Homework Assignment 3

Practice Solved Problems

1. Smith, J. M., Van Ness, H. C., & Abbott, M. M. (2005). Introduction to Chemical Engineering Thermodynamics, 7th ed.
   - Chapter 6: 6.2, 6.3, 6.4, 6.5, 6.6
   - Chapter 10: 10.1, 10.2, 10.3
   - Chapter 11: 11.2, 11.3, 11.4, 11.5, 11.6, 11.7, 11.8

HW Problems (Due 14th June in-class 2pm)

1. [40 points] Derive departure function for enthalpy, Gibbs free-energy and entropy for Beattie-Bridgman equation of state:
$$P = \frac{RT}{v^2}\left(1 - \frac{C}{vT^3}\right)\left(v + B_0 - \frac{bB_0}{v}\right) - \frac{A_0}{v^2}\left(1 - \frac{a}{v}\right) \tag{1}$$
Now compute these departure functions for O_2 at 350K and 40bar. Given that for O_2: $A_0 = 0.1511\frac{Pa\cdot m^3}{mol^2}$; $B_0 = 0.04624 \times 10^{-3}\frac{m^3}{mol}$; $a = 0.02562 \times 10^{-3}\frac{m^3}{mol}$; $b = 0.004208 \times 10^{-3}$; $C = 48\frac{m^3K^3}{mol}$.

2. [10 points] Liquid isobutane is throttled through a valve from an initial state of 360K and 4000 kPa to a final pressure of 2000 kPa. Estimate the temperature change and the entropy change of the isobutane. The specific heat of liquid isobutane at 360K is 2.78J/g/°C. Estimates of V and β may be found from Rackett equation ($V^{sat} = V_c Z_c^{(1-T_r)^{2/7}}$).

3. [10 points] A rigid vessel of 0.4 m^3 capacity is filled with steam at 800 kPa and 350 °C. How much heat must be transferred from the steam to bring its temperature to 200°C.

4. [10 points] The constants for carbon dioxide, as described by the van der Waals equation of state
$$\left(p + \frac{a}{v^2}\right)(v - b) = RT, \tag{2}$$
are $a = 3.592$atm L^2/mol^2 and $b = 0.04267$ L/mol. What is the vapor pressure of carbon dioxide at 275 K? What are the specific volumes of the coexisting vapor and liquid phases at that temperature?

5. [20 points] Below the triple point (-56.2 °C)the vapor pressure of solid carbon dioxide may be expressed by the relation:
$$\log_{10} p = -\frac{1353}{T} + 9.832 \tag{3}$$
where p is in mmHg and T in K. The enthalpy of melting is 8382 J/mol. Make an estimate of the vapor pressure of liquid carbon dioxide at 0°C and indicate the sources of inaccuracy in the method used.

6. [20 points] Assuming Raoult's law to apply to the system $n-$pentane(1)/$n-$heptane(2),
   (a) What are the values of x_1 and y_1 at T=55°C and $P = \frac{1}{2}\left(P_1^{sat} + P_2^{sat}\right)$? For these conditions plot the fraction of system that is vapor vs. overall composition z_1.
   (b) For $T = 55$°C and $z_1 = 0.5$, plot P , x_1, y_1 vs vapor fraction.

7. [10 points] A concentrated binary solution containing mostly species 2 (but $x_2 \neq 1$) is in equilibrium with a vapor phase containing both species 1 and 2. The pressure of this two-phase system is 1 bar; the temperature is 25 °C. Determine from the following data good estimates of x_1 and y_1. $\mathcal{H}_1 = 200$ bar and $P_2^{sat} = 0.01$ bar. State and justify all assumptions.

8. [20 points] 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 T (K) and P (bar) for the separator. Assume modified Raoult's applies to the VLE of the system; the calculated P should validate this assumption. Data: For the liquid phase, $\ln \gamma_1 = 0.93x_2^2$ and $\ln \gamma_2 = 0.93x_1^2$. Also, $\ln P_i^{sat} = A_i - \frac{B_i}{T}$, where P_i is in bars and T is in K. Also, $A_1 = 10.08$, $B_1 = 2572.0$, $A_2 = 11.63$ and $B_2 = 6254.0$.

9. [10 points] What is the change in entropy when 0.7m^3 of CO_2 and 0.3 m^3 of N_2m each at 1 bar and 25 °C blend to form a gas mixture at the same conditions? Assume ideal gasses.

10. [20 points] Estimate the fugaicty of cyclopentane at 110°C and 275 bar. AT 110°C the vapor pressure of cyclopentane is 5.267 bar. Assume Redlich-Kwong equation of state to estimate fugacity coefficient.

11. [10 points] A vessel, divided into two parts by a partition, contains 4 mol of nitrogen gas at 75°C and 30 bar on one side and 2.5 mol of argon gas at 130°C and 20 bar on the other. If the partition is removed and the gases mix adiabatically and completely, what is the change in entropy? Assume nitrogen to be an ideal gas with $C_v = (5/2)R$ and argon to be an ideal gas with $C_v = (3/2)R$.

12. [10 points] Solid sulfur undergoes a phase transition between the monoclinic (m) and orthorhombic (o) phases at a temperature of 368.3 K and pressure of 1 bar. Calculate the difference in Gibbs energy between monoclinic sulfur and orthorhombic sulfur at 298 K and a pressure of 1 bar. Which phase is more stable at 298 K? Take the entropy in each phase to be given by the following expressions: Monoclinic phase: $s_m = 13.8 + 0.066T$ [J/(mol K)]; Orthorhombic phase: $s_o = 11.0 + 0.071T$ [J/(mol K)]