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## Exercises of “Fundamentals of Chemical Processes”

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### Exercise 7

#### 1) Estimation of the composition of the streams at the exit of an isothermal flash unit

A flash unit is maintained at a temperature of 80°C and at a pressure of 110 kPa. A mixture of nitromethane, acetone and acetonitrile (molar composition  $z_i$  reported in the table), is sent to the flash unit. Assuming ideal gases and ideal liquid mixture:

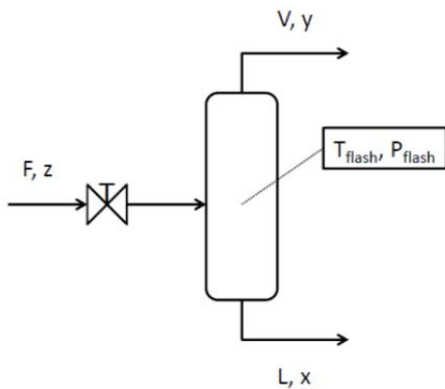
- 1) calculate the bubble pressure and the dew pressure of the mixture at the temperature of the unit
- 2) calculate the boiling temperature and the dew temperature of the mixture at the pressure of the unit
- 3) evaluate if a vapor-liquid equilibrium condition is reached at the temperature and pressure of the unit
- 4) estimate the vaporization ratio and the composition of the liquid stream and of the vapor stream that are produced in the flash unit.

For each specie,  $A_i$ ,  $B_i$  and  $C_i$  are the parameters of Antoine's equation for the estimation of the vapor pressure.

#### Data

	Specie	$A_i$	$B_i$	$C_i$
	<b>Acetone</b>	0.450	14.3145	2756.220
	<b>Acetonitrile</b>	0.350	14.8950	3413.100
	<b>Nitromethane</b>	0.200	14.7513	3331.700

$$\ln(P_i^{SAT}) = A_i - \frac{B_i}{C_i + T} \quad P_i^{SAT} = [kPa] \quad T = [^{\circ}C]$$

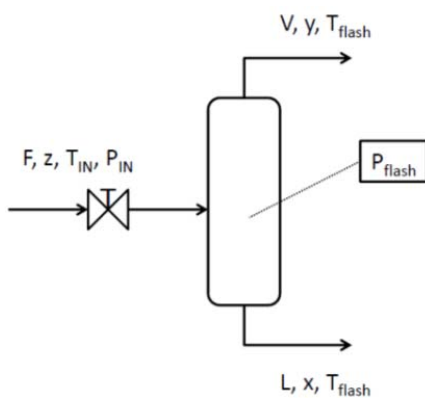


## 2) Estimation of the temperature and the composition of the streams at the exit of an adiabatic flash unit

A flash unit is maintained at 100 kPa pressure. A mixture of n-hexane, n-octane and n-decane, whose composition in terms of molar fractions ( $z_i$ ) is reported in the table, is sent to the flash unit. The mixture fed to the flash unit is at 130°C and 304 kPa. Assuming ideal gases and ideal liquid mixture, and knowing that the flash drum is adiabatic, calculate the temperature and the composition of the streams that exit the unit. For each specie, the specific heat in the liquid phase, the specific heat in the vapor phase and the enthalpy of vaporization ( $\Delta H^{VAP}$ , at the normal boiling temperature) can be assumed as constant. The enthalpies of vaporization are given at the boiling temperature at 1 atm.

### Data

Species	$A_i$	$B_i$	$C_i$	$C_p^{liq}$ [J/mol/°C]	$C_p^{gas}$ [J/mol/°C]	$\Delta H^{VAP}(T_{boil}^N)$ [J/mol]	
n-hexane	0.300	13.8193	2696.040	224.317	200	182	28850
n-octane	0.350	13.9346	3123.130	209.635	255	240	34410
n-decane	0.350	13.9748	3442.760	193.858	315	298	38750



### Exercise 1) Isothermal flash

Given that the pressure and the temperature of the flash unit are known,  $2N + 2$  unknown values must be found,  $N$  being the number of the species in the unit. The equations needed in the system are: 1 global material balance,  $N$  material balances for the species, and  $N$  equilibrium conditions for the  $i$ -th specie between the liquid and the gas phase.

$$F = V + L$$

$$F \cdot z_i = V \cdot y_i + L \cdot x_i \quad i = 1 \dots N_{\text{species}}$$

$$y_i = k_i(T, P, \vec{y}, \vec{x}) \cdot x_i \quad i = 1 \dots N_{\text{species}}$$

$z_i$  is the molar fraction of the  $i$ -th specie fed to the unit,  $F$  the inlet molar flow rate,  $x_i$  is the molar fraction of the  $i$ -th specie in the liquid stream  $L$ ,  $y_i$  is the molar fraction of the  $i$ -th specie in the vapor stream  $V$ ,  $k_i$  are the equilibrium constants for the material transfer between the liquid and the vapor phase. In general, for each specie, the equilibrium constant depends on the temperature, the pressure and the composition of both the liquid and the vapor phases. In the exercise, given that the gas is ideal and the mixture is ideal (i.e. the Raoult's law is valid), it is possible to write the constants in a simple form, starting from the Antoine's equation for the estimation of the saturation pressures of the species:

$$k_i(T, P) = \frac{P_i^{\text{SAT}}(T)}{P}$$

It is convenient to rearrange the problem by introducing the vaporization ratio  $\alpha$ : in this way, the problem of the determination the compositions of the liquid and the vapor phases is reduced to the determination of the vaporization ratio  $\alpha$ . Once this ratio is known, the compositions are easily determined. The vaporization ratio is the fraction the feed flow that is vaporized in the flash chamber.

$$\alpha = \frac{V}{F}$$

$$z_i = \alpha \cdot y_i + (1 - \alpha) \cdot x_i$$

By substitution of the equilibrium condition  $k_i \cdot x_i$  in  $y_i$ , one obtains:

$$z_i = \alpha \cdot k_i \cdot x_i + (1 - \alpha) \cdot x_i$$

$$x_i = \frac{z_i}{\alpha \cdot k_i + 1 - \alpha} = \frac{z_i}{\alpha \cdot (k_i - 1) + 1}$$

The equation required to solve for the vaporization ratio is the constraint on the molar fractions  $x_i$ :

$$\sum_1^{NSpecies} x_i = 1$$

$$\sum_1^{NSpecies} \frac{z_i}{\alpha \cdot (k_i - 1) + 1} - 1 = 0 \quad Eq.(1)$$

This equation (Eq. 1) is non-linear and must be solved with a proper numeric procedure. In this case, two solving roots are found for  $\alpha$ : a trivial solution is always found for  $\alpha = 0$ , which corresponds to the absence of vaporization. Following the same procedure of equation 1, a second equation is found (Eq. 2) for the solution of the vaporization ratio  $\alpha$  by substitution of the equilibrium constant relationship in  $x_i$ , as follows:

$$z_i = \alpha \cdot y_i + (1 - \alpha) \cdot \frac{y_i}{k_i}$$

$$k_i \cdot z_i = k_i \cdot \alpha \cdot y_i + (1 - \alpha) \cdot y_i$$

$$y_i = \frac{k_i \cdot z_i}{\alpha \cdot k_i + 1 - \alpha} = \frac{k_i \cdot z_i}{\alpha \cdot (k_i - 1) + 1}$$

$$\sum_1^{NSpecies} y_i = 1$$

$$\sum_1^{NSpecies} \frac{k_i \cdot z_i}{\alpha \cdot (k_i - 1) + 1} - 1 = 0 \quad Eq.(2)$$

Equation 2 is also non-linear and must be solved numerically. Also in this case, two solving roots are found for the  $\alpha$  ratio:  $\alpha = 1$  is a trivial solution for this equation, which corresponds to the complete vaporization of the incoming feed. If the functions corresponding to equations 1 and 2 are considered (Fig. 1a), it is noted that both the curves show a minimum. Additionally, unless an appropriate value of  $\alpha$  is assigned as a first attempt, some numerical procedures can diverge.

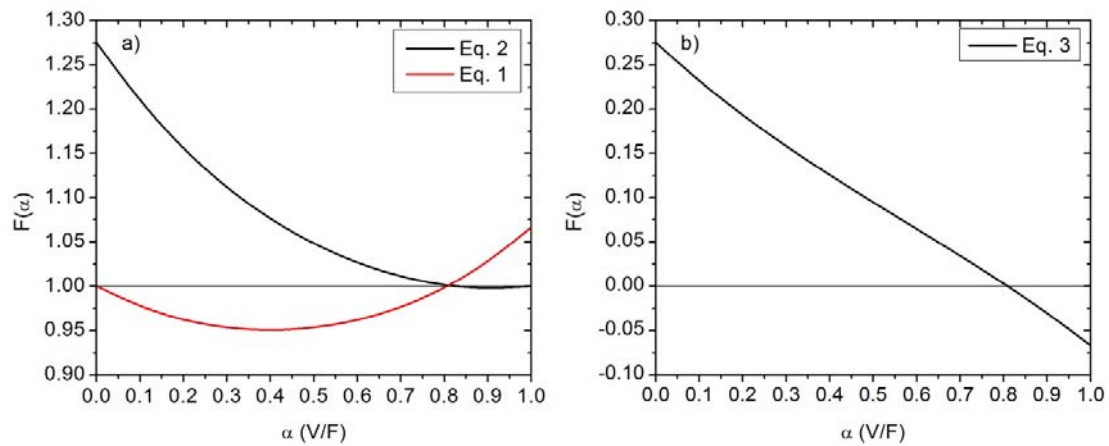


Figure 1 – solving functions Eq 1 and 2 as a function of the vaporization ratio  $\alpha$ .

If equations 1 and 2 are combined (by subtraction), equation 3 is found, also known as the Rachford-Rice equation. This equation is stable from a numerical viewpoint, since it decreases monotonically and has only one solving root between 0 and 1 (Fig. 1b).

$$\sum_1^{NSpecies} (y_i - x_i) = 1$$

$$\sum_1^{NSpecies} \frac{z_i (k_i - 1)}{\alpha \cdot (k_i - 1) + 1} = 0 \quad Eq.(3)$$

Before addressing the numerical solution, it is convenient to verify whether or not the operating conditions allow for a non-trivial solution of the vaporization ratio. In order to perform this verification, it is sufficient to calculate the bubble pressure and the dew pressure of the feed stream at the flash temperature and to verify if the pressure of the flash unit is comprised in between:

$$P_{dew}(T_{flash}) < P_{flash} < P_{bubble}(T_{flash})$$

If this condition is verified, the vaporization ratio  $\alpha$  is comprised between 0 and 1, and a liquid current and a vapor current exist at the equilibrium under the operating conditions of the flash unit. In the exercise, the dew and bubble pressures are:

$$P_{BUBBLE} = 140 \text{ kPa}$$

$$P_{DEW} = 103 \text{ kPa}$$

Similarly, the dew temperature and the bubble temperature can be calculated at the flash pressure and a vaporization ratio exists between 0 and 1 in case the flash temperature is comprised between their values:

$$T_{\text{BUBBLE}} = 72.1^{\circ}\text{C}$$

$$T_{\text{DEW}} = 82.0^{\circ}\text{C}$$

In the exercise, a non-trivial solution exists. The final vaporization ratio has the following value:

$$\alpha = 0.8107$$

With this value, the following compositions are calculated for the outgoing streams:

Species	$P_{\text{SAT}}$ [kPa]	$K_i$	$y_i$	$x_i$
Acetone	214.321	1.948	0.496	0.254
Acetonitrile	96.413	0.876	0.341	0.389
Nitromethane	50.402	0.458	0.163	0.357

### Exercise 2) Adiabatic Flash Unit

In this case, the pressure of the flash unit is known, but the temperature is unknown. Compared to the solving system of the previous exercise, in this case an additional equation is required, which is the enthalpy balance on the unit. Given that the flash unit is adiabatic, the enthalpy balance reads as follows:

$$\dot{H}_{IN}^F(T_{IN}) - \dot{H}_{OUT}^V(T_{flash}) - \dot{H}_{OUT}^L(T_{flash}) = 0$$

Similarly to the previous case, it is convenient to reduce the problem to the determination of two unknowns only, the vaporization ratio  $\alpha$  and the flash temperature  $T_{flash}$ , instead of solving for the compositions of the two streams. The enthalpy balance must be coupled with the Rachford-Rice equation:

$$\sum_1^{N_{\text{Species}}} \frac{z_i (k_i(T_{flash}, P_{flash}) - 1)}{\alpha \cdot (k_i(T_{flash}, P_{flash}) - 1) + 1} = 0$$

In the exercise, the mixtures are ideal and the gas is ideal. The equilibrium constants  $k_i$  are a function of the pressure of the flash unit and of its temperature, which is unknown. Therefore, the Rachford-Rice equation must be solved simultaneously with the enthalpy balance, giving rise to a system of two equations in two unknowns,  $T_{flash}$  and  $\alpha$ . The enthalpy balance can be written as:

$$\sum_1^{NS} F \cdot z_i \cdot \dot{h}_i^F(T_{IN}) - \sum_1^{NS} V \cdot y_i \cdot \dot{h}_i^V(T_{flash}) - \sum_1^{NS} L \cdot x_i \cdot \dot{h}_i^L(T_{flash}) = 0$$

$$\sum_1^{NS} z_i \cdot \dot{h}_i^F(T_{IN}) - \sum_1^{NS} \alpha \cdot y_i \cdot \dot{h}_i^V(T_{flash}) - \sum_1^{NS} (1 - \alpha) \cdot x_i \cdot \dot{h}_i^L(T_{flash}) = 0$$

From the estimation of the dew temperature and of the bubble temperature of the inlet feed, the inlet feed is liquid, being its temperature (130°C) lower than the bubble temperature:

$$T_{bubble}(P_{feed}) = 149.13^\circ C$$

$$T_{dew}(P_{feed}) = 190.34^\circ C$$

In the enthalpy balance, it is possible to choose as the reference the inlet feed, taken in the liquid state, at the temperature  $T_{IN}$ , pressure  $P_{feed}$  and composition  $z$ . Thus, the enthalpy of the inlet feed is null:

$$\dot{h}_i^F(T_{IN}) = 0$$

Chosen the reference, it is possible to derive the specific molar enthalpy of the species in each of the outgoing streams. For the liquid current, neglecting the pressure effects, it results:

$$\dot{h}_i^L(T_{flash}) = \int_{T_{IN}}^{T_{FLASH}} \bar{c}_{p,i}^{Liq}(T) \cdot dT$$

For the vapor stream, for each specie, the value of the  $\Delta H^{VAP}$  in the data is given at the normal boiling point (that is, at the boiling temperature of the pure specie at 1 atm,  $P = 1 \text{ atm}$ ,  $T = T_{boil}^N$ ). It is then reasonable to follow the enthalpy pathway:

$$\dot{h}_i^V(T_{flash}) = \int_{T_{IN}}^{T_{boil,i}^N} \bar{c}_{p,i}^{Liq}(T) \cdot dT + \Delta H_i^{VAP}(T_{boil,i}^N) + \int_{T_{boil,i}^N}^{T_{FLASH}} \bar{c}_{p,i}^{Vap}(T) \cdot dT$$

For both phases, the specific heats are considered constant. By substituting the specific molar enthalpy values in the enthalpy balance, the second equation of the system is obtained:

$$\sum_1^{NS} \alpha \cdot y_i \cdot [\bar{c}_{p,i}^{Liq} \cdot (T_{boil,i}^N - T_{IN}) + \Delta H_i^{VAP}(T_{boil,i}^N) + \bar{c}_{p,i}^{Vap} \cdot (T_{FLASH} - T_{boil,i}^N)] + \sum_1^{NS} (1 - \alpha) \cdot x_i \cdot \bar{c}_{p,i}^{Liq} \cdot (T_{FLASH} - T_{IN}) = 0$$

An iterative procedure can be adopted for the numerical solution. First, it is possible to solve the enthalpy balance as a function of the vaporization ratio  $\alpha$  by assuming a flash temperature; then, the Rachford-Rice equation is solved for the  $T_{flash}$  value, given the value of  $\alpha$  calculated in the previous step. The procedure is then repeated up to the convergence. Differently from the isothermal flash, in the adiabatic flash it is not possible to verify a priori the existence of a non-trivial solution of the vaporization ratio  $\alpha$ . The condition:

$$T_{IN} > T_{bubble}(P_{flash})$$

is in fact only necessary, but not sufficient for the existence of a vaporization ratio different from 0 or 1. On the one hand, the depressurization of the inlet feed from  $P_{IN}$  to  $P_{flash}$  as a consequence of the isenthalpic lamination may not be sufficient to vaporize part of the inlet current; on the other hand, the cooling of the inlet temperature from  $T_{IN}$  to  $T_{feed}$  may bring the inlet feed under its bubble temperature at  $P_{flash}$ . In the present case, the following values can be used as first attempts:  $\alpha = 0.5$  and  $T_{flash} = 115^\circ\text{C}$ . At the end of the iterative procedure, the solving values are:

$$\alpha = 0.1679$$

$$T_{flash} = 110.366^\circ\text{C}$$

The compositions of the outlet currents are:

	$K_i$	$y_i$	$x_i$	$T_{boiling}^N$ [ $^\circ\text{C}$ ]	$h_i$ liquid [J/mol]	$h_i$ vapor [J/mol]
<b>n-hexane</b>	3.186	0.699	0.219	68.700	-717.091	2837.487
<b>n-octane</b>	0.650	0.242	0.372	125.599	-1549.036	1202.999
<b>n-decane</b>	0.143	0.058	0.409	174.097	-2104.008	329.648