0.6959$$

$$\underline{L = 70 \text{ mol/s}, x_1 = 0.2761, V = 80 \text{ mol/s and } y_1 = 0.6959}$$

4

The main point here is to compare batch (dynamic) and continuous (steady-state) operation of single-stage flash (also known as flash distillation) for a binary mixture where one can assume constant relative volatility $\alpha = 2.45$. Note that the relative volatility for a binary mixture between components A and B is

$$\alpha = \frac{y_A/x_A}{y_B/x_B} = \frac{y/x}{(1-y)/(1-x)}$$

The feed (initial) composition is in both cases $x' = 0.357$ (mole fraction of light component). In both cases, the pressure is constant.

i) Draw flowsheets of the two alternative flash processes (batch and continuous)

ii) **Batch flash (Simple batch distillation).**

a) Derive an analytical expression for the Rayleigh integral

$$\int_{L^0}^{L^1} \frac{dL}{L} = \int_{x^0}^{x^1} \frac{dx}{y-x}$$

assuming constant relative volatility

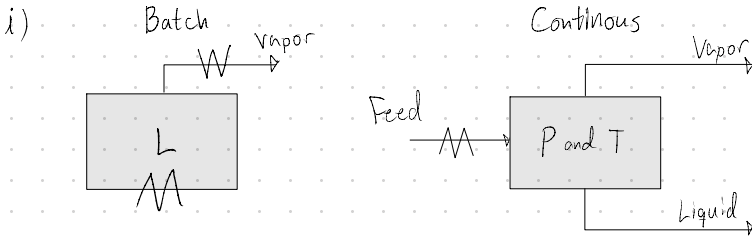
$$\text{Hint: Show that } \frac{1}{y-x} = \frac{1}{\alpha-1} \left(\frac{1}{x} + \frac{\alpha}{1-x} \right)$$

b) Apply this expression to our mixture, which has $\alpha = 2.45$ and $x' = 0.357$. What fraction of the liquid must be evaporated in order to obtain a final composition $x_1 = 0.258$?

iii) **Continuous flash.**

a) What fraction of the liquid must be evaporated to reach the same end concentration if the operation mode is changed to continuous flash?

b) Which flash is more effective: Batch or continuous?



ii) a) Showing that $\frac{1}{y-x} = \frac{1}{\alpha-1} \left(\frac{1}{x} + \frac{\alpha}{1-x} \right)$:

Given: Relative volatility

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

$$\alpha x(1-y) = y(1-x)$$

$$\alpha x - \alpha xy - y + yx = 0$$

$$y - yx + \alpha xy = \alpha x$$

$$y(1-x + \alpha x) = \alpha x$$

$$y(1 + (\alpha-1)x) = \alpha x$$

$$y = \frac{\alpha x}{1 + (\alpha-1)x}$$

$$y-x = \frac{\alpha x}{1 + (\alpha-1)x} - \frac{x(1 + (\alpha-1)x)}{1 + (\alpha-1)x} = \frac{x((\alpha-1) - (\alpha-1)x)}{1 + (\alpha-1)x}$$

$$y-x = \frac{x(\alpha-1)(1-x)}{1 + (\alpha-1)x}$$

$$\begin{aligned} \frac{1}{y-x} &= \frac{1 + (\alpha-1)x}{x(\alpha-1)(1-x)} = \frac{1}{\alpha-1} \left(\frac{1}{x(1-x)} + \frac{x(\alpha-1)}{x(1-x)} \right) = \frac{1}{\alpha-1} \left(\frac{1}{x} - \frac{1}{1-x} + \frac{\alpha-1}{1-x} \right) \\ &= \frac{1}{\alpha-1} \left(\frac{1}{x} - \frac{1}{1-x} + \frac{\alpha-1}{1-x} \right) = \frac{1}{\alpha-1} \left(\frac{1}{x} + \frac{\alpha}{1-x} \right) \end{aligned}$$

$$\Rightarrow \boxed{\frac{1}{y-x} = \frac{1}{\alpha-1} \left(\frac{1}{x} + \frac{\alpha}{1-x} \right)}$$

Rayleigh Integral

$$\int_{L_0}^{L_1} \frac{dL}{L} = \int_{x_0}^{x_1} \frac{dx}{y-x}$$

Left side $\int_{L_0}^{L_1} \frac{dL}{L} = \ln|L| \Big|_{L_0}^{L_1} = \ln\left(\frac{L_1}{L_0}\right) \quad (L > 0)$

Right side

$$\begin{aligned}\int_{x^0}^{x_1} \frac{dx}{y-x} &= \int_{x^0}^{x_1} \frac{1}{\alpha-1} \left(\frac{1}{x} + \frac{\alpha}{1-x} \right) dx = \frac{1}{\alpha-1} \int_{x^0}^{x_1} \left(\frac{1}{x} + \frac{\alpha}{1-x} \right) dx \\ &= \frac{1}{\alpha-1} \left(\ln \frac{x_1}{x^0} - \alpha \ln \frac{1-x_1}{1-x^0} \right)\end{aligned}$$

ln total:

$$\ln \frac{L_1}{L^0} = \frac{1}{\alpha-1} \left(\ln \frac{x_1}{x^0} + \alpha \ln \frac{1-x^0}{1-x_1} \right)$$

$$\frac{L_1}{L^0} = \exp \left(\frac{1}{\alpha-1} \left(\ln \frac{x_1}{x^0} + \alpha \ln \frac{1-x^0}{1-x_1} \right) \right)$$

$$\frac{L_1}{L^0} = \exp \left(\frac{1}{\alpha-1} \ln \frac{x_1}{x^0} \right) \cdot \exp \left(\frac{\alpha}{\alpha-1} \ln \frac{1-x^0}{1-x_1} \right)$$

$$\frac{L_1}{L^0} = \left(\frac{x_1}{x^0} \right)^{\frac{1}{\alpha-1}} \cdot \left(\frac{1-x^0}{1-x_1} \right)^{\frac{\alpha}{\alpha-1}}$$

b) Inputting $x^0 = 0,357$, $\alpha = 2,45$, $x_1 = 0,258$:

$$\frac{L_1}{L^0} = \left(\frac{0,258}{0,357} \right)^{\frac{1}{2,45-1}} \left(\frac{1-0,357}{1-0,258} \right)^{\frac{2,45}{2,45-1}}$$

$$\frac{L_1}{L^0} = 0,6275$$

$$1 - 0,6275 = 0,3725 = 37,25\%$$

$\Rightarrow 37,25\%$ of the liquid must be evaporated

iii) a) Mass balances:

$$F x^0 = Lx + Vy \Rightarrow V = \frac{F x^0 - Lx}{y}$$

$$F = L + V \Rightarrow F = L + \frac{F x^0 - Lx}{y}$$

$$F y - F x^0 = L y - L x$$

$$\underline{\frac{L}{F} = \frac{y - x^0}{y - x}}$$

In ii) a) we found that $y = \frac{\alpha x}{1 + x(\alpha - 1)}$

Using $\alpha = 2,45$, $x^0 = 0,357$, $X = 0,258$

$$y = \frac{2,45 \cdot 0,258}{1 + 0,258(2,45 - 1)} = 0,460$$

$$\Rightarrow \frac{L}{F} = \frac{0,460 - 0,357}{0,460 - 0,258} = 0,510$$

$$1 - 0,510 = 0,490 = 49\%$$

$\Rightarrow 49\%$ of the liquid needs to be evaporated

b) Batch is more efficient than continuous flash.

We need to evaporate more liquid in continuous flash than in batch distillation, evaporation requires energy, which makes batch flash more efficient than continuous flash (in this case).