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Exercises of "*Fundamentals of Chemical Processes*"

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Exercise 8

Estimation of the composition of the liquid and vapor streams exiting a flash unit with a supercritical component

A mixture of hydrogen, n-heptane, n-hexane and n-butane (molar composition z_i reported in the table) is sent to a flash unit.

	z_i	A_i	B_i	C_i
H_2	0.40	-	-	-
n-heptane	0.30	15.8737	2911.32	-56.51
n-hexane	0.20	15.8366	2697.55	-48.78
n-butane	0.10	15.6782	2154.90	-34.42

For each specie, A_i, B_i and C_i are the parameters of Antoine's equation for the estimation of the vapor pressure. The mixture is initially at 10 bar. Assuming ideal gases, ideal liquid mixture and assuming that H_2 is absent from the liquid phase (H_2 is an incondensable component), estimate:

- the dew temperature of the mixture at 10 bar
- the vaporization ratio and the composition of the liquid and vapor streams obtained in a flash unit maintained at a temperature of 350 K and at a pressure of 10 bar.

Re-estimate the flash unit (vaporization ratio and outlet streams composition) assuming that the H_2 dissolves in the liquid phase according to the Henry's law. The Henry's constant of H_2 varies with the temperature and the composition of the liquid mixture, accounting the data reported in the table and the equations listed below.

	$H^0_{H2,i}$(298K) [bar]	$\Delta H_{DES}/R$
H_2 in n-heptane	1268.8	-734.4
H_2 in n-hexane	1054.7	-397.7
H_2 in n-butane	1677.2	-1418.0

Variation of the Henry's constant with the temperature for H_2 in the i-th specie: H is bar, T is K

$$H_{H_2,i} = H^0_{H_2,i}(298K) \cdot \exp\left(\frac{\Delta H_{DES}}{R} \cdot \left(-\frac{1}{T} + \frac{1}{298} \right) \right)$$

Variation of the Henry's constant with the composition of the liquid mixture:

$$\ln\left(H_{H_2,mix}\right) = \sum_{i \neq H_2}^{NC} x_i \cdot \ln\left(H_{H_2,i}\right)$$

Antoine's equation: P_{SAT} is mmHg, T is K

$$\ln P_{SAT} = A_i - \frac{B_i}{T + C_i}$$

Solution

H_2 is absent in the liquid phase. This case is very interesting, since its results can be conveniently assumed as first attempts for more complex cases. It is possible to verify the presence of a liquid phase under the operating conditions of the flash unit by comparing the dew temperature of the mixture at P_{flash} with the temperature of the flash unit. Assuming ideal gas and ideal mixtures, the equation for the dew point is:

$$\sum_{i}^{NSpecie} \frac{P_{flash} \cdot y_i}{P_i^{sat}(T_{Dew})} = 1$$

Given that the supercritical component is absent from the liquid phase ($x_{H2} = 0$), the equation includes only the condensable species (for which a saturation temperature does exist):

$$\sum_{i}^{N\,CondensableSpecie} \frac{P_{flash} \cdot y_i}{P_i^{sat}(T_{Dew})} = 1 \rightarrow \frac{P_{flash} \cdot y_{nC4}}{P_{nC4}^{sat}(T_{Dew})} + \frac{P_{flash} \cdot y_{nC6}}{P_{nC6}^{sat}(T_{Dew})} + \frac{P_{flash} \cdot y_{nC7}}{P_{nC7}^{sat}(T_{Dew})} = 1$$

The dew temperature is equal to 427.98 K, higher than that of the flash unit. It is concluded that a liquid phase is formed in the flash unit, at the equilibrium with the vapor phase. The vapor phase is always present due to the presence of the supercritical specie. Hence, the bubble temperature of the mixture cannot be defined. Once the formation of the liquid phase is verified, the value of the vaporization ratio α is determined by following the same procedure shown for the Rachford-Rice equation. The material balances are considered for all the species, while the equilibrium conditions are considered exclusively for the condensable species:

$$z_i = \alpha \cdot y_i + (1-\alpha) \cdot x_i \quad i = 1 \ldots N_{specie} \quad \textit{condensable}$$

$$y_i = \frac{P_i^{sat}\left(T_{flash}\right)}{P_{flash}} \cdot x_i = k_i\left(T_{flash}, P_{flash}\right) \cdot x_i \quad i = 1 \ldots N_{specie} \quad \textit{condensable}$$

$$z_i = \alpha \cdot y_i \quad i = 1 \ldots N_{specie} \quad \text{supercrtical}$$

$$x_i = 0 \quad i = 1 \ldots N_{specie} \quad \text{supercritical}$$

From these equations, one obtains:

$$x_i = \frac{z_i}{\alpha \cdot (k_i - 1) + 1} \quad i = 1 \ldots N_{specie} \quad \textit{condensable}$$

$$y_i = \frac{z_i \cdot k_i}{\alpha \cdot (k_i - 1) + 1} \quad i = 1 \ldots N_{specie} \quad \textit{condensable}$$

$$y_i = \frac{z_i}{\alpha} \quad i = 1 \ldots N_{specie} \quad \text{supercritical}$$

$$x_i = 0 \quad i = 1 \ldots N_{specie} \quad \text{supercritical}$$

By combining the stoichiometric relations of x_i e y_i, it results:

$$\sum_{1}^{NSpecie}(y_i - x_i) = 1$$

$$\sum_{1}^{NCondensableSpecie} \frac{z_i \cdot (k_i - 1)}{\alpha \cdot (k_i - 1) + 1} + \sum_{1}^{NSupercrticalSpecie} \frac{z_i}{\alpha} = 0 \qquad Eq.(1)$$

Since the temperature and the pressure of the flash unit are known, the only unknown value of Equation 1 is the vaporization ratio α. In the present case, Equation 1 leads to the following form:

$$\frac{z_{nC4} \cdot (k_{nC4} - 1)}{\alpha \cdot (k_{nC4} - 1) + 1} + \frac{z_{nC6} \cdot (k_{nC6} - 1)}{\alpha \cdot (k_{nC6} - 1) + 1} + \frac{z_{nC6} \cdot (k_{nC6} - 1)}{\alpha \cdot (k_{nC6} - 1) + 1} + \frac{z_{H_2}}{\alpha} = 0$$

The solving value is α = 0.4815. The corresponding compositions for the liquid and the vapor phases are:

	y_i	x_i
H_2	0.8307	0.0000
n-heptane	0.0284	0.5523
n-hexane	0.0447	0.3442
n-butane	0.0962	0.1035

It is interesting to note that the Rachford-Rice equation in the presence of supercritical components can be obtained by considering that the equilibrium constant k_i for the mass transfer between the liquid and the vapor phase is infinite in the case of supercritical components.

$$k_i(T_{flash}, P_{flash}) = \frac{y_i}{x_i} \to +\infty \quad \text{with } x_i \to 0 \qquad \text{(supercritical)}$$

The limit of the Rachford-Rice equation for k_i tending to infinite is in fact:

$$\lim_{k_i \to +\infty} \sum_{1}^{NSupercriticalSpecie} \frac{z_i \cdot (k_i - 1)}{\alpha \cdot (k_i - 1) + 1} = \sum_{1}^{NSupercriticalSpecie} \frac{z_i}{\alpha}$$

From which Equation 1 is obtained.

H_2 is present in the liquid phase. Under the assumption of ideal gas and ideal mixtures, the presence of H_2 in the liquid mixture is accounted for via the Henry's equation. The equilibrium constant for the mass transfer between the vapor and the liquid phase has a finite value also in the case of the supercritical compound, and the Rachford-Rice equation can be applied in its general form.

$$y_i = \frac{P_i^{sat}\left(T_{flash}\right)}{P_{flash}} \cdot x_i \qquad i = 1 \ldots N_{specie}$$

$$y_{H_2} = \frac{H_{H_2 mix}\left(T_{flash}, \vec{x}\right)}{P_{flash}} \cdot x_{H_2}$$

$$\sum_{1}^{NSpecie} \frac{z_i \cdot \left(k_i - 1\right)}{\alpha \cdot \left(k_i - 1\right) + 1} = 1$$

The Henry's coefficient for H_2 in the liquid mixture H_{H2mix} is defined as a function of the composition of the condensable components. The following formulas are applied:

$$\ln\left(H_{H_2,mix}\right) = \sum_{i \neq H_2}^{NC} x_i \cdot \ln\left(H_{H_2,i}\right)$$

$$H_{H_2,mix} = \exp\left[x_{nC4} \cdot \ln\left(H_{H_2,nC4}\right) + x_{nC6} \cdot \ln\left(H_{H_2,nC6}\right) + x_{nC7} \cdot \ln\left(H_{H_2,nC7}\right)\right]$$

The Henry's coefficients for H_2 dissolved in each individual condensable specie are estimated at the flash temperature by application of the following equation:

$$H_{H_2,i} = H_{H_2,i}^{0}\left(298K\right) \cdot \exp\left(\frac{\Delta H_{DES}}{R} \cdot \left(-\frac{1}{T} + \frac{1}{298}\right)\right)$$

From which, it is obtained:

	$H^0_{H2,i}$ (298 K) [bar]	$\Delta H_{DES}/R$	$H_{H2,i}$ (350 K) [bar]
H_2 in n-heptane	1268.8	-734.4	879.79
H_2 in n-hexane	1054.7	-397.7	865.00
H_2 in n-butane	1677.2	-1418.0	827.10

In order to rearrange the Rachford-Rice equation back to the only unknown value α, the molar fractions of the condensable components in the liquid phase must be expressed as a function of their feed composition z_i and of the vaporization ratio α itself.

$$x_i = \frac{z_i}{\alpha \cdot (k_i - 1) + 1} \quad i = 1 \dots N_{specie} \quad condensable$$

$$H_{H_2,mix} = \exp\left[\frac{z_{nC4}}{\alpha \cdot (k_{nC4} - 1) + 1} \cdot \ln(H_{H_2,nC4}) + \frac{z_{nC6}}{\alpha \cdot (k_{nC6} - 1) + 1} \cdot \ln(H_{H_2,nC6}) + \frac{z_{nC7}}{\alpha \cdot (k_{nC7} - 1) + 1} \cdot \ln(H_{H_2,nC7})\right]$$

By substituting this latter equation into the Rachford-Rice, the final solving equation in the only unknown α is obtained:

$$\sum_{1}^{NCondensableSpecie} \frac{z_i \cdot (k_i - 1)}{\alpha \cdot (k_i - 1) + 1} + \frac{z_{H_2} \cdot (k_{H_2} - 1)}{\alpha \cdot (k_{H_2} - 1) + 1} = 0 \qquad Eq.(2)$$

The equation is solved for α = 0.4745. It is worthy to note that the solution obtained under the assumption of the absence of H_2 from the liquid phase (α = 0.4815) is a very good first attempt to solve the current case. The compositions of the liquid phase and of the vapor phase are:

	x_i	y_i
H_2	0.0103	0.8316
n-heptane	0.5456	0.0280
n-hexane	0.3407	0.0442
n-butane	0.1035	0.0962