

Chemical Engineering Thermodynamics II

Worksheet – III and IV

Submission Date: 22-May-2018

- Starting with the fact that for a spontaneous process $\Delta S^{total} = \Delta S^{sys} + \Delta S^{sur} \geq 0$, derive criterion for equilibrium of a closed system at constant temperature and pressure.
- Assuming validity of Raoult's law for benzene (1)/toluene (2) system, calculate the following: (Iterate till the two successive temperature values are within 1%.)
 - y_1 and P given $x_1 = 0.33$ and $T = 100^\circ\text{C}$
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$$\ln P_i^{sat} / \text{kPa} = A_i - \frac{B_i}{T/^\circ\text{C} + C_i};$$

$$A_1 = 13.8594; \quad B_1 = 2773.78; \quad C_1 = 220.07$$

$$A_2 = 14.0098; \quad B_2 = 3103.01; \quad C_2 = 219.79$$

- A process stream contains light species 1 and heavy species 2. A relatively pure liquid stream containing mostly 2 is desired, obtained by a single-stage liquid/vapor separation. Specifications on the equilibrium composition are: $x_1 = 0.002$ and $y_1 = 0.950$. Use data given below to determine BUBL and DEW P(bar) at $T=350\text{K}$ for the separator. Assume that Eq. (10.5) applies; the calculated P should validate this assumption. Data: For the liquid phase:

$$\ln \gamma_1 = 0.93x_2^2 \quad \ln \gamma_2 = 0.93x_1^2$$

$$\ln P_i^{sat} / \text{bar} = A_i - \frac{B_i}{T/\text{K}}$$

$$A_1 = 10.08, \quad B_1 = 2572.0, \quad A_2 = 11.63, \quad B_2 = 6254.0$$

- What is the change in entropy when 0.7 m^3 of CO_2 and 0.3 m^3 of N_2 , each at 1 bar and 298.15 K (25°C) blend to form a gas mixture at the same conditions? Assume ideal gases.
- The molar volume ($\text{cm}^3 \text{ mol}^{-1}$) of a binary liquid mixture at T and P is given by:

$$V = 120x_1 + 70x_2 + (15x_1 + 8x_2)x_1x_2$$

- Find expressions for the partial molar volumes of species 1 and 2 at T and P.
- Show that when these expressions are combined in accord with Eq. (11.11) the given equation for V is recovered.

c. Show that these expressions satisfy Eq. (11.14), the Gibbs/Duhem equation.

d. Show that $\left(\frac{d\bar{V}_1}{dx_1}\right)_{x_1=1} = \left(\frac{d\bar{V}_2}{dx_1}\right)_{x_1=0} = 0$.

6. Estimate the fugacity of isobutylene as a gas:

a. At 553.15 K (280°C) and 20bar. (Generalized fugacity charts)

b. At 553.15 K (280°C) and 100bar. (Lee-Kesler Correlation)

7. From data in the steam tables, determine a good estimate for f/f^{sat} for liquid water at 423.15 K (150°C) and 150 bar, where f^{sat} is the fugacity of saturated liquid at 423.15 K (150°C).

8. For the system ethylene (1)/propylene (2) as a gas, estimate $\hat{f}_1, \hat{f}_2, \hat{\phi}_1$ and $\hat{\phi}_2$ at $T/t = 423.15$ K (150°C), $P = 30$ bar, and $y_1 = 0.35$: