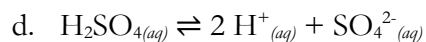
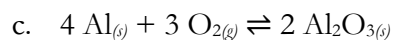
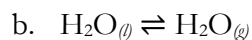
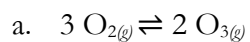


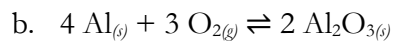
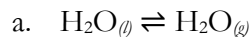
**Chem 160 Chapter 17: Thermodynamics: Entropy, Free Energy, and Equilibrium**

1. What is a *spontaneous* process? What determines spontaneity? Define Gibb's free energy, enthalpy, and entropy, and the relationship between them.

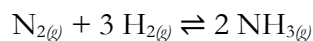
2. Predict the sign of  $\Delta S$  in the following processes. Briefly explain your answer:



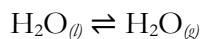
3. Calculate  $\Delta S^\circ$ ,  $\Delta H^\circ$ , and  $\Delta G^\circ$  for following reactions using standard values of formation. Are products or reactants favored?



4. Calculate the free energy change of the following reaction at 0 °C and 0.5 atm N<sub>2</sub>, 0.7 atm H<sub>2</sub>, and 1.5 atm NH<sub>3</sub>. Is the reaction spontaneous under these conditions?



5. Calculate the equilibrium constant for the following reaction at 25 °C. What species is dominant in the equilibrium mixture?



6. A mixture of 14.0 g of N<sub>2</sub> and 3.024 g of H<sub>2</sub> in a 2.00 L container is heated to 350 °C.
- Calculate the molar concentrations of each species present in the mixture at equilibrium, assume that  $\Delta S^\circ$  and  $\Delta H^\circ$  are independent of temperature, and remember that the standard state of a gas is defined in terms of pressure.
  - Does the yield of the product increase or decrease on raising the temperature from 350 °C to 500 °C. Explain your answer using thermodynamic properties?

### Solutions

1. A spontaneous process is a process that happens without intervention in a given set of conditions. In a spontaneous reaction, the formation of products is more favorable. Spontaneity is determined by the overall change in Gibb's free energy ( $\Delta G$ ), i.e. energy available to do work. A reaction is spontaneous when  $\Delta G^\circ < 0$  and is nonspontaneous when  $\Delta G^\circ > 0$

Gibb's free energy can be calculated from enthalpy change ( $\Delta H$ ) and entropy change ( $\Delta S$ , randomness or degree of disorder).

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

(Note:  $^\circ$  denotes standard conditions: 298.15 K (25  $^\circ$ C) and 1 atm)

$\Delta H^\circ$	$\Delta S^\circ$	$\Delta G^\circ$
Positive	Negative	Always positive
Positive	Positive	Positive at low T, negative at high T
Negative	Positive	Always negative
Negative	Negative	Negative at low T, positive at high T

2.

- a. Negative. A process that increases the number of particles increases the entropy of the system.
- b. Positive. Liquids have larger entropy than solids.
- c. Negative. A process that decreases the number of particles decreases the entropy of the system.
- d. Positive. A process that increases the number of particles increases the entropy of the system.

3. (Values obtained from Table B.13, *Chemistry: Structures and Dynamics*, 5<sup>th</sup> edition, by James N. Spencer)

$$\begin{aligned} \text{a. } \Delta H^\circ &= \sum(\Delta H^\circ_{\text{products}} \times n_{\text{products}}) - \sum(\Delta H^\circ_{\text{reactants}} \times n_{\text{reactants}}) \\ &= (-926.29 \text{ kJ/mol} \times 1 \text{ mol } H_2O_{(g)}) - (-970.30 \text{ kJ/mol} \times 1 \text{ mol } H_2O_{(l)}) = 44.01 \text{ kJ} \\ &\rightarrow \text{endothermic} \end{aligned}$$

$$\begin{aligned} \Delta S^\circ &= \sum(\Delta S^\circ_{\text{products}} \times n_{\text{products}}) - \sum(\Delta S^\circ_{\text{reactants}} \times n_{\text{reactants}}) \\ &= (-202.23 \text{ J/mol} \times 1 \text{ mol } H_2O_{(g)}) - (-320.57 \text{ J/mol} \times 1 \text{ mol } H_2O_{(l)}) = 118.34 \text{ J} \end{aligned}$$

$$\begin{aligned}\Delta G^\circ &= \sum(\Delta G^\circ_{\text{products}} \times n_{\text{products}}) - \sum(\Delta G^\circ_{\text{reactants}} \times n_{\text{reactants}}) \\ &= (-866.797 \text{ kJ/mol} \times 1 \text{ mol } H_2O_{(g)}) - (-875.354 \text{ kJ/mol} \times 1 \text{ mol } H_2O_{(l)}) \\ &= 8.557 \text{ kJ}\end{aligned}$$

$$\text{or } \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\begin{aligned}&= 44.01 \text{ kJ} - 298.15 \text{ K} \times 0.11834 \text{ kJ} = 8.727 \text{ kJ} \rightarrow \\ &\text{nonspontaneous, favoring reactants.}\end{aligned}$$

$$\begin{aligned}\text{b. } \Delta H^\circ &= \sum(\Delta H^\circ_{\text{products}} \times n_{\text{products}}) - \sum(\Delta H^\circ_{\text{reactants}} \times n_{\text{reactants}}) \\ &= (-3076.0 \text{ kJ} \times 2Al_2O_{3(s)}) - (-498.340 \text{ kJ} \times 3 O_{2(g)} - 326.4 \text{ kJ} \times 4 Al_{(s)}) \\ &= -3351.4 \text{ kJ} \rightarrow \text{exothermic}\end{aligned}$$

$$\begin{aligned}\Delta S^\circ &= \sum(\Delta S^\circ_{\text{products}} \times n_{\text{products}}) - \sum(\Delta S^\circ_{\text{reactants}} \times n_{\text{reactants}}) \\ &= (-761.33 \text{ J} \times 2Al_2O_{3(s)}) - (-116.972 \text{ J} \times 3 O_{2(g)} - 136.21 \text{ J} \times 4 Al_{(s)}) \\ &= -626.9 \text{ J}\end{aligned}$$

$$\begin{aligned}\Delta G^\circ &= \sum(\Delta G^\circ_{\text{products}} \times n_{\text{products}}) - \sum(\Delta G^\circ_{\text{reactants}} \times n_{\text{reactants}}) \\ &= (-2848.9 \text{ kJ} \times 2Al_2O_{3(s)}) - (-463.462 \text{ kJ} \times 3 O_{2(g)} - 285.7 \text{ kJ} \times 4 Al_{(s)}) \\ &= -3164.6 \text{ kJ}\end{aligned}$$

$$\text{or } \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\begin{aligned}&= 3351.4 \text{ kJ} - 298.15 \text{ K} \times -0.6269 \text{ kJ} = -3164.5 \text{ kJ} \rightarrow \\ &\text{spontaneous, favoring products.}\end{aligned}$$

$$\begin{aligned}4. \Delta G^\circ &= \sum(\Delta G^\circ_{\text{products}} \times n_{\text{products}}) - \sum(\Delta G^\circ_{\text{reactants}} \times n_{\text{reactants}}) \\ &= (-1081.82 \text{ kJ} \times 2 NH_{3(g)}) - (-406.494 \text{ kJ} \times 3 H_{2(g)} - 911.26 \text{ kJ} \times 1 N_{2(g)}) \\ &= -32.898 \text{ kJ}\end{aligned}$$

$$Q_P = \frac{(P_{NH_3})^2}{(P_{N_2})^1 (P_{H_2})^3} = \frac{(1.5)^2}{(0.5)(0.7)^3} = 13.1195$$

$$\Delta G = \Delta G^\circ + RT \ln Q$$

$$\begin{aligned}&= (-32.898 \times 10^3 \text{ J/mol}) + (8.314 \text{ J/mol} \\ &\cdot \text{K})(273.15 \text{ K})(\ln 13.1195) = -30 \text{ kJ} < 0 \rightarrow \rightarrow \text{spontaneous.}\end{aligned}$$

5. From question 3b,  $\Delta G^\circ = 8.557 \text{ kJ}$

$$\Delta G^\circ = -RT \ln K \rightarrow \ln K = -\frac{\Delta G^\circ}{RT}$$

$$\ln K = -\frac{8.557 \times 10^3 \text{ J/mol}}{(8.314 \text{ J/mol} \cdot \text{K})(298.15 \text{ K})} = -3.452$$

$$K = e^{-3.452} = 0.0316 < 1 \rightarrow \text{the equilibrium mixture is mostly reactants.}$$

6. The reaction is the same as question 4:  $\text{N}_{2(g)} + 3 \text{H}_{2(g)} \rightleftharpoons 2 \text{NH}_{3(g)}$

$$\begin{aligned} \text{a. } \Delta H^\circ_{298 \text{ K}} &= \sum(\Delta H^\circ_{\text{products}} \times n_{\text{products}}) - \sum(\Delta H^\circ_{\text{reactants}} \times n_{\text{reactants}}) \\ &= (-1171.76 \text{ kJ} \times 2 \text{NH}_{3(s)}) - (-435.30 \text{ kJ} \times 3 \text{H}_{2(g)} - 945.408 \text{ kJ} \times 1 \text{N}_{2(s)}) = \\ &= -92.212 \text{ kJ} \end{aligned}$$

$$\begin{aligned} \Delta S^\circ_{298 \text{ K}} &= \sum(\Delta S^\circ_{\text{products}} \times n_{\text{products}}) - \sum(\Delta S^\circ_{\text{reactants}} \times n_{\text{reactants}}) \\ &= (-304.99 \text{ J} \times 2 \text{NH}_{3(s)}) - (-98.742 \text{ J} \times 3 \text{H}_{2(g)} - 114.99 \text{ J} \times 1 \text{N}_{2(s)}) \\ &= -198.764 \text{ J} \end{aligned}$$

$$\begin{aligned} \Delta G^\circ_{573.15 \text{ K}} &= \Delta H^\circ - T\Delta S^\circ \\ &= (-92.212 \text{ kJ}) - (623.15 \text{ K})(-0.198764 \text{ kJ}) = 31.6478 \text{ kJ} \end{aligned}$$

$$\Delta G^\circ = -RT \ln K \rightarrow \ln K = -\frac{\Delta G^\circ}{RT}$$

$$\ln K = -\frac{31.6478 \times 10^3 \text{ J/mol}}{(8.314 \text{ J/mol} \cdot \text{K})(623.15 \text{ K})} = -6.10859$$

$$K = K_p = e^{-6.10859} = 2.22369 \times 10^{-3}$$

(Note: Since all species are gaseous, and the standard state of a gas is identified in terms of pressure, the equilibrium constant is  $K_p$ )

$$K_p = K_c(RT)^{\Delta n} \rightarrow K_c = \frac{K_p}{(RT)^{\Delta n}}$$

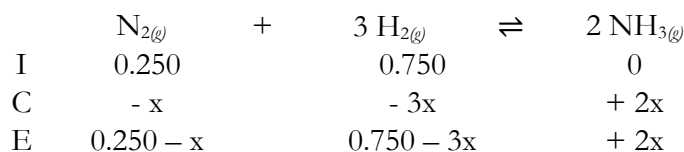
$$K_c = \frac{2.22369 \times 10^{-3}}{(0.08206 \times 623.15)^{2-(3+1)}} = \frac{2.22369 \times 10^{-3}}{(51.13569)^{-2}} = 5.76234$$

(Note: gas constant R used should be 0.08206 atm.L/mol.K, not 8.314 J/mol.K like in  $\Delta G^\circ$ .)

$$[N_2] = 14.0 \text{ g} \times \frac{1 \text{ mol}}{28.014 \text{ g}} \times \frac{1}{2.00L} = 0.250 \text{ M}$$

$$[H_2] = 3.024 \text{ g} \times \frac{1 \text{ mol}}{2.016 \text{ g}} \times \frac{1}{2.00L} = 0.750 \text{ M}$$

Make an ICE table to find concentrations at equilibrium:



$$K_C = \frac{[NH_3]^2}{[N_2]^1[H_2]^3} = \frac{(2x)^2}{(0.250 - x)(0.750 - 3x)^3} = 5.76234$$

$$\frac{(2x)^2}{(0.250 - x)[3 \times (0.250 - x)]^3} = 5.76234 \text{ (factoring out 3 from } (0.750 - 3x))$$

$$\frac{(2x)^2}{(0.250 - x)^4} = 5.76234 \times 3^3 = 155.583 \text{ (multiplying both sides by } 3^3)$$

$$\sqrt{\frac{(2x)^2}{(0.250 - x)^4}} = \frac{2x}{(0.250 - x)^2} = \sqrt{155.583}$$

$$= 12.4733 \text{ (taking squareroot both sides)}$$

$$2x = 12.4733(0.0625 - 0.500x + x^2) = 0.77958 - 6.23665x + 12.4733x^2$$

$$12.4733x^2 - 8.23665x + 0.77958 = 0$$

$$\left( \text{Use the quadratic formula } x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}, \text{ with } a = 12.4733, b = -8.23665, c = 0.77958 \right)$$

$$x = 0.1145 \text{ (accepted)} \quad \text{or} \quad x = 0.54584 \text{ (rejected, since } x > [N_2]_{\text{initial}})$$

$$[NH_3]_{eq} = 2x = 2 \times (0.1145) = 0.229 \text{ M}$$

$$[H_2]_{eq} = 0.750 - 3x = 0.750 - 3 \times (0.1145) = 0.296 \text{ M}$$

$$[N_2]_{eq} = 0.250 - x = 0.250 - (0.1145) = 0.136 \text{ M}$$

- b. The yield of ammonia decreases. Since  $\Delta H^\circ$  is negative, the reaction is releasing heat. As a result, adding more heat by raising the temperature will cause the reaction to shift to the left to dissipate the added heat and re-establish equilibrium, according to Le Chatelier's Principle.

This can also be explained using  $\Delta G^\circ$

$$\Delta G^\circ_{773.15 K} = \Delta H^\circ - T\Delta S^\circ$$

$$= (-92.212 \text{ kJ}) - (773.15 K)(-0.198764 \text{ kJ}) = 61.462 \text{ kJ}$$

$$\Delta G^\circ = -RT \ln K \rightarrow \ln K = -\frac{\Delta G^\circ}{RT}$$

$$\ln K_{773.15 K} = -\frac{61462 \times (10^3 \text{ J})/\text{mol}}{(8.314 \text{ J/mol} \cdot \text{K})(773.15 \text{ K})} = -9.56165$$

$$K_{773.15 K} = e^{-9.56165} = 7.03765 \times 10^{-5}.$$

Meanwhile, at 350 °C,  $K_{623.15 K} = 2.22369 \times 10^{-3}$ , so at 500 °C, equilibrium constant is lower, so the equilibrium is shifted to the left, resulting in a decrease in production of  $\text{NH}_3$ .