

# ChE-304 Problem Set 6

Week 7

## Problem 1

The Margules model represents the excess Gibbs energy for a binary mixture as a simple function of the mole fraction of each component multiplied by an empirical parameter:

$$\bar{G}_E/RT = A x_1 x_2$$

From this model, could you derive a formula that describes the activity coefficient of substance 1 (i.e.  $\gamma_1$ ) in a mixture with just two components (1 and 2)?

## Solution

We use the formula that we saw in class:

$$RT \ln \gamma_\alpha = \bar{G}_\alpha^E = \frac{\partial}{\partial n_\alpha} \left[ \left( \sum_k n_k \right) (\bar{G}_E) \right] = \frac{\partial}{\partial n_\alpha} \left[ \left( \sum_k n_k \right) f(x_\alpha, x_\beta, \dots, T) \right]$$

and replace  $f(x_\alpha, x_\beta, \dots, T)$  by our model.

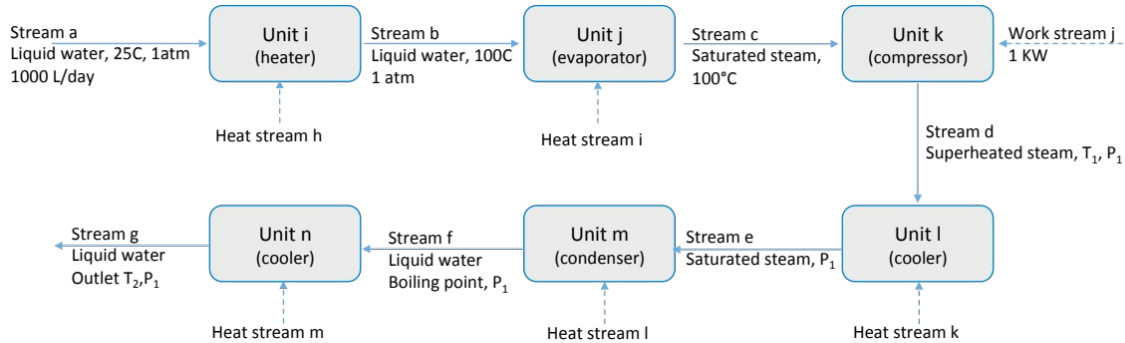
$$RT \ln \gamma_1 = \frac{\partial}{\partial n_1} \left[ \left( \sum_k n_k \right) (A x_1 x_2 RT) \right] \rightarrow \ln \gamma_1 = \frac{\partial}{\partial n_1} \left[ (n_1 + n_2) \left( \frac{A n_1 n_2}{(n_1 + n_2)^2} \right) \right] = \textcolor{red}{\frac{\partial}{\partial n_1} \left( \frac{A n_1 n_2}{(n_1 + n_2)^2} \right)}$$

$$\frac{\partial}{\partial n_1} \left[ \left( \frac{A n_1 n_2}{(n_1 + n_2)^2} \right) \right] = A \frac{n_2 (n_1 + n_2) - n_1 n_2}{(n_1 + n_2)^2} = A \frac{n_2^2}{(n_1 + n_2)^2} = A x_2^2$$

with  $\left( \frac{f}{g} \right)' = \frac{f'g - g'f}{g^2}$

## Problem 2

Last week, we came up with the following flowsheet and specifications for the slingshot process:



Assume that we specify  $T_2$ . We can also assume that the pump is a reversible adiabatic compression. Do we have enough information to fully characterize this system?

Recall that the total number of required specifications for independent streams is:

$$N_{\text{specifications}} = N_{\text{streams}, Q} + N_{\text{streams}, W_{el}} + 2 N_{\square \text{streams}, W_{mech}} + N_{\text{streams}, material} (2 + N_c)$$

### Solution:

The number of required specifications are:

$$N_{\text{specifications}} = N_{\text{streams}, Q} + N_{\text{streams}, W_{el}} + 2 N_{\square \text{streams}, W_{mech}} + N_{\text{streams}, material} (2 + N_c) = 5 + 1 + 7 * (2 + 1) = 27$$

How many specifications have we made?

Stream a: 3

Stream b: 2

Stream c: 2 (temperature and saturation conditions, which sets the pressure)

Stream d: -

Stream e: 2 (saturation  $T^\circ$  at  $P_1$ )

Stream f: 2 (boiling water at  $P_1$ )

Stream g: 2 ( $T_2$  and  $P_1$ )

Stream j: 1

Streams h, i, k, l, m: -

**Total: 14**

We are missing 13 specifications. However, this is for isolated streams. We have unit relations that will reduce the number of required specifications.

For each unit we have a mass and energy balance:

6 units\*2 balances = 12 equations

For the pump, we also have the relation for isentropic (= reversible adiabatic) compression → 1 extra equation!

Therefore, this will reduce the number of required specifications by 12+1=13, meaning our system is fully specified!

### Problem 3

Last week, we started analyzing the Slingshot process by drawing a flowsheet and by calculating the temperature and pressure of the fluid after compression.

At this temperature and pressure, is the fluid in its liquid or vapor phase? Once you have determined the phase, you can calculate the enthalpy and entropy of the fluid at this temperature.

Coefficients needed for the Antoine equation and the Cp equation of water and the standard enthalpy and entropy are shown below (from the NIST webbook).

Antoine's equation:

$$C_p(T) = A_\alpha + B_\alpha T + C_\alpha T^2 + D_\alpha T^3 + \frac{E_\alpha}{T^2}, \text{ where } T = \frac{\text{temperature} \in K}{1000}$$

Antoine's parameters, valid 370-573K:

$$A = 3.55959 \quad B = 643.748 \quad C = -198.043$$

Cp equation coefficients, vapor phase:

$$A = 30.092 \quad B = 6.832514 \quad C = 6.793435 \quad D = -2.53448 \quad E = 0.082139$$

Standard enthalpy and entropy, vapor phase:

$$\text{Standard enthalpy, kJ/mol} = -241.83 \quad \text{Standard entropy, J/molK} = 188.84$$

Cp equation coefficients, liquid phase:

$$A = -203.6060 \quad B = 1523.290 \quad C = -3196.413 \quad D = 2474.455 \quad E = 3.855326$$

Standard entropy, liquid phase, J/molK = 69.95

Enthalpy of vaporization, water at 100C, kJ/mol = 40.6

Critical temperature, pressure of water: 647.3K, 221.2 bar

### Solution:

(From last week's solution:  $T = 430.7 \text{ K}$ ,  $P = 1.836 \text{ atm}$  or  $1.86 \text{ bar}$ )

First, using the Antoine equation:

$$\log_{10}(P_{sat, \alpha}) = A_\alpha - \frac{B_\alpha}{T_{sat, \alpha} + C_\alpha} \quad (\text{Equation 2.4 in the notes})$$

$$\log_{10}(P_{sat, \alpha}) = 3.55959 - \frac{643.748}{430.7 - 198.043}$$

$$P_{sat, \alpha} = 6.20369 \text{ bar}$$

At this temperature, saturation pressure is 6.2 bar. Since our pressure is lower, we know our fluid is in The vapor phase.

Thus, we use the vapor phase Cp coefficients to determine enthalpy and entropy at this temperature from  $H_0$  and  $S_0$ .

We know that  $C_p(T) = A_\alpha + B_\alpha T + C_\alpha T^2 + D_\alpha T^3 + \frac{E_\alpha}{T^2}$ , where  $T = \frac{temp}{1000}$

And  $dH = C_p dT$ ,

So,

$$H = \int_{T_0}^{T_1} C_p dT$$

$$\Delta H = A_\alpha (T_1 - T_0) + \frac{B_\alpha (T_1^2 - T_0^2)}{2} + \frac{C_\alpha (T_1^3 - T_0^3)}{3} + \frac{D_\alpha (T_1^4 - T_0^4)}{4} - E_\alpha \left( \frac{1}{T_1} - \frac{1}{T_0} \right)$$

Plugging values in,

$$\Delta H = (30.092) * (431 - 298) + \frac{6.832514 * (431^2 - 298^2)}{1000} + \frac{6.793435 * (431^3 - 298^3)}{1000^2} + \frac{-2.53448 * (431^4 - 298^4)}{1000^3} -$$

$$\Delta H = 4.508 \text{ kJ/mol}$$

Thus,

$$H_{430.7} = H_{298.15} + \Delta H = -241.83 + 4.508$$

$$H_{430.7} = -237.3 \text{ kJ/mol}$$

Now, let look at entropy. We know that

$$dS = \frac{C_p}{T} dT - \frac{R}{P} dP$$

$$S = \int_{T_0}^{T_1} \frac{C_p}{T} dT - \int_{P_0}^{P_1} \frac{R}{P} dP$$

$$\Delta S_\alpha = \left[ A_\alpha \ln \left( \frac{T_1}{T_0} \right) + \frac{B_\alpha}{1000} (T_1 - T_0) + \frac{C_\alpha}{1000^2} (T_1^2 - T_0^2) + \frac{D_\alpha}{1000^3} (T_1^3 - T_0^3) - \frac{E_\alpha * 1000^2}{2} \left( \frac{1}{T_1^2} - \frac{1}{T_0^2} \right) \right] - \left[ R * \ln \left( \frac{P_1}{P_0} \right) \right]$$

Plugging values ( $T_1 = 431 \text{ K}$ ,  $T_0 = 298 \text{ K}$ ,  $P_1 = 1.86 \text{ bar}$ ,  $P_0 = 1 \text{ bar}$ ) in and solving,

$$\Delta S = 7.338 \text{ J/(K mol)}$$

Thus,

$$S_{430.7} = S_{298.15} + \Delta S = 188.84 + 7.34$$

$$S_{430.7} = 196.18 \text{ J/(K mol)}$$