

**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.

- 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  $a = 1.39000 \text{ L}^2 \text{ atm mole}^{-2}$  and  $b = 0.03913 \text{ L mole}^{-1}$ . Compare your result with that obtained using the following data:  $H_m(130 \text{ K}, 1 \text{ atm}) = 10.655 \text{ kJ/mol}$ ,  $H_m(298.15 \text{ K}, 1 \text{ atm}) = 15.586 \text{ kJ/mol}$ ,  $H_m(130 \text{ K}, 600 \text{ atm}) = 7.305 \text{ kJ/mol}$ ,  $S_m(130 \text{ K}, 1 \text{ atm}) = 16.710 \text{ kJ/mol K}$ ,  $S_m(298.15 \text{ K}, 1 \text{ atm}) = 19.137 \text{ kJ/mol K}$ ,  $S_m(130 \text{ K}, 600 \text{ atm}) = 0.09633 \text{ kJ/mol K}$ .

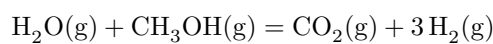
- The Gibbs energy of a binary mixture of species  $a$  and species  $b$  at 300 K and 10 bar is given by the following expression:

$$g = 40x_a - 60x_b + RT(x_a \ln x_a + x_b \ln x_b) + 5x_a x_b \quad [\text{kJ/mol}]$$

- For a system containing 1 mole of species  $a$  and 4 moles of species  $b$ , find  $\Delta G_{\text{mix}}$  and  $\Delta S_{\text{mix}}$ . (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.
- (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. (c) At 25 °C, calculate the Gibbs energy of mixing  $1 - \xi$  mol of nitrogen,  $3(1 - \xi)$  mol of hydrogen, and  $2\xi$  mol of ammonia as a function of  $\xi$ . Plot the values from  $\xi = 0$  to  $\xi = 1$  at intervals of 0.2 (d) If  $\Delta G_f^\circ(\text{NH}_3) = -16.5 \text{ kJ/mol}$  at 25 °C, calculate the Gibbs energy of the mixture for values of  $\xi = 0$  to  $\xi = 1$  at intervals of 0.2. Plot  $G$  versus  $\xi$  if the initial state is the mixture of 1 mol  $N_2$  and 3 mol of  $H_2$ . (e) Calculate  $G$  for  $\xi_e$  at  $p = 1 \text{ atm}$ .

- The reaction  $\text{SO}_2(\text{g}) + \frac{1}{2}\text{O}_2 \rightarrow \text{SO}_3$  is performed starting with 1.2 moles of  $\text{SO}_2$ , 0.8 mole of  $\text{O}_2$ , and 0.07 moles of  $\text{SO}_3$ . 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.

- 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:

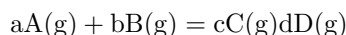


The reaction is carried out at 60 °C and low pressure, with a feed of twice as much water as methanol. The equilibrium extent of reaction is  $\xi = 0.87$ . How many moles of  $H_2$  can be produced per mole of  $\text{CH}_3\text{OH}$  in the feed? What is the mole fraction of  $H_2$ ?

- Calculate the equilibrium constant at 298 K for the reaction of problem 5.
- Calculate the equilibrium constant at 60 °C for the reaction of problem 5.
- We wish to produce formaldehyde,  $\text{CH}_2\text{O}$ , by the gas-phase pyrolysis of methanol,  $\text{CH}_3\text{OH}$ , according to:

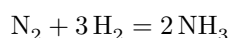


- What is the equilibrium constant at room temperature? Would you expect an appreciable yield of product?
  - Consider the reaction at 600 °C and 1 bar. What is the equilibrium constant (i) assuming  $\Delta H_{\text{rxn}}^\circ = \text{constant}$ ? (ii) using  $\Delta H_{\text{rxn}}^\circ = \Delta H_{\text{rxn}}^\circ(T)$ ?
- Consider the following general gas-phase reaction:



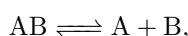
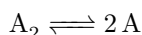
The constant-pressure reactor also contains an inert species,  $I$ . Describe how the following reactor conditions affect yield of reaction products: (a) temperature; (b) pressure; (c) addition of inert species; (d) additional (nonstoichiometric) reactant in feed.

- Consider the production of ammonia from the catalytic reaction of a stoichiometric feed of nitrogen and hydrogen. The reaction temperature is 500 °C and the reactor pressure is 1 bar.



What is the maximum possible conversion? (a) Take  $\Delta H_{\text{rxn}}^\circ = \text{constant}$ . (b) Take  $\Delta H_{\text{rxn}}^\circ = \Delta H_{\text{rxn}}^\circ(T)$ .

- Consider the two equilibria,



and assume that the  $\Delta_r G^\circ$  and therefore  $K$  is the same for both. Show that the equilibrium value of  $\xi_2$  is greater than the equilibrium value of  $\xi_1$ ? What is the physical reason for this result?