

## 13.10: Problems

1. Ethylene is the most important feedstock for the organic chemicals industry. The ethylene-production process with the lowest processing cost is the “thermal cracking” of ethane to produce hydrogen and ethylene. The table below gives  $\Delta_f G^\circ$  for ethane and ethylene at 1000 K, 1100 K, and 1200 K.

T, K	$C_6H_6$	$C_6H_4$
1000	110,750	119,067
1100	132,385	127,198
1200	154,096	135,402

- Calculate  $\Delta_r G^\circ$  and  $K_P$  at each temperature.
  - At each temperature, calculate the extent of reaction when one mole of pure ethane reacts to reach equilibrium, while the pressure of the system is maintained constant at one bar.
  - At each temperature, calculate the extent of reaction when one mole of pure ethane reacts to reach equilibrium, while the pressure of the system is maintained constant at 0.100 bar.
  - To minimize side reactions, it is desirable to operate a cracking reactor at the lowest possible temperature. The feed to a cracking reactor contains many moles of water (steam) for every mole of ethane. Steam is simply an inexpensive inert gas in this system. Why is steam fed to cracking reactors?
2. A system initially contains one mole of ethane. The cracking reaction occurs while the system is maintained at a constant pressure of 0.1 bar and a constant temperature of 1000 K.
- Write the equations for the molar Gibbs free energies of ethane, ethylene, and hydrogen as a function of the extent of reaction,  $\xi$ .
  - Write the equation for  $\Delta_r G^\circ$  as a function of the extent of reaction. For a constant system pressure of 0.1 bar, calculate  $\Delta_r G^\circ$  for  $\xi = 0, 0.4, 0.7, 0.8, 0.9$ , and 1.0. Roughly, what extent of reaction corresponds to  $\Delta_r G^\circ = 0$ ?
  - Write the equation for the Gibbs free energy of the system,  $G_{system}$ , as a function of the extent of reaction,  $\xi$ . For a constant system pressure of 0.1 bar, calculate  $G_{system}$  for  $\xi = 0, 0.4, 0.7, 0.8, 0.9$ , and 1.0. Roughly, at what extent of reaction is  $G_{system}$  a minimum?
  - From the equation for  $G_{system}$  in part (c), find  $(\partial G_{system} / \partial \xi)_{T,P,n_j}$ . (When the  $n_j$  are constant, the composition of the system is fixed:  $\bar{G}_{C_6H_6}$ ,  $\bar{G}_{C_6H_4}$ , and  $\bar{G}_{H_2}$  are constants.)
3. At  $-56.6^\circ\text{C}$ , the vapor pressure of solid  $CO_2$  is 5.18 bar. (This is the triple point.) At  $-78.5^\circ\text{C}$ , the vapor pressure of solid  $CO_2$  is 1.01 bar.
- A cold bath is prepared by mixing solid  $CO_2$  with methanol in a Dewar flask that is open to the atmosphere. What is the temperature of this cold bath?
  - Use the Clausius-Clapeyron equation to estimate the enthalpy of sublimation of  $CO_2$ .
  - Assume that we know the Gibbs free energy of formation for both solid and ideal-gas  $CO_2$  at a particular temperature, T. That is, we know  $\Delta_f G^\circ(CO_2, g, T)$  and  $\Delta_f G^\circ(CO_2, s, T)$ . What is the Gibbs free energy of gaseous  $CO_2$  as a function of pressure at constant temperature, T?
  - What is the Gibbs free energy of solid  $CO_2$  at a constant temperature, T?
  - Assume that the variation of the Gibbs free energy of the solid with pressure is negligible. Using your answers to (c) and (d), write the Gibbs free energy change,  $\Delta G$ , for the process  $CO_2(\text{solid}, P, T) \rightarrow CO_2(\text{gas}, P, T)$ . If  $(P, T)$  is a point of solid—gas equilibrium, what is the value of  $\Delta G$ ? How is the equilibrium constant for this process related to  $P_{CO_2}$ ?
  - Use the Gibbs-Helmholtz equation to estimate the enthalpy of sublimation of  $CO_2$ .
  - Compare the equation you used in part (b) to the equation that you used in part (f).

4. Ethanol is manufactured by the addition of water to ethylene over a solid-acid catalyst. The process is known as “the hydration of ethylene.” One mole of ethylene, 10 moles of water, and a quantity of solid catalyst are charged to a reactor. When equilibrium is reached at 400 K, the system pressure is 10.00 bar and the conversion to ethanol is 64.17%. Assume that ethylene, water, and ethanol behave as ideal gases. What is  $\Delta_r G^\circ$  for the hydration of ethylene at 400 K?

5. At 298.15 K, the Gibbs free energies for formation of  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$ , in their hypothetical ideal gas standard states, are 51.3 and 99.8 kJ mol<sup>−1</sup>, respectively.

(a) At this temperature, what is the value of the equilibrium constant for the reaction  $\text{N}_2\text{O}_4 \rightleftharpoons 2 \text{NO}_2$ ?

(b) A 10 L sample of gas initially contains one mole of  $\text{N}_2\text{O}_4$ . The balance of the sample is  $\text{N}_2$ . The pressure and temperature of the system are maintained constant at 3 bar and 298.15 K. How many moles of  $\text{NO}_2$  are present at equilibrium? What fraction of the  $\text{N}_2\text{O}_4$  is converted to  $\text{NO}_2$ ?

(c) A 10 L sample of gas initially contains only one mole of  $\text{N}_2\text{O}_4$  at 298.15 K. The volume and temperature of the system are maintained constant. What fraction of the  $\text{N}_2\text{O}_4$  is converted to  $\text{NO}_2$ ?

(d) A 10 L sample of gas initially contains only 10<sup>−1</sup> mole of  $\text{N}_2\text{O}_4$  at 298.15 K. The pressure and temperature of the system are maintained constant. What fraction of the  $\text{N}_2\text{O}_4$  is converted to  $\text{NO}_2$ ?

(e) A 10 L sample of gas initially contains only 10<sup>−1</sup> mole of  $\text{N}_2\text{O}_4$  at 298.15 K. The volume and temperature of the system are maintained constant. What fraction of the  $\text{N}_2\text{O}_4$  is converted to  $\text{NO}_2$ ?

6. At 800 K, the Gibbs free energies for formation of methanol and formaldehyde, in their hypothetical ideal gas standard states, are −88.063 and −87.893 kJ mol<sup>−1</sup>, respectively.

(a) At 800 K, what is the value of the equilibrium constant for the reaction  $\text{CH}_3\text{OH} \rightleftharpoons \text{CH}_2\text{O} + \text{H}_2$ ?

(b) Initially, one mole of pure methanol occupies 1 m<sup>3</sup> at 800 K. The volume and temperature of this system are maintained constant. Assume that the presence of a catalyst allows this reaction to occur selectively. How many moles of formaldehyde are present at equilibrium? What fraction of the methanol is converted to formaldehyde?

(c) The initial system in (b) is allowed to equilibrate at constant pressure and temperature. What fraction of the methanol is converted to formaldehyde?

(d) Initially, one mole of hydrogen and one mole of methanol occupy 1 m<sup>3</sup> at 800 K. The volume and temperature of this system are maintained constant. What fraction of the methanol is converted to formaldehyde at equilibrium?

7. At 298.15 K, the Gibbs free energies of formation of  $\text{Br}_2$  and  $\text{BrCl}$ , in their hypothetical ideal gas standard states, are +3.1 and −1.0 kJ mol<sup>−1</sup>, respectively. Why is  $\Delta_f G^\circ(\text{Br}_2, \text{HIG}^\circ, 298.15 \text{ K})$  not zero? A 1 m<sup>3</sup> vessel initially contains 0.100 mole of  $\text{Br}_2$  and 0.200 mole of  $\text{Cl}_2$  at 298.15 K. The volume and temperature are maintained constant. What are the partial pressures of  $\text{Br}_2$ ,  $\text{Cl}_2$ , and  $\text{BrCl}$  at equilibrium?

8. Devise a non-isothermal process for the reversible mixing of two gases. (Suppose that one of the substances can be condensed to a liquid, whose vapor pressure is negligible, at a temperature at which the other substance remains a gas.)

9. The following thermodynamic data are available:

$$\Delta_f G^\circ(\text{SO}_2, \text{g}, 298.15 \text{ K}) = -300.1 \text{ kJ mol}^{-1}$$

$$\Delta_f G^\circ(\text{SO}_3, \text{g}, 298.15 \text{ K}) = -371.1 \text{ kJ mol}^{-1}$$

$$\Delta_f H^\circ(\text{SO}_2, \text{g}, 298.15 \text{ K}) = -296.8 \text{ kJ mol}^{-1}$$

$$\Delta_f H^\circ(\text{SO}_3, \text{g}, 298.15 \text{ K}) = -395.7 \text{ kJ mol}^{-1}$$

(a) What are  $\Delta_r G^\circ$  and  $\Delta_r H^\circ$  for the reaction  $2 \text{SO}_2 + \text{O}_2 \rightleftharpoons 2 \text{SO}_3$  at 298.15 K?

(b) Estimate the temperature,  $T_0$ , at which the standard Gibbs free energy change for this reaction is zero.

(c) A mixture is prepared to contain 1.00 mole of  $\text{SO}_2$  and 1.00 mole of  $\text{O}_2$ . The mixture is allowed to equilibrate at  $T_0$  and a pressure of 10.0 bar. What fraction of the  $\text{SO}_2$  is converted to  $\text{SO}_3$ ?

(d) A mixture is prepared to contain 1.00 mole of  $\text{SO}_2$  and 10.0 mole of  $\text{O}_2$ . The mixture is allowed to equilibrate at  $T_0$  and a pressure of 10.0 bar. What fraction of the  $\text{SO}_2$  is converted to  $\text{SO}_3$ ?

10. At 400 K, the Gibbs free energies of formation for carbon monoxide and methanol are  $-146.341 \text{ kJ mol}^{-1}$  and  $-148.509 \text{ kJ mol}^{-1}$ , respectively. What is  $\Delta_r G^\circ$  for the reaction  $\text{CO} + 2 \text{H}_2 \rightleftharpoons \text{CH}_3\text{OH}$ ? A mixture of carbon monoxide and hydrogen in the stoichiometric proportions is prepared. Assume that the presence of a catalyst allows this reaction to occur selectively. When this mixture reaches equilibrium at 400 K and 1.00 bar, what fraction of the carbon monoxide is converted to methanol?
11. At 500 K, the Gibbs free energies of formation for carbon monoxide and methanol are  $-155.412 \text{ kJ mol}^{-1}$  and  $-134.109 \text{ kJ mol}^{-1}$ , respectively. What is  $\Delta_r G^\circ$  for the reaction  $\text{CO} + 2 \text{H}_2 \rightleftharpoons \text{CH}_3\text{OH}$ ? Assume that the presence of a catalyst allows this reaction to occur selectively. What ratio of hydrogen to carbon monoxide must be charged to a reactor in order for 50% of the carbon monoxide to be converted to methanol when the system reaches equilibrium at a pressure of 100.0 bar?
12. The reaction of carbon monoxide with water to produce carbon dioxide and hydrogen,  $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$ , is known as “the water-gas shift reaction.” It is used in the commercial manufacture of hydrogen. The Gibbs free energy change for this reaction becomes less favorable as the temperature increases. At 1100 K, the standard Gibbs free energy change for this reaction is  $\Delta_r G^\circ = +0.152 \text{ kJ mol}^{-1}$ . Equal numbers of moles of carbon monoxide and water are charged to a reactor. What fraction of the water is converted to hydrogen when the system reaches equilibrium at 1100 K and 10.0 bar?

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