

# CHAPTER 18

## ENTROPY, FREE ENERGY, AND EQUILIBRIUM

- 18.6** The probability ( $P$ ) of finding all the molecules in the same flask becomes progressively smaller as the number of molecules increases. An equation that relates the probability to the number of molecules is given in the text.

$$P = \left(\frac{1}{2}\right)^N$$

where,

$N$  is the total number of molecules present.

Using the above equation, we find:

(a)  $P = 0.02$       (b)  $P = 9 \times 10^{-19}$       (c)  $P = 2 \times 10^{-181}$

- 18.9**
- (a) This is easy. The liquid form of any substance always has greater entropy (more microstates).
  - (b) This is hard. At first glance there may seem to be no apparent difference between the two substances that might affect the entropy (molecular formulas identical). However, the first has the  $-O-H$  structural feature which allows it to participate in hydrogen bonding with other molecules. This allows a more ordered arrangement of molecules in the liquid state. The standard entropy of  $CH_3OCH_3$  is larger.
  - (c) This is also difficult. Both are monatomic species. However, the Xe atom has a greater molar mass than Ar. Xenon has the higher standard entropy.
  - (d) Same argument as part (c). Carbon dioxide gas has the higher standard entropy (see Appendix 3).
  - (e)  $O_3$  has a greater molar mass than  $O_2$  and thus has the higher standard entropy.
  - (f) Using the same argument as part (c), one mole of  $N_2O_4$  has a larger standard entropy than one mole of  $NO_2$ . Compare values in Appendix 3.

Use the data in Appendix 3 to compare the standard entropy of one mole of  $N_2O_4$  with that of two moles of  $NO_2$ . In this situation the number of atoms is the same for both. Which is higher and why?

- 18.10** In order of increasing entropy per mole at  $25^\circ C$ :

(c) < (d) < (e) < (a) < (b)

- (c)  $Na(s)$ : ordered, crystalline material.
- (d)  $NaCl(s)$ : ordered crystalline material, but with more particles per mole than  $Na(s)$ .
- (e)  $H_2$ : a diatomic gas, hence of higher entropy than a solid.
- (a)  $Ne(g)$ : a monatomic gas of higher molar mass than  $H_2$ .
- (b)  $SO_2(g)$ : a polyatomic gas of higher molar mass than  $Ne$ .

- 18.11** Using Equation (18.7) of the text to calculate  $\Delta S_{rxn}^\circ$

(a)  $\Delta S_{rxn}^\circ = S^\circ(SO_2) - [S^\circ(O_2) + S^\circ(S)]$

$$\Delta S_{rxn}^\circ = (1)(248.5 \text{ J/K} \cdot \text{mol}) - (1)(205.0 \text{ J/K} \cdot \text{mol}) - (1)(31.88 \text{ J/K} \cdot \text{mol}) = \mathbf{11.6 \text{ J/K} \cdot \text{mol}}$$

$$(b) \quad \Delta S_{\text{rxn}}^{\circ} = S^{\circ}(\text{MgO}) + S^{\circ}(\text{CO}_2) - S^{\circ}(\text{MgCO}_3)$$

$$\Delta S_{\text{rxn}}^{\circ} = (1)(26.78 \text{ J/K}\cdot\text{mol}) + (1)(213.6 \text{ J/K}\cdot\text{mol}) - (1)(65.69 \text{ J/K}\cdot\text{mol}) = \mathbf{174.7 \text{ J/K}\cdot\text{mol}}$$

**18.12 Strategy:** To calculate the standard entropy change of a reaction, we look up the standard entropies of reactants and products in Appendix 3 of the text and apply Equation (18.7). As in the calculation of enthalpy of reaction, the stoichiometric coefficients have no units, so  $\Delta S_{\text{rxn}}^{\circ}$  is expressed in units of J/K·mol.

**Solution:** The standard entropy change for a reaction can be calculated using the following equation.

$$\Delta S_{\text{rxn}}^{\circ} = \sum n S^{\circ}(\text{products}) - \sum m S^{\circ}(\text{reactants})$$

$$(a) \quad \Delta S_{\text{rxn}}^{\circ} = S^{\circ}(\text{Cu}) + S^{\circ}(\text{H}_2\text{O}) - [S^{\circ}(\text{H}_2) + S^{\circ}(\text{CuO})]$$

$$= (1)(33.3 \text{ J/K}\cdot\text{mol}) + (1)(188.7 \text{ J/K}\cdot\text{mol}) - [(1)(131.0 \text{ J/K}\cdot\text{mol}) + (1)(43.5 \text{ J/K}\cdot\text{mol})]$$

$$= \mathbf{47.5 \text{ J/K}\cdot\text{mol}}$$

$$(b) \quad \Delta S_{\text{rxn}}^{\circ} = S^{\circ}(\text{Al}_2\text{O}_3) + 3S^{\circ}(\text{Zn}) - [2S^{\circ}(\text{Al}) + 3S^{\circ}(\text{ZnO})]$$

$$= (1)(50.99 \text{ J/K}\cdot\text{mol}) + (3)(41.6 \text{ J/K}\cdot\text{mol}) - [(2)(28.3 \text{ J/K}\cdot\text{mol}) + (3)(43.9 \text{ J/K}\cdot\text{mol})]$$

$$= \mathbf{-12.5 \text{ J/K}\cdot\text{mol}}$$

$$(c) \quad \Delta S_{\text{rxn}}^{\circ} = S^{\circ}(\text{CO}_2) + 2S^{\circ}(\text{H}_2\text{O}) - [S^{\circ}(\text{CH}_4) + 2S^{\circ}(\text{O}_2)]$$

$$= (1)(213.6 \text{ J/K}\cdot\text{mol}) + (2)(69.9 \text{ J/K}\cdot\text{mol}) - [(1)(186.2 \text{ J/K}\cdot\text{mol}) + (2)(205.0 \text{ J/K}\cdot\text{mol})]$$

$$= \mathbf{-242.8 \text{ J/K}\cdot\text{mol}}$$

Why was the entropy value for water different in parts (a) and (c)?

**18.13** All parts of this problem rest on two principles. First, the entropy of a solid is always less than the entropy of a liquid, and the entropy of a liquid is always much smaller than the entropy of a gas. Second, in comparing systems in the same phase, the one with the most complex particles has the higher entropy.

(a) Positive entropy change (increase). One of the products is in the gas phase (more microstates).

(b) Negative entropy change (decrease). Liquids have lower entropies than gases.

(c) Positive. Same as (a).

(d) Positive. There are two gas-phase species on the product side and only one on the reactant side.

**18.14** (a)  $\Delta S < 0$ ; gas reacting with a liquid to form a solid (decrease in number of moles of gas, hence a decrease in microstates).

(b)  $\Delta S > 0$ ; solid decomposing to give a liquid and a gas (an increase in microstates).

(c)  $\Delta S > 0$ ; increase in number of moles of gas (an increase in microstates).

(d)  $\Delta S < 0$ ; gas reacting with a solid to form a solid (decrease in number of moles of gas, hence a decrease in microstates).

**18.17** Using Equation (18.12) of the text to solve for the change in standard free energy,

$$(a) \quad \Delta G^\circ = 2\Delta G_f^\circ(\text{NO}) - \Delta G_f^\circ(\text{N}_2) - \Delta G_f^\circ(\text{O}_2) = (2)(86.7 \text{ kJ/mol}) - 0 - 0 = \mathbf{173.4 \text{ kJ/mol}}$$

$$(b) \quad \Delta G^\circ = \Delta G_f^\circ[\text{H}_2\text{O}(g)] - \Delta G_f^\circ[\text{H}_2\text{O}(l)] = (1)(-228.6 \text{ kJ/mol}) - (1)(-237.2 \text{ kJ/mol}) = \mathbf{8.6 \text{ kJ/mol}}$$

$$(c) \quad \Delta G^\circ = 4\Delta G_f^\circ(\text{CO}_2) + 2\Delta G_f^\circ(\text{H}_2\text{O}) - 2\Delta G_f^\circ(\text{C}_2\text{H}_2) - 5\Delta G_f^\circ(\text{O}_2) \\ = (4)(-394.4 \text{ kJ/mol}) + (2)(-237.2 \text{ kJ/mol}) - (2)(209.2 \text{ kJ/mol}) - (5)(0) = \mathbf{-2470 \text{ kJ/mol}}$$

**18.18 Strategy:** To calculate the standard free-energy change of a reaction, we look up the standard free energies of formation of reactants and products in Appendix 3 of the text and apply Equation (18.12). Note that all the stoichiometric coefficients have no units so  $\Delta G_{\text{rxn}}^\circ$  is expressed in units of kJ/mol. The standard free energy of formation of any element in its stable allotropic form at 1 atm and 25°C is zero.

**Solution:** The standard free energy change for a reaction can be calculated using the following equation.

$$\Delta G_{\text{rxn}}^\circ = \sum n\Delta G_f^\circ(\text{products}) - \sum m\Delta G_f^\circ(\text{reactants})$$

$$(a) \quad \Delta G_{\text{rxn}}^\circ = 2\Delta G_f^\circ(\text{MgO}) - [2\Delta G_f^\circ(\text{Mg}) + \Delta G_f^\circ(\text{O}_2)]$$

$$\Delta G_{\text{rxn}}^\circ = (2)(-569.6 \text{ kJ/mol}) - [(2)(0) + (1)(0)] = \mathbf{-1139 \text{ kJ/mol}}$$

$$(b) \quad \Delta G_{\text{rxn}}^\circ = 2\Delta G_f^\circ(\text{SO}_3) - [2\Delta G_f^\circ(\text{SO}_2) + \Delta G_f^\circ(\text{O}_2)]$$

$$\Delta G_{\text{rxn}}^\circ = (2)(-370.4 \text{ kJ/mol}) - [(2)(-300.4 \text{ kJ/mol}) + (1)(0)] = \mathbf{-140.0 \text{ kJ/mol}}$$

$$(c) \quad \Delta G_{\text{rxn}}^\circ = 4\Delta G_f^\circ[\text{CO}_2(g)] + 6\Delta G_f^\circ[\text{H}_2\text{O}(l)] - \{2\Delta G_f^\circ[\text{C}_2\text{H}_6(g)] + 7\Delta G_f^\circ[\text{O}_2(g)]\}$$

$$\Delta G_{\text{rxn}}^\circ = (4)(-394.4 \text{ kJ/mol}) + (6)(-237.2 \text{ kJ/mol}) - [(2)(-32.89 \text{ kJ/mol}) + (7)(0)] = \mathbf{-2935.0 \text{ kJ/mol}}$$

**18.19** Reaction A: First apply Equation (18.10) of the text to compute the free energy change at 25°C (298 K)

$$\Delta G = \Delta H - T\Delta S = 10,500 \text{ J/mol} - (298 \text{ K})(30 \text{ J/K}\cdot\text{mol}) = 1560 \text{ J/mol}$$

The +1560 J/mol shows the reaction is not spontaneous at 298 K. The  $\Delta G$  will change sign (i.e., the reaction will become spontaneous) above the temperature at which  $\Delta G = 0$ .

$$T = \frac{\Delta H}{\Delta S} = \frac{10500 \text{ J/mol}}{30 \text{ J/K}\cdot\text{mol}} = \mathbf{350 \text{ K}}$$

Reaction B: Calculate  $\Delta G$ .

$$\Delta G = \Delta H - T\Delta S = 1800 \text{ J/mol} - (298 \text{ K})(-113 \text{ J/K}\cdot\text{mol}) = \mathbf{35,500 \text{ J/mol}}$$

The free energy change is positive, which shows that the reaction is not spontaneous at 298 K. Since both terms are positive, there is no temperature at which their sum is negative. The reaction is not spontaneous at any temperature.

**18.20 Reaction A:** Calculate  $\Delta G$  from  $\Delta H$  and  $\Delta S$ .

$$\Delta G = \Delta H - T\Delta S = -126,000 \text{ J/mol} - (298 \text{ K})(84 \text{ J/K}\cdot\text{mol}) = -151,000 \text{ J/mol}$$

The free energy change is negative so the reaction is spontaneous at 298 K. Since  $\Delta H$  is negative and  $\Delta S$  is positive, **the reaction is spontaneous at all temperatures.**

**Reaction B:** Calculate  $\Delta G$ .

$$\Delta G = \Delta H - T\Delta S = -11,700 \text{ J/mol} - (298 \text{ K})(-105 \text{ J/K}\cdot\text{mol}) = +19,600 \text{ J}$$

The free energy change is positive at 298 K which means the reaction is not spontaneous at that temperature. The positive sign of  $\Delta G$  results from the large negative value of  $\Delta S$ . At lower temperatures, the  $-T\Delta S$  term will be smaller thus allowing the free energy change to be negative.

$\Delta G$  will equal zero when  $\Delta H = T\Delta S$ .

Rearranging,

$$T = \frac{\Delta H}{\Delta S} = \frac{-11700 \text{ J/mol}}{-105 \text{ J/K}\cdot\text{mol}} = \mathbf{111 \text{ K}}$$

At temperatures **below 111 K**,  $\Delta G$  will be negative and the reaction will be spontaneous.

**18.23** Find the value of  $K$  by solving Equation (18.14) of the text.

$$K_p = e^{\frac{-\Delta G^\circ}{RT}} = e^{\frac{-2.60 \times 10^3 \text{ J/mol}}{(8.314 \text{ J/K}\cdot\text{mol})(298 \text{ K})}} = e^{-1.05} = \mathbf{0.35}$$

**18.24 Strategy:** According to Equation (18.14) of the text, the equilibrium constant for the reaction is related to the standard free energy change; that is,  $\Delta G^\circ = -RT \ln K$ . Since we are given the equilibrium constant in the problem, we can solve for  $\Delta G^\circ$ . What temperature unit should be used?

**Solution:** The equilibrium constant is related to the standard free energy change by the following equation.

$$\Delta G^\circ = -RT \ln K$$

Substitute  $K_w$ ,  $R$ , and  $T$  into the above equation to calculate the standard free energy change,  $\Delta G^\circ$ . The temperature at which  $K_w = 1.0 \times 10^{-14}$  is  $25^\circ\text{C} = 298 \text{ K}$ .

$$\Delta G^\circ = -RT \ln K_w$$

$$\Delta G^\circ = -(8.314 \text{ J/mol}\cdot\text{K})(298 \text{ K}) \ln(1.0 \times 10^{-14}) = \mathbf{8.0 \times 10^4 \text{ J/mol} = 8.0 \times 10^1 \text{ kJ/mol}$$

**18.25**  $K_{sp} = [\text{Fe}^{2+}][\text{OH}^-]^2 = 1.6 \times 10^{-14}$ 

$$\Delta G^\circ = -RT \ln K_{sp} = -(8.314 \text{ J/K}\cdot\text{mol})(298 \text{ K}) \ln(1.6 \times 10^{-14}) = \mathbf{7.9 \times 10^4 \text{ J/mol} = 79 \text{ kJ/mol}$$

**18.26** Use standard free energies of formation from Appendix 3 to find the standard free energy difference.

$$\Delta G_{\text{rxn}}^\circ = 2\Delta G_f^\circ[\text{H}_2(\text{g})] + \Delta G_f^\circ[\text{O}_2(\text{g})] - 2\Delta G_f^\circ[\text{H}_2\text{O}(\text{g})]$$

$$\Delta G_{\text{rxn}}^\circ = (2)(0) + (1)(0) - (2)(-228.6 \text{ kJ/mol})$$

$$\Delta G_{\text{rxn}}^\circ = \mathbf{457.2 \text{ kJ/mol} = 4.572 \times 10^5 \text{ J/mol}$$

We can calculate  $K_P$  using the following equation. We carry additional significant figures in the calculation to minimize rounding errors when calculating  $K_P$ .

$$\begin{aligned}\Delta G^\circ &= -RT \ln K_P \\ 4.572 \times 10^5 \text{ J/mol} &= -(8.314 \text{ J/mol}\cdot\text{K})(298 \text{ K}) \ln K_P \\ -184.54 &= \ln K_P\end{aligned}$$

Taking the antiln of both sides,

$$\begin{aligned}e^{-184.54} &= K_P \\ \mathbf{K_P} &= \mathbf{7.2 \times 10^{-81}}\end{aligned}$$

- 18.27 (a)** We first find the standard free energy change of the reaction.

$$\begin{aligned}\Delta G_{\text{rxn}}^\circ &= \Delta G_f^\circ[\text{PCl}_3(\text{g})] + \Delta G_f^\circ[\text{Cl}_2(\text{g})] - \Delta G_f^\circ[\text{PCl}_5(\text{g})] \\ &= (1)(-286 \text{ kJ/mol}) + (1)(0) - (1)(-325 \text{ kJ/mol}) = \mathbf{39 \text{ kJ/mol}}\end{aligned}$$

We can calculate  $K_P$  using Equation (18.14) of the text.

$$K_P = e^{\frac{-\Delta G^\circ}{RT}} = e^{\frac{-39 \times 10^3 \text{ J/mol}}{(8.314 \text{ J/K}\cdot\text{mol})(298 \text{ K})}} = e^{-16} = \mathbf{1 \times 10^{-7}}$$

- (b)** We are finding the free energy difference between the reactants and the products at their nonequilibrium values. The result tells us the direction of and the potential for further chemical change. We use the given nonequilibrium pressures to compute  $Q_P$ .

$$Q_P = \frac{P_{\text{PCl}_3} P_{\text{Cl}_2}}{P_{\text{PCl}_5}} = \frac{(0.27)(0.40)}{0.0029} = 37$$

The value of  $\Delta G$  (notice that this is not the standard free energy difference) can be found using Equation (18.13) of the text and the result from part (a).

$$\Delta G = \Delta G^\circ + RT \ln Q = (39 \times 10^3 \text{ J/mol}) + (8.314 \text{ J/K}\cdot\text{mol})(298 \text{ K}) \ln(37) = \mathbf{48 \text{ kJ/mol}}$$

Which way is the direction of spontaneous change for this system? What would be the value of  $\Delta G$  if the given data were equilibrium pressures? What would be the value of  $Q_P$  in that case?

- 18.28 (a)** The equilibrium constant is related to the standard free energy change by the following equation.

$$\Delta G^\circ = -RT \ln K$$

Substitute  $K_P$ ,  $R$ , and  $T$  into the above equation to the standard free energy change,  $\Delta G^\circ$ .

$$\begin{aligned}\Delta G^\circ &= -RT \ln K_P \\ \Delta G^\circ &= -(8.314 \text{ J/mol}\cdot\text{K})(2000 \text{ K}) \ln(4.40) = -2.464 \times 10^4 \text{ J/mol} = \mathbf{-24.6 \text{ kJ/mol}}\end{aligned}$$

- (b)**

**Strategy:** From the information given we see that neither the reactants nor products are at their standard state of 1 atm. We use Equation (18.13) of the text to calculate the free-energy change under non-standard-state conditions. Note that the partial pressures are expressed as dimensionless quantities in the reaction quotient  $Q_P$ .

**Solution:** Under non-standard-state conditions,  $\Delta G$  is related to the reaction quotient  $Q_P$  by the following equation.

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

We are using  $Q_P$  in the equation because this is a gas-phase reaction.

**Step 1:**  $\Delta G^\circ$  was calculated in part (a). We must calculate  $Q_P$ . We carry additional significant figures in this calculation to minimize rounding errors.

$$Q_P = \frac{P_{\text{H}_2\text{O}} \cdot P_{\text{CO}}}{P_{\text{H}_2} \cdot P_{\text{CO}_2}} = \frac{(0.66)(1.20)}{(0.25)(0.78)} = 4.062$$

**Step 2:** Substitute  $\Delta G^\circ = -2.46 \times 10^4$  J/mol and  $Q_P$  into the following equation to calculate  $\Delta G$ .

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

$$\Delta G = -2.464 \times 10^4 \text{ J/mol} + (8.314 \text{ J/mol}\cdot\text{K})(2000 \text{ K}) \ln(4.062)$$

$$\Delta G = (-2.464 \times 10^4 \text{ J/mol}) + (2.331 \times 10^4 \text{ J/mol})$$

$$\Delta G = -1.33 \times 10^3 \text{ J/mol} = \mathbf{-1.33 \text{ kJ/mol}}$$

**18.29** The expression of  $K_P$  is:  $K_P = P_{\text{CO}_2}$

Thus you can predict the equilibrium pressure directly from the value of the equilibrium constant. The only task at hand is computing the values of  $K_P$  using Equations (18.10) and (18.14) of the text.

(a) At 25°C,  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = (177.8 \times 10^3 \text{ J/mol}) - (298 \text{ K})(160.5 \text{ J/K}\cdot\text{mol}) = 130.0 \times 10^3 \text{ J/mol}$

$$P_{\text{CO}_2} = K_P = e^{\frac{-\Delta G^\circ}{RT}} = e^{\frac{-130.0 \times 10^3 \text{ J/mol}}{(8.314 \text{ J/K}\cdot\text{mol})(298 \text{ K})}} = e^{-52.47} = \mathbf{1.6 \times 10^{-23} \text{ atm}}$$

(b) At 800°C,  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = (177.8 \times 10^3 \text{ J/mol}) - (1073 \text{ K})(160.5 \text{ J/K}\cdot\text{mol}) = 5.58 \times 10^3 \text{ J/mol}$

$$P_{\text{CO}_2} = K_P = e^{\frac{-\Delta G^\circ}{RT}} = e^{\frac{-5.58 \times 10^3 \text{ J/mol}}{(8.314 \text{ J/K}\cdot\text{mol})(1073 \text{ K})}} = e^{-0.625} = \mathbf{0.535 \text{ atm}}$$

What assumptions are made in the second calculation?

**18.30** We use the given  $K_P$  to find the standard free energy change.

$$\Delta G^\circ = -RT \ln K$$

$$\Delta G^\circ = -(8.314 \text{ J/K}\cdot\text{mol})(298 \text{ K}) \ln(5.62 \times 10^{35}) = 2.04 \times 10^5 \text{ J/mol} = \mathbf{-204 \text{ kJ/mol}}$$

The standard free energy of formation of one mole of  $\text{COCl}_2$  can now be found using the standard free energy of reaction calculated above and the standard free energies of formation of  $\text{CO}(g)$  and  $\text{Cl}_2(g)$ .

$$\Delta G_{\text{rxn}}^\circ = \sum n \Delta G_f^\circ(\text{products}) - \sum m \Delta G_f^\circ(\text{reactants})$$

$$\Delta G_{\text{rxn}}^\circ = \Delta G_f^\circ[\text{COCl}_2(g)] - \{\Delta G_f^\circ[\text{CO}(g)] + \Delta G_f^\circ[\text{Cl}_2(g)]\}$$

$$-204 \text{ kJ/mol} = (1)\Delta G_f^\circ[\text{COCl}_2(g)] - [(1)(-137.3 \text{ kJ/mol}) + (1)(0)]$$

$$\Delta G_f^\circ[\text{COCl}_2(g)] = \mathbf{-341 \text{ kJ/mol}}$$

**18.31** The equilibrium constant expression is:  $K_P = P_{\text{H}_2\text{O}}$

We are actually finding the equilibrium vapor pressure of water (compare to Problem 18.29). We use Equation (18.14) of the text.

$$P_{\text{H}_2\text{O}} = K_P = e^{\frac{-\Delta G^\circ}{RT}} = e^{\frac{-8.6 \times 10^3 \text{ J/mol}}{(8.314 \text{ J/K}\cdot\text{mol})(298 \text{ K})}} = e^{-3.47} = \mathbf{3.1 \times 10^{-2} \text{ atm}}$$

The positive value of  $\Delta G^\circ$  implies that reactants are favored at equilibrium at 25°C. Is that what you would expect?

**18.32** The standard free energy change is given by:

$$\Delta G_{\text{rxn}}^\circ = \Delta G_f^\circ(\text{graphite}) - \Delta G_f^\circ(\text{diamond})$$

You can look up the standard free energy of formation values in Appendix 3 of the text.

$$\Delta G_{\text{rxn}}^\circ = (1)(0) - (1)(2.87 \text{ kJ/mol}) = \mathbf{-2.87 \text{ kJ/mol}}$$

Thus, the formation of graphite from diamond is **favored** under standard-state conditions at 25°C. However, the rate of the diamond to graphite conversion is very slow (due to a high activation energy) so that it will take millions of years before the process is complete.

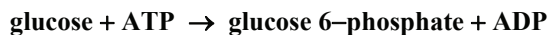
**18.35**  $\text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2 \rightarrow 6\text{CO}_2 + 6\text{H}_2\text{O}$        $\Delta G^\circ = -2880 \text{ kJ/mol}$

$\text{ADP} + \text{H}_3\text{PO}_4 \rightarrow \text{ATP} + \text{H}_2\text{O}$        $\Delta G^\circ = +31 \text{ kJ/mol}$

Maximum number of ATP molecules synthesized:

$$2880 \text{ kJ/mol} \times \frac{1 \text{ ATP molecule}}{31 \text{ kJ/mol}} = \mathbf{93 \text{ ATP molecules}}$$

**18.36** The equation for the coupled reaction is:



$$\Delta G^\circ = 13.4 \text{ kJ/mol} - 31 \text{ kJ/mol} = -18 \text{ kJ/mol}$$

As an estimate:

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

$$\ln K = \frac{-(-18 \times 10^3 \text{ J/mol})}{(8.314 \text{ J/K}\cdot\text{mol})(298 \text{ K})} = 7.3$$

$$\mathbf{K = 1 \times 10^3}$$

**18.37** When Humpty broke into pieces, he became more disordered (spontaneously). The king was unable to reconstruct Humpty.

**18.38** In each part of this problem we can use the following equation to calculate  $\Delta G$ .

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

or,

$$\Delta G = \Delta G^\circ + RT \ln [\text{H}^+][\text{OH}^-]$$

- (a) In this case, the given concentrations are equilibrium concentrations at 25°C. Since the reaction is at equilibrium,  $\Delta G = 0$ . This is advantageous, because it allows us to calculate  $\Delta G^\circ$ . Also recall that at equilibrium,  $Q = K$ . We can write:

$$\Delta G^\circ = -RT \ln K_w$$

$$\Delta G^\circ = -(8.314 \text{ J/K}\cdot\text{mol})(298 \text{ K}) \ln(1.0 \times 10^{-14}) = 8.0 \times 10^4 \text{ J/mol}$$

- (b)  $\Delta G = \Delta G^\circ + RT \ln Q = \Delta G^\circ + RT \ln [H^+][OH^-]$

$$\Delta G = (8.0 \times 10^4 \text{ J/mol}) + (8.314 \text{ J/K}\cdot\text{mol})(298 \text{ K}) \ln[(1.0 \times 10^{-3})(1.0 \times 10^{-4})] = 4.0 \times 10^4 \text{ J/mol}$$

- (c)  $\Delta G = \Delta G^\circ + RT \ln Q = \Delta G^\circ + RT \ln [H^+][OH^-]$

$$\Delta G = (8.0 \times 10^4 \text{ J/mol}) + (8.314 \text{ J/K}\cdot\text{mol})(298 \text{ K}) \ln[(1.0 \times 10^{-12})(2.0 \times 10^{-8})] = -3.2 \times 10^4 \text{ J/mol}$$

- (d)  $\Delta G = \Delta G^\circ + RT \ln Q = \Delta G^\circ + RT \ln [H^+][OH^-]$

$$\Delta G = (8.0 \times 10^4 \text{ J/mol}) + (8.314 \text{ J/K}\cdot\text{mol})(298 \text{ K}) \ln[(3.5)(4.8 \times 10^{-4})] = 6.4 \times 10^4 \text{ J/mol}$$

18.39 Only  $E$  and  $H$  are associated with the first law alone.

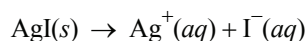
18.40 One possible explanation is simply that no reaction is possible, namely that there is an unfavorable free energy difference between products and reactants ( $\Delta G > 0$ ).

A second possibility is that the potential for spontaneous change is there ( $\Delta G < 0$ ), but that the reaction is extremely slow (very large activation energy).

A remote third choice is that the student accidentally prepared a mixture in which the components were already at their equilibrium concentrations.

Which of the above situations would be altered by the addition of a catalyst?

18.41 We can use data in Appendix 3 of the text to calculate the standard free energy change for the reaction. Then, we can use Equation (18.14) of the text to calculate the equilibrium constant,  $K$ .



$$\Delta G^\circ = \Delta G_f^\circ(\text{Ag}^+) + \Delta G_f^\circ(\text{I}^-) - \Delta G_f^\circ(\text{AgI})$$

$$\Delta G^\circ = (1)(77.1 \text{ kJ/mol}) + (1)(-51.67 \text{ kJ/mol}) - (1)(-66.3 \text{ kJ/mol}) = 91.73 \text{ kJ/mol}$$

$$\Delta G^\circ = -RT \ln K$$

$$\ln K = -\frac{91.73 \times 10^3 \text{ J/mol}}{(8.314 \text{ J/K}\cdot\text{mol})(298 \text{ K})} = -37.024$$

$$K = 8.3 \times 10^{-17}$$

The calculated value of  $K$  matches the  $K_{sp}$  value in Table 16.2 of the text.

18.42 For a solid to liquid phase transition (melting) the entropy always increases ( $\Delta S > 0$ ) and the reaction is always endothermic ( $\Delta H > 0$ ).

- (a) Melting is always spontaneous above the melting point, so  $\Delta G < 0$ .

(b) At the melting point ( $-77.7^{\circ}\text{C}$ ), solid and liquid are in equilibrium, so  $\Delta G = 0$ .

(c) Melting is not spontaneous below the melting point, so  $\Delta G > 0$ .

**18.43** For a reaction to be spontaneous,  $\Delta G$  must be negative. If  $\Delta S$  is negative, as it is in this case, then the reaction must be exothermic (why?). When water freezes, it gives off heat (exothermic). Consequently, the entropy of the surroundings increases and  $\Delta S_{\text{universe}} > 0$ .

**18.44** If the process is *spontaneous* as well as *endothermic*, the signs of  $\Delta G$  and  $\Delta H$  must be negative and positive, respectively. Since  $\Delta G = \Delta H - T\Delta S$ , the sign of  $\Delta S$  must be **positive** ( $\Delta S > 0$ ) for  $\Delta G$  to be negative.

**18.45** The equation is:  $\text{BaCO}_3(s) \rightleftharpoons \text{BaO}(s) + \text{CO}_2(g)$

$$\Delta G^{\circ} = \Delta G_{\text{f}}^{\circ}(\text{BaO}) + \Delta G_{\text{f}}^{\circ}(\text{CO}_2) - \Delta G_{\text{f}}^{\circ}(\text{BaCO}_3)$$

$$\Delta G^{\circ} = (1)(-528.4 \text{ kJ/mol}) + (1)(-394.4 \text{ kJ/mol}) - (1)(-1138.9 \text{ kJ/mol}) = 216.1 \text{ kJ/mol}$$

$$\Delta G^{\circ} = -RT \ln K_P$$

$$\ln K_P = \frac{-2.16 \times 10^5 \text{ J/mol}}{(8.314 \text{ J/K} \cdot \text{mol})(298 \text{ K})} = -87.2$$

$$K_P = P_{\text{CO}_2} = e^{-87.2} = 1 \times 10^{-38} \text{ atm}$$

**18.46** (a) Using the relationship:

$$\frac{\Delta H_{\text{vap}}}{T_{\text{b.p.}}} = \Delta S_{\text{vap}} \approx 90 \text{ J/K} \cdot \text{mol}$$

$$\text{benzene} \quad \Delta S_{\text{vap}} = 87.8 \text{ J/K} \cdot \text{mol}$$

$$\text{hexane} \quad \Delta S_{\text{vap}} = 90.1 \text{ J/K} \cdot \text{mol}$$

$$\text{mercury} \quad \Delta S_{\text{vap}} = 93.7 \text{ J/K} \cdot \text{mol}$$

$$\text{toluene} \quad \Delta S_{\text{vap}} = 91.8 \text{ J/K} \cdot \text{mol}$$

Most liquids have  $\Delta S_{\text{vap}}$  approximately equal to a constant value because the order of the molecules in the liquid state is similar. The order of most gases is totally random; thus,  $\Delta S$  for liquid  $\rightarrow$  vapor should be similar for most liquids.

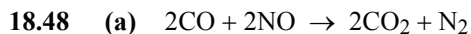
(b) Using the data in Table 11.6 of the text, we find:

$$\text{ethanol} \quad \Delta S_{\text{vap}} = 111.9 \text{ J/K} \cdot \text{mol}$$

$$\text{water} \quad \Delta S_{\text{vap}} = 109.4 \text{ J/K} \cdot \text{mol}$$

Both water and ethanol have a larger  $\Delta S_{\text{vap}}$  because the liquid molecules are more ordered due to hydrogen bonding (there are fewer microstates in these liquids).

**18.47** Evidence shows that HF, which is strongly hydrogen-bonded in the liquid phase, is still considerably hydrogen-bonded in the vapor state such that its  $\Delta S_{\text{vap}}$  is smaller than most other substances.



(b) The oxidizing agent is NO; the reducing agent is CO.

(c)  $\Delta G^\circ = 2\Delta G_f^\circ(\text{CO}_2) + \Delta G_f^\circ(\text{N}_2) - 2\Delta G_f^\circ(\text{CO}) - 2\Delta G_f^\circ(\text{NO})$

$$\Delta G^\circ = (2)(-394.4 \text{ kJ/mol}) + (0) - (2)(-137.3 \text{ kJ/mol}) - (2)(86.7 \text{ kJ/mol}) = -687.6 \text{ kJ/mol}$$

$$\Delta G^\circ = -RT \ln K_P$$

$$\ln K_P = \frac{6.876 \times 10^5 \text{ J/mol}}{(8.314 \text{ J/K} \cdot \text{mol})(298 \text{ K})} = 277.5$$

$$K_P = 3 \times 10^{120}$$

(d)  $Q_P = \frac{P_{\text{N}_2} P_{\text{CO}_2}^2}{P_{\text{CO}}^2 P_{\text{NO}}^2} = \frac{(0.80)(0.030)^2}{(5.0 \times 10^{-5})^2 (5.0 \times 10^{-7})^2} = 1.2 \times 10^{18}$

Since  $Q_P \ll K_P$ , the reaction will proceed from **left to right**.

(e)  $\Delta H^\circ = 2\Delta H_f^\circ(\text{CO}_2) + \Delta H_f^\circ(\text{N}_2) - 2\Delta H_f^\circ(\text{CO}) - 2\Delta H_f^\circ(\text{NO})$

$$\Delta H^\circ = (2)(-393.5 \text{ kJ/mol}) + (0) - (2)(-110.5 \text{ kJ/mol}) - (2)(90.4 \text{ kJ/mol}) = -746.8 \text{ kJ/mol}$$

Since  $\Delta H^\circ$  is negative, raising the temperature will decrease  $K_P$ , thereby increasing the amount of reactants and decreasing the amount of products. **No**, the formation of  $\text{N}_2$  and  $\text{CO}_2$  is not favored by raising the temperature.

18.49 (a) At two different temperatures  $T_1$  and  $T_2$ ,

$$\Delta G_1^\circ = \Delta H^\circ - T_1 \Delta S^\circ = -RT \ln K_1 \quad (1)$$

$$\Delta G_2^\circ = \Delta H^\circ - T_2 \Delta S^\circ = -RT \ln K_2 \quad (2)$$

Rearranging Equations (1) and (2),

$$\ln K_1 = \frac{-\Delta H^\circ}{RT_1} + \frac{\Delta S^\circ}{R} \quad (3)$$

$$\ln K_2 = \frac{-\Delta H^\circ}{RT_2} + \frac{\Delta S^\circ}{R} \quad (4)$$

Subtracting equation (3) from equation (4) gives,

$$\ln K_2 - \ln K_1 = \left( \frac{-\Delta H^\circ}{RT_2} + \frac{\Delta S^\circ}{R} \right) - \left( \frac{-\Delta H^\circ}{RT_1} + \frac{\Delta S^\circ}{R} \right)$$

$$\ln \frac{K_2}{K_1} = \frac{\Delta H^\circ}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\ln \frac{K_2}{K_1} = \frac{\Delta H^\circ}{R} \left( \frac{T_2 - T_1}{T_1 T_2} \right)$$

(b) Using the equation that we just derived, we can calculate the equilibrium constant at 65°C.

$$K_1 = 4.63 \times 10^{-3} \quad T_1 = 298 \text{ K}$$

$$K_2 = ? \quad T_2 = 338 \text{ K}$$

$$\ln \frac{K_2}{4.63 \times 10^{-3}} = \frac{58.0 \times 10^3 \text{ J/mol}}{8.314 \text{ J/K} \cdot \text{mol}} \left( \frac{338 \text{ K} - 298 \text{ K}}{(338 \text{ K})(298 \text{ K})} \right)$$

$$\ln \frac{K_2}{4.63 \times 10^{-3}} = 2.77$$

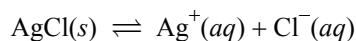
Taking the antiln of both sides of the equation,

$$\frac{K_2}{4.63 \times 10^{-3}} = e^{2.77}$$

$$K_2 = 0.074$$

$K_2 > K_1$ , as we would predict for a positive  $\Delta H^\circ$ . Recall that an increase in temperature will shift the equilibrium towards the endothermic reaction; that is, the decomposition of  $\text{N}_2\text{O}_4$ .

**18.50** The equilibrium reaction is:



$$K_{\text{sp}} = [\text{Ag}^+][\text{Cl}^-] = 1.6 \times 10^{-10}$$

We can calculate the standard enthalpy of reaction from the standard enthalpies of formation in Appendix 3 of the text.

$$\Delta H^\circ = \Delta H_f^\circ(\text{Ag}^+) + \Delta H_f^\circ(\text{Cl}^-) - \Delta H_f^\circ(\text{AgCl})$$

$$\Delta H^\circ = (1)(105.9 \text{ kJ/mol}) + (1)(-167.2 \text{ kJ/mol}) - (1)(-127.0 \text{ kJ/mol}) = 65.7 \text{ kJ/mol}$$

From Problem 18.49(a):

$$\ln \frac{K_2}{K_1} = \frac{\Delta H^\circ}{R} \left( \frac{T_2 - T_1}{T_1 T_2} \right)$$

$$K_1 = 1.6 \times 10^{-10} \quad T_1 = 298 \text{ K}$$

$$K_2 = ? \quad T_2 = 333 \text{ K}$$

$$\ln \frac{K_2}{1.6 \times 10^{-10}} = \frac{6.57 \times 10^4 \text{ J}}{8.314 \text{ J/K} \cdot \text{mol}} \left( \frac{333 \text{ K} - 298 \text{ K}}{(333 \text{ K})(298 \text{ K})} \right)$$

$$\ln \frac{K_2}{1.6 \times 10^{-10}} = 2.79$$

$$\frac{K_2}{1.6 \times 10^{-10}} = e^{2.79}$$

$$K_2 = 2.6 \times 10^{-9}$$

The increase in  $K$  indicates that the solubility increases with temperature.

**18.51** At absolute zero. A substance can never have a negative entropy.

**18.52** Assuming that both  $\Delta H^\circ$  and  $\Delta S^\circ$  are temperature independent, we can calculate both  $\Delta H^\circ$  and  $\Delta S^\circ$ .

$$\Delta H^\circ = \Delta H_f^\circ(\text{CO}) + \Delta H_f^\circ(\text{H}_2) - [\Delta H_f^\circ(\text{H}_2\text{O}) + \Delta H_f^\circ(\text{C})]$$

$$\Delta H^\circ = (1)(-110.5 \text{ kJ/mol}) + (1)(0) - [(1)(-241.8 \text{ kJ/mol}) + (1)(0)]$$

$$\Delta H^\circ = 131.3 \text{ kJ/mol}$$

$$\Delta S^\circ = S^\circ(\text{CO}) + S^\circ(\text{H}_2) - [S^\circ(\text{H}_2\text{O}) + S^\circ(\text{C})]$$

$$\Delta S^\circ = [(1)(197.9 \text{ J/K}\cdot\text{mol}) + (1)(131.0 \text{ J/K}\cdot\text{mol})] - [(1)(188.7 \text{ J/K}\cdot\text{mol}) + (1)(5.69 \text{ J/K}\cdot\text{mol})]$$

$$\Delta S^\circ = 134.5 \text{ J/K}\cdot\text{mol}$$

It is obvious from the given conditions that the reaction must take place at a fairly high temperature (in order to have red-hot coke). Setting  $\Delta G^\circ = 0$

$$0 = \Delta H^\circ - T\Delta S^\circ$$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{131.3 \text{ kJ/mol} \times \frac{1000 \text{ J}}{1 \text{ kJ}}}{134.5 \text{ J/K}\cdot\text{mol}} = 976 \text{ K} = 703^\circ\text{C}$$

The temperature must be greater than  $703^\circ\text{C}$  for the reaction to be spontaneous.

**18.53 (a)** We know that HCl is a strong acid and HF is a weak acid. Thus, the equilibrium constant will be less than 1 ( $K < 1$ ).

**(b)** The number of particles on each side of the equation is the same, so  $\Delta S^\circ \approx 0$ . Therefore  $\Delta H^\circ$  will dominate.

**(c)** HCl is a weaker bond than HF (see Table 9.4 of the text), therefore  $\Delta H^\circ > 0$ .

**18.54** For a reaction to be spontaneous at constant temperature and pressure,  $\Delta G < 0$ . The process of crystallization proceeds with more order (less disorder), so  $\Delta S < 0$ . We also know that

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

Since  $\Delta G$  must be negative, and since the entropy term will be positive ( $-T\Delta S$ , where  $\Delta S$  is negative), then  $\Delta H$  must be negative ( $\Delta H < 0$ ). The reaction will be exothermic.

**18.55** For the reaction:  $\text{CaCO}_3(s) \rightleftharpoons \text{CaO}(s) + \text{CO}_2(g)$   $K_p = P_{\text{CO}_2}$

Using the equation from Problem 18.49:

$$\ln \frac{K_2}{K_1} = \frac{\Delta H^\circ}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) = \frac{\Delta H^\circ}{R} \left( \frac{T_2 - T_1}{T_1 T_2} \right)$$

Substituting,

$$\ln \frac{1829}{22.6} = \frac{\Delta H^\circ}{8.314 \text{ J/K}\cdot\text{mol}} \left( \frac{1223 \text{ K} - 973 \text{ K}}{(973 \text{ K})(1223 \text{ K})} \right)$$

Solving,

$$\Delta H^\circ = 1.74 \times 10^5 \text{ J/mol} = 174 \text{ kJ/mol}$$

- 18.56** For the reaction to be spontaneous,  $\Delta G$  must be negative.

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

Given that  $\Delta H = 19 \text{ kJ/mol} = 19,000 \text{ J/mol}$ , then

$$\Delta G = 19,000 \text{ J/mol} - (273 \text{ K} + 72 \text{ K})(\Delta S)$$

Solving the equation with the value of  $\Delta G = 0$

$$0 = 19,000 \text{ J/mol} - (273 \text{ K} + 72 \text{ K})(\Delta S)$$

$$\Delta S = 55 \text{ J/K}\cdot\text{mol}$$

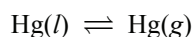
This value of  $\Delta S$  which we solved for is the value needed to produce a  $\Delta G$  value of zero. The *minimum* value of  $\Delta S$  that will produce a spontaneous reaction will be any value of entropy *greater than* 55 J/K·mol.

- 18.57** (a)  $\Delta S > 0$       (b)  $\Delta S < 0$       (c)  $\Delta S > 0$       (d)  $\Delta S > 0$

- 18.58** The second law states that the entropy of the universe must increase in a spontaneous process. But the entropy of the universe is the sum of two terms: the entropy of the system plus the entropy of the surroundings. One of the entropies can decrease, but not both. In this case, the decrease in system entropy is offset by an increase in the entropy of the surroundings. The reaction in question is exothermic, and the heat released raises the temperature (and the entropy) of the surroundings.

Could this process be spontaneous if the reaction were endothermic?

- 18.59** At the temperature of the normal boiling point the free energy difference between the liquid and gaseous forms of mercury (or any other substances) is zero, i.e. the two phases are in equilibrium. We can therefore use Equation (18.10) of the text to find this temperature. For the equilibrium,



$$\Delta G = \Delta H - T\Delta S = 0$$

$$\Delta H = \Delta H_f^\circ[\text{Hg}(g)] - \Delta H_f^\circ[\text{Hg}(l)] = 60,780 \text{ J/mol} - 0 = 60780 \text{ J/mol}$$

$$\Delta S = S^\circ[\text{Hg}(g)] - S^\circ[\text{Hg}(l)] = 174.7 \text{ J/K}\cdot\text{mol} - 77.4 \text{ J/K}\cdot\text{mol} = 97.3 \text{ J/K}\cdot\text{mol}$$

$$T_{\text{bp}} = \frac{\Delta H}{\Delta S} = \frac{60780 \text{ J/mol}}{97.3 \text{ J/K}\cdot\text{mol}} = 625 \text{ K} = 352^\circ\text{C}$$

What assumptions are made? Notice that the given enthalpies and entropies are at standard conditions, namely 25°C and 1.00 atm pressure. In performing this calculation we have tacitly assumed that these quantities don't depend upon temperature. The actual normal boiling point of mercury is 356.58°C. Is the assumption of the temperature independence of these quantities reasonable?

- 18.60 Strategy:** At the boiling point, liquid and gas phase ethanol are at equilibrium, so  $\Delta G = 0$ . From Equation (18.10) of the text, we have  $\Delta G = 0 = \Delta H - T\Delta S$  or  $\Delta S = \Delta H/T$ . To calculate the entropy change for the liquid ethanol  $\rightarrow$  gas ethanol transition, we write  $\Delta S_{\text{vap}} = \Delta H_{\text{vap}}/T$ . What temperature unit should we use?

**Solution:** The entropy change due to the phase transition (the vaporization of ethanol), can be calculated using the following equation. Recall that the temperature must be in units of Kelvin ( $78.3^\circ\text{C} = 351 \text{ K}$ ).

$$\Delta S_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T_{\text{b.p.}}}$$

$$\Delta S_{\text{vap}} = \frac{39.3 \text{ kJ/mol}}{351 \text{ K}} = 0.112 \text{ kJ/mol} \cdot \text{K} = 112 \text{ J/mol} \cdot \text{K}$$

The problem asks for the change in entropy for the vaporization of 0.50 moles of ethanol. The  $\Delta S$  calculated above is for 1 mole of ethanol.

$$\Delta S \text{ for } 0.50 \text{ mol} = (112 \text{ J/mol} \cdot \text{K})(0.50 \text{ mol}) = \mathbf{56 \text{ J/K}}$$

- 18.61** There is no connection between the spontaneity of a reaction predicted by  $\Delta G$  and the rate at which the reaction occurs. A negative free energy change tells us that a reaction has the potential to happen, but gives no indication of the rate.

Does the fact that a reaction occurs at a measurable rate mean that the free energy difference  $\Delta G$  is negative?

- 18.62** For the given reaction we can calculate the standard free energy change from the standard free energies of formation (see Appendix 3 of the text). Then, we can calculate the equilibrium constant,  $K_P$ , from the standard free energy change.

$$\Delta G^\circ = \Delta G_f^\circ[\text{Ni}(\text{CO})_4] - [4\Delta G_f^\circ(\text{CO}) + \Delta G_f^\circ(\text{Ni})]$$

$$\Delta G^\circ = (1)(-587.4 \text{ kJ/mol}) - [(4)(-137.3 \text{ kJ/mol}) + (1)(0)] = -38.2 \text{ kJ/mol} = -3.82 \times 10^4 \text{ J/mol}$$

Substitute  $\Delta G^\circ$ ,  $R$ , and  $T$  (in K) into the following equation to solve for  $K_P$ .

$$\Delta G^\circ = -RT \ln K_P$$

$$\ln K_P = \frac{-\Delta G^\circ}{RT} = \frac{-(-3.82 \times 10^4 \text{ J/mol})}{(8.314 \text{ J/K} \cdot \text{mol})(353 \text{ K})}$$

$$\mathbf{K_P = 4.5 \times 10^5}$$

- 18.63 (a)**  $\Delta G^\circ = 2\Delta G_f^\circ(\text{HBr}) - \Delta G_f^\circ(\text{H}_2) - \Delta G_f^\circ(\text{Br}_2) = (2)(-53.2 \text{ kJ/mol}) - (1)(0) - (1)(0)$

$$\Delta G^\circ = -106.4 \text{ kJ/mol}$$

$$\ln K_P = \frac{-\Delta G^\circ}{RT} = \frac{106.4 \times 10^3 \text{ J/mol}}{(8.314 \text{ J/K} \cdot \text{mol})(298 \text{ K})} = 42.9$$

$$\mathbf{K_P = 4 \times 10^{18}}$$

- (b)**  $\Delta G^\circ = \Delta G_f^\circ(\text{HBr}) - \frac{1}{2}\Delta G_f^\circ(\text{H}_2) - \frac{1}{2}\Delta G_f^\circ(\text{Br}_2) = (1)(-53.2 \text{ kJ/mol}) - (\frac{1}{2})(0) - (\frac{1}{2})(0)$

$$\Delta G^\circ = -53.2 \text{ kJ/mol}$$

$$\ln K_P = \frac{-\Delta G^\circ}{RT} = \frac{53.2 \times 10^3 \text{ J/mol}}{(8.314 \text{ J/K} \cdot \text{mol})(298 \text{ K})} = 21.5$$

$$\mathbf{K_P = 2 \times 10^9}$$

The  $K_P$  in (a) is the square of the  $K_P$  in (b). Both  $\Delta G^\circ$  and  $K_P$  depend on the number of moles of reactants and products specified in the balanced equation.

- 18.64** We carry additional significant figures throughout this calculation to minimize rounding errors. The equilibrium constant is related to the standard free energy change by the following equation:

$$\Delta G^\circ = -RT \ln K_P$$

$$2.12 \times 10^5 \text{ J/mol} = -(8.314 \text{ J/mol}\cdot\text{K})(298 \text{ K}) \ln K_P$$

$$K_P = 6.894 \times 10^{-38}$$

We can write the equilibrium constant expression for the reaction.

$$K_P = \sqrt{P_{\text{O}_2}}$$

$$P_{\text{O}_2} = (K_P)^2$$

$$P_{\text{O}_2} = (6.894 \times 10^{-38})^2 = \mathbf{4.8 \times 10^{-75} \text{ atm}}$$

This pressure is far too small to measure.

- 18.65** Talking involves various biological processes (to provide the necessary energy) that lead to an increase in the entropy of the universe. Since the overall process (talking) is spontaneous, the entropy of the universe must increase.

- 18.66** Both (a) and (b) apply to a reaction with a negative  $\Delta G^\circ$  value. Statement (c) is not always true. An endothermic reaction that has a positive  $\Delta S^\circ$  (increase in entropy) will have a negative  $\Delta G^\circ$  value at high temperatures.

- 18.67** (a) If  $\Delta G^\circ$  for the reaction is 173.4 kJ/mol,

$$\text{then, } \Delta G_f^\circ = \frac{173.4 \text{ kJ/mol}}{2} = \mathbf{86.7 \text{ kJ/mol}}$$

- (b)  $\Delta G^\circ = -RT \ln K_P$

$$173.4 \times 10^3 \text{ J/mol} = -(8.314 \text{ J/K}\cdot\text{mol})(298 \text{ K}) \ln K_P$$

$$\mathbf{K_P = 4 \times 10^{-31}}$$

- (c)  $\Delta H^\circ$  for the reaction is  $2 \times \Delta H_f^\circ(\text{NO}) = (2)(86.7 \text{ kJ/mol}) = 173.4 \text{ kJ/mol}$

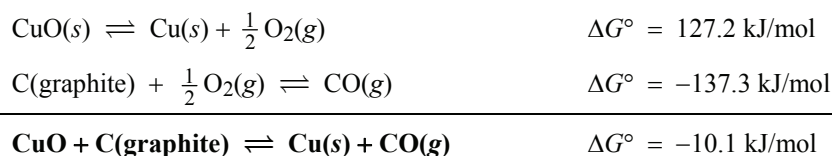
Using the equation in Problem 18.49:

$$\ln \frac{K_2}{4 \times 10^{-31}} = \frac{173.4 \times 10^3 \text{ J/mol}}{8.314 \text{ J/mol}\cdot\text{K}} \left( \frac{1373 \text{ K} - 298 \text{ K}}{(1373 \text{ K})(298 \text{ K})} \right)$$

$$\mathbf{K_2 = 3 \times 10^{-7}}$$

- (d) Lightning promotes the formation of NO (from  $\text{N}_2$  and  $\text{O}_2$  in the air) which eventually leads to the formation of nitrate ion ( $\text{NO}_3^-$ ), an essential nutrient for plants.

- 18.68** We write the two equations as follows. The standard free energy change for the overall reaction will be the sum of the two steps.



We can now calculate the equilibrium constant from the standard free energy change,  $\Delta G^\circ$ .

$$\ln K = \frac{-\Delta G^\circ}{RT} = \frac{-(-10.1 \times 10^3 \text{ J/mol})}{(8.314 \text{ J/K} \cdot \text{mol})(673 \text{ K})}$$

$$\ln K = 1.81$$

$$\mathbf{K = 6.1}$$

- 18.69** Using the equation in the Chemistry in Action entitled “The Efficiency of Heat Engines” in Chapter 18:

$$\text{Efficiency} = \frac{T_2 - T_1}{T_2} = \frac{2473 \text{ K} - 1033 \text{ K}}{2473 \text{ K}} = 0.5823$$

The work done by moving the car:

$$mgh = (1200 \text{ kg})(9.81 \text{ m/s}^2) \times h = \text{heat generated by the engine.}$$

The heat generated by the gas:

$$1.0 \text{ gal} \times \frac{3.1 \text{ kg}}{1 \text{ gal}} \times \frac{1000 \text{ g}}{1 \text{ kg}} \times \frac{1 \text{ mol}}{114.2 \text{ g}} \times \frac{5510 \times 10^3 \text{ J}}{1 \text{ mol}} = 1.5 \times 10^8 \text{ J}$$

The maximum use of the energy generated by the gas is:

$$(\text{energy})(\text{efficiency}) = (1.5 \times 10^8 \text{ J})(0.5823) = 8.7 \times 10^7 \text{ J}$$

Setting the (useable) energy generated by the gas equal to the work done moving the car:

$$8.7 \times 10^7 \text{ J} = (1200 \text{ kg})(9.81 \text{ m/s}^2) \times h$$

$$\mathbf{h = 7.4 \times 10^3 \text{ m}}$$

- 18.70** As discussed in Chapter 18 of the text for the decomposition of calcium carbonate, a reaction favors the formation of products at equilibrium when

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ < 0$$

If we can calculate  $\Delta H^\circ$  and  $\Delta S^\circ$ , we can solve for the temperature at which decomposition begins to favor products. We use data in Appendix 3 of the text to solve for  $\Delta H^\circ$  and  $\Delta S^\circ$ .

$$\Delta H^\circ = \Delta H_f^\circ[\text{MgO}(s)] + \Delta H_f^\circ[\text{CO}_2(g)] - \Delta H_f^\circ[\text{MgCO}_3(s)]$$

$$\Delta H^\circ = -601.8 \text{ kJ/mol} + (-393.5 \text{ kJ/mol}) - (-1112.9 \text{ kJ/mol}) = 117.6 \text{ kJ/mol}$$

$$\Delta S^\circ = S^\circ[\text{MgO}(s)] + S^\circ[\text{CO}_2(g)] - S^\circ[\text{MgCO}_3(s)]$$

$$\Delta S^\circ = 26.78 \text{ J/K} \cdot \text{mol} + 213.6 \text{ J/K} \cdot \text{mol} - 65.69 \text{ J/K} \cdot \text{mol} = 174.7 \text{ J/K} \cdot \text{mol}$$

For the reaction to begin to favor products,

$$\Delta H^\circ - T\Delta S^\circ < 0$$

or

$$T > \frac{\Delta H^\circ}{\Delta S^\circ}$$

$$T > \frac{117.6 \times 10^3 \text{ J/mol}}{174.7 \text{ J/K} \cdot \text{mol}}$$

$$T > 673.2 \text{ K}$$

- 18.71 (a)** The first law states that energy can neither be created nor destroyed. We cannot obtain energy out of nowhere.
- (b)** If we calculate the efficiency of such an engine, we find that  $T_h = T_c$ , so the efficiency is zero! See Chemistry in Action on p. 796 of the text.

**18.72 (a)**  $\Delta G^\circ = \Delta G_f^\circ(\text{H}_2) + \Delta G_f^\circ(\text{Fe}^{2+}) - \Delta G_f^\circ(\text{Fe}) - 2\Delta G_f^\circ(\text{H}^+)$

$$\Delta G^\circ = (1)(0) + (1)(-84.9 \text{ kJ/mol}) - (1)(0) - (2)(0)$$

$$\Delta G^\circ = -84.9 \text{ kJ/mol}$$

$$\Delta G^\circ = -RT \ln K$$

$$-84.9 \times 10^3 \text{ J/mol} = -(8.314 \text{ J/mol} \cdot \text{K})(298 \text{ K}) \ln K$$

$$K = 7.6 \times 10^{14}$$

**(b)**  $\Delta G^\circ = \Delta G_f^\circ(\text{H}_2) + \Delta G_f^\circ(\text{Cu}^{2+}) - \Delta G_f^\circ(\text{Cu}) - 2\Delta G_f^\circ(\text{H}^+)$

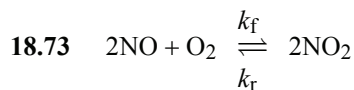
$$\Delta G^\circ = 64.98 \text{ kJ/mol}$$

$$\Delta G^\circ = -RT \ln K$$

$$64.98 \times 10^3 \text{ J/mol} = -(8.314 \text{ J/mol} \cdot \text{K})(298 \text{ K}) \ln K$$

$$K = 4.1 \times 10^{-12}$$

The activity series is correct. The very large value of  $K$  for reaction (a) indicates that *products* are highly favored; whereas, the very small value of  $K$  for reaction (b) indicates that *reactants* are highly favored.



$$\Delta G^\circ = (2)(51.8 \text{ kJ/mol}) - (2)(86.7 \text{ kJ/mol}) - 0 = -69.8 \text{ kJ/mol}$$

$$\Delta G^\circ = -RT \ln K$$

$$-69.8 \times 10^3 \text{ J/mol} = -(8.314 \text{ J/mol} \cdot \text{K})(298 \text{ K}) \ln K$$

$$K = 1.7 \times 10^{12} \text{ M}^{-1}$$

$$K = \frac{k_f}{k_r}$$

$$1.7 \times 10^{12} M^{-1} = \frac{7.1 \times 10^9 M^{-2} s^{-1}}{k_r}$$

$$k_r = 4.2 \times 10^{-3} M^{-1} s^{-1}$$

**18.74 (a)** It is a “reverse” disproportionation redox reaction.

$$(b) \Delta G^\circ = (2)(-228.6 \text{ kJ/mol}) - (2)(-33.0 \text{ kJ/mol}) - (1)(-300.4 \text{ kJ/mol})$$

$$\Delta G^\circ = -90.8 \text{ kJ/mol}$$

$$-90.8 \times 10^3 \text{ J/mol} = -(8.314 \text{ J/mol}\cdot\text{K})(298 \text{ K}) \ln K$$

$$K = 8.2 \times 10^{15}$$

Because of the large value of  $K$ , this method is efficient for removing  $\text{SO}_2$ .

$$(c) \Delta H^\circ = (2)(-241.8 \text{ kJ/mol}) + (3)(0) - (2)(-20.15 \text{ kJ/mol}) - (1)(-296.1 \text{ kJ/mol})$$

$$\Delta H^\circ = -147.2 \text{ kJ/mol}$$

$$\Delta S^\circ = (2)(188.7 \text{ J/K}\cdot\text{mol}) + (3)(31.88 \text{ J/K}\cdot\text{mol}) - (2)(205.64 \text{ J/K}\cdot\text{mol}) - (1)(248.5 \text{ J/K}\cdot\text{mol})$$

$$\Delta S^\circ = -186.7 \text{ J/K}\cdot\text{mol}$$

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

Due to the negative entropy change,  $\Delta S^\circ$ , the free energy change,  $\Delta G^\circ$ , will become positive at higher temperatures. Therefore, the reaction will be **less effective** at high temperatures.

**18.75 (1)** Measure  $K$  and use  $\Delta G^\circ = -RT \ln K$

**(2)** Measure  $\Delta H^\circ$  and  $\Delta S^\circ$  and use  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

**18.76**  $2\text{O}_3 \rightleftharpoons 3\text{O}_2$

$$\Delta G^\circ = 3\Delta G_f^\circ(\text{O}_2) - 2\Delta G_f^\circ(\text{O}_3) = 0 - (2)(163.4 \text{ kJ/mol})$$

$$\Delta G^\circ = -326.8 \text{ kJ/mol}$$

$$-326.8 \times 10^3 \text{ J/mol} = -(8.314 \text{ J/mol}\cdot\text{K})(243 \text{ K}) \ln K_P$$

$$K_P = 1.8 \times 10^{70}$$

Due to the large magnitude of  $K$ , you would expect this reaction to be spontaneous in the forward direction. However, this reaction has a **large activation energy**, so the rate of reaction is extremely slow.

**18.77** First convert to moles of ice.

$$74.6 \text{ g H}_2\text{O}(s) \times \frac{1 \text{ mol H}_2\text{O}(s)}{18.02 \text{ g H}_2\text{O}(s)} = 4.14 \text{ mol H}_2\text{O}(s)$$

For a phase transition:

$$\Delta S_{\text{sys}} = \frac{\Delta H_{\text{sys}}}{T}$$

$$\Delta S_{\text{sys}} = \frac{(4.14)(6010 \text{ J/mol})}{273 \text{ K}} = \mathbf{91.1 \text{ J/K} \cdot \text{mol}}$$

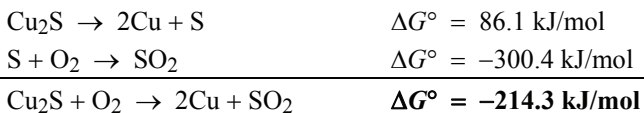
$$\Delta S_{\text{surr}} = \frac{-\Delta H_{\text{sys}}}{T}$$

$$\Delta S_{\text{surr}} = \frac{-(4.14)(6010 \text{ J/mol})}{273 \text{ K}} = \mathbf{-91.1 \text{ J/K} \cdot \text{mol}}$$

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = \mathbf{0}$$

This is an equilibrium process. There is no net change.

**18.78** Heating the ore alone is not a feasible process. Looking at the coupled process:



Since  $\Delta G^\circ$  is a large negative quantity, the coupled reaction is feasible for extracting sulfur.

**18.79** Since we are dealing with the same ion ( $\text{K}^+$ ), Equation (18.13) of the text can be written as:

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

$$\Delta G = 0 + (8.314 \text{ J/mol} \cdot \text{K})(310 \text{ K}) \ln \left( \frac{400 \text{ mM}}{15 \text{ mM}} \right)$$

$$\Delta G = \mathbf{8.5 \times 10^3 \text{ J/mol} = 8.5 \text{ kJ/mol}}$$

**18.80** First, we need to calculate  $\Delta H^\circ$  and  $\Delta S^\circ$  for the reaction in order to calculate  $\Delta G^\circ$ .

$$\Delta H^\circ = -41.2 \text{ kJ/mol} \qquad \Delta S^\circ = -42.0 \text{ J/K} \cdot \text{mol}$$

Next, we calculate  $\Delta G^\circ$  at  $300^\circ\text{C}$  or  $573 \text{ K}$ , assuming that  $\Delta H^\circ$  and  $\Delta S^\circ$  are temperature independent.

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

$$\Delta G^\circ = -41.2 \times 10^3 \text{ J/mol} - (573 \text{ K})(-42.0 \text{ J/K} \cdot \text{mol})$$

$$\Delta G^\circ = -1.71 \times 10^4 \text{ J/mol}$$

Having solved for  $\Delta G^\circ$ , we can calculate  $K_p$ .

$$\Delta G^\circ = -RT \ln K_p$$

$$-1.71 \times 10^4 \text{ J/mol} = -(8.314 \text{ J/K} \cdot \text{mol})(573 \text{ K}) \ln K_p$$

$$\ln K_p = 3.59$$

$$\mathbf{K_p = 36}$$

Due to the negative entropy change calculated above, we expect that  $\Delta G^\circ$  will become positive at some temperature higher than  $300^\circ\text{C}$ . We need to find the temperature at which  $\Delta G^\circ$  becomes zero. This is the temperature at which reactants and products are equally favored ( $K_P = 1$ ).

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ 0 &= \Delta H^\circ - T\Delta S^\circ \\ T &= \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{-41.2 \times 10^3 \text{ J/mol}}{-42.0 \text{ J/K}\cdot\text{mol}} \\ \mathbf{T} &= \mathbf{981 \text{ K} = 708^\circ\text{C}}\end{aligned}$$

This calculation shows that at  $708^\circ\text{C}$ ,  $\Delta G^\circ = 0$  and the equilibrium constant  $K_P = 1$ . Above  $708^\circ\text{C}$ ,  $\Delta G^\circ$  is positive and  $K_P$  will be smaller than 1, meaning that reactants will be favored over products. Note that the temperature  $708^\circ\text{C}$  is only an estimate, as we have assumed that both  $\Delta H^\circ$  and  $\Delta S^\circ$  are independent of temperature.

Using a more efficient catalyst will *not* increase  $K_P$  at a given temperature, because the catalyst will speed up both the forward and reverse reactions. The value of  $K_P$  will stay the same.

**18.81 (a)**  $\Delta G^\circ$  for  $\text{CH}_3\text{COOH}$ :

$$\begin{aligned}\Delta G^\circ &= -(8.314 \text{ J/mol}\cdot\text{K})(298 \text{ K})\ln(1.8 \times 10^{-5}) \\ \Delta G^\circ &= 2.7 \times 10^4 \text{ J/mol} = \mathbf{27 \text{ kJ/mol}}\end{aligned}$$

$\Delta G^\circ$  for  $\text{CH}_2\text{ClCOOH}$ :

$$\begin{aligned}\Delta G^\circ &= -(8.314 \text{ J/mol}\cdot\text{K})(298 \text{ K})\ln(1.4 \times 10^{-3}) \\ \Delta G^\circ &= 1.6 \times 10^4 \text{ J/mol} = \mathbf{16 \text{ kJ/mol}}\end{aligned}$$

**(b)** The  $T\Delta S^\circ$  is the dominant term.

**(c)** The breaking of the O–H bond in ionization of the acid and the forming of the O–H bond in  $\text{H}_3\text{O}^+$ .

**(d)** The  $\text{CH}_3\text{COO}^-$  ion is smaller than  $\text{CH}_2\text{ClCOO}^-$  and can participate in hydration to a greater extent, leading to a more ordered solution.

**18.82** butane  $\rightarrow$  isobutane

$$\begin{aligned}\Delta G^\circ &= \Delta G_f^\circ(\text{isobutane}) - \Delta G_f^\circ(\text{butane}) \\ \Delta G^\circ &= (1)(-18.0 \text{ kJ/mol}) - (1)(-15.9 \text{ kJ/mol}) \\ \Delta G^\circ &= -2.1 \text{ kJ/mol}\end{aligned}$$

For a mixture at equilibrium at  $25^\circ\text{C}$ :

$$\begin{aligned}\Delta G^\circ &= -RT\ln K_P \\ -2.1 \times 10^3 \text{ J/mol} &= -(8.314 \text{ J/mol}\cdot\text{K})(298 \text{ K})\ln K_P \\ K_P &= 2.3\end{aligned}$$

$$K_P = \frac{P_{\text{isobutane}}}{P_{\text{butane}}} \propto \frac{\text{mol isobutane}}{\text{mol butane}}$$

$$2.3 = \frac{\text{mol isobutane}}{\text{mol butane}}$$

This shows that there are 2.3 times as many moles of isobutane as moles of butane. Or, we can say for every one mole of butane, there are 2.3 moles of isobutane.

$$\text{mol \% isobutane} = \frac{2.3 \text{ mol}}{2.3 \text{ mol} + 1.0 \text{ mol}} \times 100\% = \mathbf{70\%}$$

By difference, the mole % of butane is **30%**.

**Yes**, this result supports the notion that straight-chain hydrocarbons like butane are less stable than branched-chain hydrocarbons like isobutane.

**18.83** Heat is absorbed by the rubber band, so  $\Delta H$  is positive. Since the contraction occurs spontaneously,  $\Delta G$  is negative. For the reaction to be spontaneous,  $\Delta S$  must be positive meaning that the rubber becomes more disordered upon heating. This is consistent with what we know about the structure of rubber; The rubber molecules become more disordered upon contraction (See the Figure in the Chemistry in Action Essay on p. 807 of the text).

**18.84** We can calculate  $K_P$  from  $\Delta G^\circ$ .

$$\Delta G^\circ = (1)(-394.4 \text{ kJ/mol}) + (0) - (1)(-137.3 \text{ kJ/mol}) - (1)(-255.2 \text{ kJ/mol})$$

$$\Delta G^\circ = -1.9 \text{ kJ/mol}$$

$$-1.9 \times 10^3 \text{ J/mol} = -(8.314 \text{ J/mol}\cdot\text{K})(1173 \text{ K}) \ln K_P$$

$$K_P = 1.2$$

Now, from  $K_P$ , we can calculate the mole fractions of CO and CO<sub>2</sub>.

$$K_P = \frac{P_{\text{CO}_2}}{P_{\text{CO}}} = 1.2 \quad P_{\text{CO}_2} = 1.2P_{\text{CO}}$$

$$X_{\text{CO}} = \frac{P_{\text{CO}}}{P_{\text{CO}} + P_{\text{CO}_2}} = \frac{P_{\text{CO}}}{P_{\text{CO}} + 1.2P_{\text{CO}}} = \frac{1}{2.2} = \mathbf{0.45}$$

$$X_{\text{CO}_2} = 1 - 0.45 = \mathbf{0.55}$$

We assumed that  $\Delta G^\circ$  calculated from  $\Delta G_f^\circ$  values was temperature independent. The  $\Delta G_f^\circ$  values in Appendix 3 of the text are measured at 25°C, but the temperature of the reaction is 900°C.

**18.85**  $\Delta G^\circ = -RT \ln K$

and,

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

Substituting,

$$\Delta G = -RT \ln K + RT \ln Q$$

$$\Delta G = RT(\ln Q - \ln K)$$

$$\Delta G = RT \ln \left( \frac{Q}{K} \right)$$

If  $Q > K$ ,  $\Delta G > 0$ , and the net reaction will proceed from right to left (see Figure 14.5 of the text).

If  $Q < K$ ,  $\Delta G < 0$ , and the net reaction will proceed from left to right.

If  $Q = K$ ,  $\Delta G = 0$ . The system is at equilibrium.

**18.86** For a phase transition,  $\Delta G = 0$ . We write:

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

$$0 = \Delta H - T\Delta S$$

$$\Delta S_{\text{sub}} = \frac{\Delta H_{\text{sub}}}{T}$$

Substituting  $\Delta H$  and the temperature,  $(-78^\circ + 273^\circ)\text{K} = 195 \text{ K}$ , gives

$$\Delta S_{\text{sub}} = \frac{\Delta H_{\text{sub}}}{T} = \frac{25.2 \times 10^3 \text{ J}}{195 \text{ K}} = 129 \text{ J/K} \cdot \text{mol}$$

This value of  $\Delta S_{\text{sub}}$  is for the sublimation of 1 mole of  $\text{CO}_2$ . We convert to the  $\Delta S$  value for the sublimation of 84.8 g of  $\text{CO}_2$ .

$$84.8 \text{ g CO}_2 \times \frac{1 \text{ mol CO}_2}{44.01 \text{ g CO}_2} \times \frac{129 \text{ J}}{\text{K} \cdot \text{mol}} = \mathbf{249 \text{ J/K}}$$

**18.87** The second law of thermodynamics states that the entropy of the universe increases in a spontaneous process and remains unchanged in an equilibrium process. Therefore, the entropy of the universe is increasing with time, and thus entropy could be used to determine the forward direction of time.

**18.88** First, let's convert the age of the universe from units of years to units of seconds.

$$(13 \times 10^9 \text{ yr}) \times \frac{365 \text{ days}}{1 \text{ yr}} \times \frac{24 \text{ h}}{1 \text{ day}} \times \frac{3600 \text{ s}}{1 \text{ h}} = 4.1 \times 10^{17} \text{ s}$$

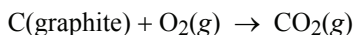
The probability of finding all 100 molecules in the same flask is  $8 \times 10^{-31}$ . Multiplying by the number of seconds gives:

$$(8 \times 10^{-31})(4.1 \times 10^{17} \text{ s}) = \mathbf{3 \times 10^{-13} \text{ s}}$$

**18.89** Equation (18.10) represents the standard free-energy change for a reaction, and not for a particular compound like  $\text{CO}_2$ . The correct form is:

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

For a given reaction,  $\Delta G^\circ$  and  $\Delta H^\circ$  would need to be calculated from standard formation values (graphite, oxygen, and carbon dioxide) first, before plugging into the equation. Also,  $\Delta S^\circ$  would need to be calculated from standard entropy values.



- 18.90** We can calculate  $\Delta S_{\text{sys}}$  from standard entropy values in Appendix 3 of the text. We can calculate  $\Delta S_{\text{surr}}$  from the  $\Delta H_{\text{sys}}$  value given in the problem. Finally, we can calculate  $\Delta S_{\text{univ}}$  from the  $\Delta S_{\text{sys}}$  and  $\Delta S_{\text{surr}}$  values.

$$\Delta S_{\text{sys}} = (2)(69.9 \text{ J/K}\cdot\text{mol}) - [(2)(131.0 \text{ J/K}\cdot\text{mol}) + (1)(205.0 \text{ J/K}\cdot\text{mol})] = \mathbf{-327 \text{ J/K}\cdot\text{mol}}$$

$$\Delta S_{\text{surr}} = \frac{-\Delta H_{\text{sys}}}{T} = \frac{-(-571.6 \times 10^3 \text{ J/mol})}{298 \text{ K}} = \mathbf{1918 \text{ J/K}\cdot\text{mol}}$$

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = (-327 + 1918) \text{ J/K}\cdot\text{mol} = \mathbf{1591 \text{ J/K}\cdot\text{mol}}$$

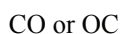
- 18.91**  $\Delta H^\circ$  is endothermic. Heat must be added to denature the protein. Denaturation leads to more disorder (an increase in microstates). The magnitude of  $\Delta S^\circ$  is fairly large (1600 J/K·mol). Proteins are large molecules and therefore denaturation would lead to a large increase in microstates. The temperature at which the process favors the denatured state can be calculated by setting  $\Delta G^\circ$  equal to zero.

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

$$0 = \Delta H^\circ - T\Delta S^\circ$$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{512 \text{ kJ/mol}}{1.60 \text{ kJ/K}\cdot\text{mol}} = \mathbf{320 \text{ K} = 47^\circ\text{C}}$$

- 18.92**  $q$ , and  $w$  are *not* state functions. Recall that state functions represent properties that are determined by the state of the system, regardless of how that condition is achieved. Heat and work are not state functions because they are not properties of the system. They manifest themselves only during a process (during a change). Thus their values depend on the path of the process and vary accordingly.
- 18.93** (d) will not lead to an increase in entropy of the system. The gas is returned to its original state. The entropy of the system does not change.
- 18.94** Since the adsorption is spontaneous,  $\Delta G$  must be negative ( $\Delta G < 0$ ). When hydrogen bonds to the surface of the catalyst, the system becomes more ordered ( $\Delta S < 0$ ). Since there is a decrease in entropy, the adsorption must be exothermic for the process to be spontaneous ( $\Delta H < 0$ ).
- 18.95** (a) An ice cube melting in a glass of water at  $20^\circ\text{C}$ . The value of  $\Delta G$  for this process is negative so it must be spontaneous.
- (b) A "perpetual motion" machine. In one version, a model has a flywheel which, once started up, drives a generator which drives a motor which keeps the flywheel running at a constant speed and also lifts a weight.
- (c) A perfect air conditioner; it extracts heat energy from the room and warms the outside air without using any energy to do so. (Note: this process does not violate the first law of thermodynamics.)
- (d) Same example as (a).
- (e) A closed flask at  $25^\circ\text{C}$  containing  $\text{NO}_2(\text{g})$  and  $\text{N}_2\text{O}_4(\text{g})$  at equilibrium.
- 18.96** (a) Each CO molecule has two possible orientations in the crystal,



If there is no preferred orientation, then for one molecule there are two, or  $2^1$ , choices of orientation. Two molecules have four or  $2^2$  choices, and for 1 mole of CO there are  $2^{N_A}$  choices. From Equation (18.1) of the text:

$$S = k \ln W$$

$$S = (1.38 \times 10^{-23} \text{ J/K}) \ln 2^{6.022 \times 10^{23}}$$

$$S = (1.38 \times 10^{-23} \text{ J/K})(6.022 \times 10^{23} / \text{mol}) \ln 2$$

$$S = \mathbf{5.76 \text{ J/K}\cdot\text{mol}}$$

(b) The fact that the actual residual entropy is 4.2 J/K·mol means that the orientation is not totally random.

**18.97** The analogy is inappropriate. Entropy is a measure of the dispersal of molecules among available energy levels. The entropy of the room is the same whether it is tidy or not.

**18.98** We use data in Appendix 3 of the text to calculate  $\Delta H^\circ$  and  $\Delta S^\circ$ .

$$\Delta H^\circ = \Delta H_{\text{vap}} = \Delta H_{\text{f}}^\circ[\text{C}_6\text{H}_6(\text{g})] - \Delta H_{\text{f}}^\circ[\text{C}_6\text{H}_6(\text{l})]$$

$$\Delta H^\circ = 82.93 \text{ kJ/mol} - 49.04 \text{ kJ/mol} = \mathbf{33.89 \text{ kJ/mol}}$$

$$\Delta S^\circ = S^\circ[\text{C}_6\text{H}_6(\text{g})] - S^\circ[\text{C}_6\text{H}_6(\text{l})]$$

$$\Delta S^\circ = 269.2 \text{ J/K}\cdot\text{mol} - 172.8 \text{ J/K}\cdot\text{mol} = \mathbf{96.4 \text{ J/K}\cdot\text{mol}}$$

We can now calculate  $\Delta G^\circ$  at 298 K.

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

$$\Delta G^\circ = 33.89 \text{ kJ/mol} - (298 \text{ K})(96.4 \text{ J/K}\cdot\text{mol}) \times \frac{1 \text{ kJ}}{1000 \text{ J}}$$

$$\Delta G^\circ = \mathbf{5.2 \text{ kJ/mol}}$$

$\Delta H^\circ$  is positive because this is an endothermic process. We also expect  $\Delta S^\circ$  to be positive because this is a liquid  $\rightarrow$  vapor phase change.  $\Delta G^\circ$  is positive because we are at a temperature that is below the boiling point of benzene (80.1°C).

**18.99** (a)  $\text{A} + \text{B} \rightarrow \text{C} + x\text{H}^+$

From Equation (18.13) of the text and using the chemical standard state of 1 M, we write

$$\Delta G = \Delta G^\circ + RT \ln \frac{\left(\frac{[\text{C}]}{1 \text{ M}}\right)\left(\frac{[\text{H}^+]}{1 \text{ M}}\right)^x}{\left(\frac{[\text{A}]}{1 \text{ M}}\right)\left(\frac{[\text{B}]}{1 \text{ M}}\right)}$$

For the biological standard state, we write

$$\Delta G = \Delta G^{\circ'} + RT \ln \frac{\left(\frac{[\text{C}]}{1 \text{ M}}\right)\left(\frac{[\text{H}^+]}{1 \times 10^{-7} \text{ M}}\right)^x}{\left(\frac{[\text{A}]}{1 \text{ M}}\right)\left(\frac{[\text{B}]}{1 \text{ M}}\right)}$$

We set the two equations equal to each other.

$$\Delta G^\circ + RT \ln \frac{\left(\frac{[C]}{1 M}\right)\left(\frac{[H^+]}{1 M}\right)^x}{\left(\frac{[A]}{1 M}\right)\left(\frac{[B]}{1 M}\right)} = \Delta G^{\circ'} + RT \ln \frac{\left(\frac{[C]}{1 M}\right)\left(\frac{[H^+]}{1 \times 10^{-7} M}\right)^x}{\left(\frac{[A]}{1 M}\right)\left(\frac{[B]}{1 M}\right)}$$

$$\Delta G^\circ + RT \ln \left(\frac{[H^+]}{1 M}\right)^x = \Delta G^{\circ'} + RT \ln \left(\frac{[H^+]}{1 \times 10^{-7} M}\right)^x$$

$$\Delta G^\circ = \Delta G^{\circ'} + RT \ln \left(\frac{[H^+]}{1 \times 10^{-7} M}\right)^x - RT \ln \left(\frac{[H^+]}{1 M}\right)^x$$

$$\Delta G^\circ = \Delta G^{\circ'} + RT \ln \left(\frac{\frac{[H^+]}{1 \times 10^{-7} M}}{\frac{[H^+]}{1 M}}\right)^x$$

$$\Delta G^\circ = \Delta G^{\circ'} + xRT \ln \left(\frac{1}{1 \times 10^{-7}}\right) \quad (1)$$

For the reverse reaction,  $C + xH^+ \rightarrow A + B$ , we can show that

$$\Delta G^\circ = \Delta G^{\circ'} - xRT \ln \left(\frac{1}{1 \times 10^{-7}}\right) \quad (2)$$

(b) To calculate  $\Delta G^{\circ'}$ , we use Equation (2) from part (a). Because  $x = 1$ , Equation (2) becomes

$$\Delta G^\circ = \Delta G^{\circ'} - (1)(8.314 \text{ J/mol} \cdot \text{K})(298 \text{ K}) \ln \frac{1}{1 \times 10^{-7}}$$

$$\Delta G^\circ = \Delta G^{\circ'} - 39.93 \text{ kJ/mol}$$

or

$$\Delta G^{\circ'} = -21.8 \text{ kJ/mol} + 39.93 \text{ kJ/mol} = \mathbf{18.1 \text{ kJ/mol}}$$

We now calculate  $\Delta G$  using both conventions.

Chemical standard state:

$$\Delta G = \Delta G^\circ + RT \ln \frac{\left(\frac{[\text{NAD}^+]}{1 M}\right)\left(\frac{P_{\text{H}_2}}{1 \text{ atm}}\right)}{\left(\frac{[\text{NADH}]}{1 M}\right)\left(\frac{[\text{H}^+]}{1 M}\right)}$$

$$\Delta G = -21.8 \times 10^3 \text{ J/mol} + (8.314 \text{ J/mol} \cdot \text{K})(298 \text{ K}) \ln \frac{(4.6 \times 10^{-3})(0.010)}{(1.5 \times 10^{-2})(3.0 \times 10^{-5})}$$

$$\Delta G = \mathbf{-10.3 \text{ kJ/mol}}$$

Biological standard state:

$$\Delta G = \Delta G^{\circ'} + RT \ln \frac{\left(\frac{[\text{NAD}^+]}{1 \text{ M}}\right)\left(\frac{P_{\text{H}_2}}{1 \text{ atm}}\right)}{\left(\frac{[\text{NADH}]}{1 \text{ M}}\right)\left(\frac{[\text{H}^+]}{1 \times 10^{-7} \text{ M}}\right)}$$

$$\Delta G = 18.1 \times 10^3 \text{ J/mol} + (8.314 \text{ J/mol} \cdot \text{K})(298 \text{ K}) \ln \frac{(4.6 \times 10^{-3})(0.010)}{(1.5 \times 10^{-2})(3.0 \times 10^{-5} / 1 \times 10^{-7})}$$

$$\Delta G = -10.3 \text{ kJ/mol}$$

As expected,  $\Delta G$  is the same regardless of which standard state we employ.

**18.100** We can calculate  $\Delta G^{\circ}$  at 872 K from the equilibrium constant,  $K_1$ .

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

$$\Delta G^{\circ} = -(8.314 \text{ J/mol} \cdot \text{K})(872 \text{ K}) \ln(1.80 \times 10^{-4})$$

$$\Delta G^{\circ} = 6.25 \times 10^4 \text{ J/mol} = \mathbf{62.5 \text{ kJ/mol}}$$

We use the equation derived in Problem 18.49 to calculate  $\Delta H^{\circ}$ .

$$\ln \frac{K_2}{K_1} = \frac{\Delta H^{\circ}}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\ln \frac{0.0480}{1.80 \times 10^{-4}} = \frac{\Delta H^{\circ}}{8.314 \text{ J/mol} \cdot \text{K}} \left( \frac{1}{872 \text{ K}} - \frac{1}{1173 \text{ K}} \right)$$

$$\Delta H^{\circ} = \mathbf{157.8 \text{ kJ/mol}}$$

Now that both  $\Delta G^{\circ}$  and  $\Delta H^{\circ}$  are known, we can calculate  $\Delta S^{\circ}$  at 872 K.

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

$$62.5 \times 10^3 \text{ J/mol} = (157.8 \times 10^3 \text{ J/mol}) - (872 \text{ K})\Delta S^{\circ}$$

$$\Delta S^{\circ} = \mathbf{109 \text{ J/K} \cdot \text{mol}}$$