CYL100 2013–14 I semester Homework 3

Handed out: August 17, 2013 Due in: August 23, 2013

Notes: 1. Unless otherwise stated, gases can be considered to behave ideally.

2. You will need a table of thermodynamic data for some of the problems. Indicate the source of your thermodynamic data.

1. Calculate the change in the chemical potential for N_2, when the temperature changes from 298.15 K to 130 K and pressure changes from 1 atm to 600 atm. Treat nitrogen as a van der Waals gas with $a = 1.39000$ L^2 atm mole^{-2} and $b = 0.03913$ L mole^{-1}. Compare your result with that obtained using the following data: H_m(130 K, 1 atm) = 10.655 kJ/mol, H_m(298.15 K, 1 atm) = 15.586 kJ/mol, H_m(130 K, 600 atm) = 7.305 kJ/mol, S_m(130 K, 1 atm) = 16.710 kJ/mol K, S_m(298.15 K, 1 atm) = 19.137 kJ/mol K, S_m(130 K, 600 atm) = 0.09633 kJ/mol K.

2. The Gibbs energy of a binary mixture of species a and species b at 300 K and 10 bar is given by the following expression:
$$g = 40x_a - 60x_b + RT(x_a \ln x_a + x_b \ln x_b) + 5x_a x_b \qquad \text{[kJ/mol]}$$
(a) For a system containing 1 mole of species a and 4 moles of species b, find ΔG_{mix} and ΔS_{mix}. (b) If the pure species are mixed together adiabatically, do you think the temperature of the system will increase, stay the same, or decrease. Explain, stating any assumptions that you make.

3. (a) Calculate the entropy of mixing 3 mol of hydrogen with 1 mol of nitrogen. (b) Calculate the Gibbs energy of mixing at 25 ℃. (c) At 25 ℃, calculate the Gibbs energy of mixing $1 - \xi$ mol of nitrogen, $3(1 - \xi)$ mol of hydrogen, and 2ξ mol of ammonia as a function of ξ. Plot the values from $\xi = 0$ to $\xi = 1$ at intervals of 0.2 (d) If $\Delta G^\circ_f(NH_3) = -16.5$ kJ/mol at 25 ℃, calculate the Gibbs energy of the mixture for values of $\xi = 0$ to $\xi = 1$ at intervals of 0.2. Plot G versus ξ if the initial state is the mixture of 1 mol N_2 and 3 mol of H_2. (e) Calculate G for ξ_e at $p = 1$ atm.

4. The reaction $SO_2(g) + \frac{1}{2}O_2 \longrightarrow SO_3$ is performed starting with 1.2 moles of SO_2, 0.8 mole of O_2, and 0.07 moles of SO_3. At some time after you start the reaction, the extent of reaction is $\xi = 0.5$. Calculate the number of moles and the mole fractions of each component at that time.

5. Fuel cells provide an attractive alternative energy source. They require an H_2 feed stream to operate. Consider a fuel cell based on the direct conversion of methanol to form hydrogen:
$$H_2O(g) + CH_3OH(g) = CO_2(g) + 3\,H_2(g)$$
The reaction is carried out at 60 ℃ and low pressure, with a feed of twice as much water as methanol. The equilibrium extent of reaction is $\xi = 0.87$. How many moles of H_2 can be produced per mole of CH_3OH in the feed? What is the mole fraction of H_2?

6. Calculate the equilibrium constant at 298 K for the reaction of problem 5.

7. Calculate the equilibrium constant at 60 ℃ for the reaction of problem 5.

8. We wish to produce formaldehyde, CH_2O, by the gas-phase pyrolysis of methanol, CH_3OH, according to:
$$CH_4O(g) = CH_2O(g) + H_2(g)$$
(a) What is the equilibrium constant at room temperature? Would you expect an appreciable yield of product?
(b) Consider the reaction at 600 ℃ and 1 bar. What is the equilibrium constant (i) assuming $\Delta H^\circ_{\text{rxn}}$ = constant? (ii) using $\Delta H^\circ_{\text{rxn}} = \Delta H^\circ_{\text{rxn}}(T)$?

9. Consider the following general gas-phase reaction:
$$\text{aA(g)} + \text{bB(g)} = \text{cC(g)dD(g)}$$
The constant-pressure reactor also contains an inert species, I. Describe how the following reactor conditions affect yield of reaction products: (a) temperature; (b) pressure; (c) addition of inert species; (d) additional (nonstoichiometric) reactant in feed.

10. Consider the production of ammonia from the catalytic reaction of a stoichiometric feed of nitrogen and hydrogen. The reaction temperature is 500 ℃ and the reactor pressure is 1 bar.
$$N_2 + 3\,H_2 = 2\,NH_3$$
What is the maximum possible conversion? (a) Take $\Delta H^\circ_{\text{rxn}}$ = constant. (b) Take $\Delta H^\circ_{\text{rxn}} = \Delta H^\circ_{\text{rxn}}(T)$.

11. Consider the two equilibria,
$$A_2 \rightleftharpoons 2\,A$$
$$AB \rightleftharpoons A + B,$$
and assume that the $\Delta_r G^\circ$ and therefore K is the same for both. Show that the equilibrium value of ξ_2 is greater than the equilibrium value of ξ_1? What is the physical reason for this result?