

# CHAPTER 20 THERMODYNAMICS: ENTROPY, FREE ENERGY, AND THE DIRECTION OF CHEMICAL REACTIONS

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## END-OF-CHAPTER PROBLEMS

- 20.1 Spontaneous processes proceed without outside intervention. The fact that a process is spontaneous does not mean that it will occur instantaneously (in an instant) or even at an observable rate. The rusting of iron is an example of a process that is spontaneous but very slow. The ignition of gasoline is an example of a process that is not spontaneous but very fast.
- 20.2 A spontaneous process occurs by itself (possibly requiring an initial input of energy), whereas a nonspontaneous process requires a continuous supply of energy to make it happen. It is possible to cause a nonspontaneous process to occur, but the process stops once the energy source is removed. A reaction that is found to be nonspontaneous under one set of conditions may be spontaneous under a different set of conditions (different temperature, different concentrations).
- 20.3 a) The energy of the universe is constant.  
b) Energy cannot be created or destroyed.  
c)  $\Delta E_{\text{system}} = -\Delta E_{\text{surroundings}}$   
The first law is concerned with balancing energy for a process but says nothing about whether the process can, in fact, occur.
- 20.4 Entropy is related to the freedom of movement of the particles. A system with greater freedom of movement has higher entropy.  
a) and b) Probability is so remote as to be virtually impossible. Both would require the simultaneous, coordinated movement of a large number of independent particles, so are very unlikely.
- 20.5 Vaporization is the change of a liquid substance to a gas so  $\Delta S_{\text{vaporization}} = S_{\text{gas}} - S_{\text{liquid}}$ . Fusion is the change of a solid substance into a liquid so  $\Delta S_{\text{fusion}} = S_{\text{liquid}} - S_{\text{solid}}$ . Vaporization involves a greater change in volume than fusion. Thus, the transition from liquid to gas involves a greater entropy change than the transition from solid to liquid.
- 20.6 In an exothermic process, the *system* releases heat to its *surroundings*. The entropy of the surroundings increases because the temperature of the surroundings increases ( $\Delta S_{\text{surr}} > 0$ ). In an endothermic process, the system absorbs heat from the surroundings and the surroundings become cooler. Thus, the entropy of the surroundings decreases ( $\Delta S_{\text{surr}} < 0$ ). A chemical cold pack for injuries is an example of a spontaneous, endothermic chemical reaction as is the melting of ice cream at room temperature.
- 20.7 a) According to the third law the entropy is **zero**.  
b) Entropy will **increase** with temperature.  
c) The third law states that the entropy of a pure, perfectly crystalline element or compound may be taken as zero at zero Kelvin. Since the standard state temperature is 25°C and entropy increases with temperature,  $S^\circ$  must be greater than zero for an element in its standard state.  
d) Since entropy values have a reference point (0 entropy at 0 K), actual entropy values can be determined, not just entropy changes.
- 20.8 Plan: A spontaneous process is one that occurs by itself without a continuous input of energy.  
Solution:  
a) **Spontaneous**, evaporation occurs because a few of the liquid molecules have enough energy to break away from the intermolecular forces of the other liquid molecules and move spontaneously into the gas phase.

- b) **Spontaneous**, a lion spontaneously chases an antelope without added force. This assumes that the lion has not just eaten.
- c) **Spontaneous**, an unstable substance decays spontaneously to a more stable substance.
- 20.9 Plan: A spontaneous process is one that occurs by itself without a continuous input of energy.  
Solution:  
 a) **Spontaneous**, with a small amount of energy input, methane will continue to burn without additional energy (the reaction itself provides the necessary energy) until it is used up.  
 b) **Spontaneous**, the dissolved sugar molecules have more states they can occupy than the crystalline sugar, so the reaction proceeds in the direction of dissolution.  
 c) **Not spontaneous**, a cooked egg will not become raw again, no matter how long it sits or how many times it is mixed.
- 20.10 Plan: Particles with more freedom of motion have higher entropy. Therefore,  $S_{\text{gas}} > S_{\text{liquid}} > S_{\text{solid}}$ . If the products of the process have more entropy than the reactants,  $\Delta S_{\text{sys}}$  is positive. If the products of the process have less entropy than the reactants,  $\Delta S_{\text{sys}}$  is negative.  
Solution:  
 a)  $\Delta S_{\text{sys}}$  **positive**, melting is the change in state from solid to liquid. The solid state of a particular substance always has lower entropy than the same substance in the liquid state. Entropy increases during melting.  
 b)  $\Delta S_{\text{sys}}$  **negative**, the entropy of most salt solutions is greater than the entropy of the solvent and solute separately, so entropy decreases as a salt precipitates.  
 c)  $\Delta S_{\text{sys}}$  **negative**, dew forms by the condensation of water vapor to liquid. Entropy of a substance in the gaseous state is greater than its entropy in the liquid state. Entropy decreases during condensation.
- 20.11 Plan: Particles with more freedom of motion have higher entropy. Therefore,  $S_{\text{gas}} > S_{\text{liquid}} > S_{\text{solid}}$ . If the products of the process have more entropy than the reactants,  $\Delta S_{\text{sys}}$  is positive. If the products of the process have less entropy than the reactants,  $\Delta S_{\text{sys}}$  is negative.  
Solution:  
 a)  $\Delta S_{\text{sys}}$  **positive**, the process described is liquid alcohol becoming gaseous alcohol. The gas molecules have greater entropy than the liquid molecules.  
 b)  $\Delta S_{\text{sys}}$  **positive**, the process described is a change from solid to gas, an increase in possible energy states for the system.  
 c)  $\Delta S_{\text{sys}}$  **positive**, the perfume molecules have more possible locations in the larger volume of the room than inside the bottle. A system that has more possible arrangements has greater entropy.
- 20.12 Plan:  $\Delta S_{\text{sys}}$  is the entropy of the products – the entropy of the reactants. Use the fact that  $S_{\text{gas}} > S_{\text{liquid}} > S_{\text{solid}}$ ; also, the greater the number of particles of a particular phase of matter, the higher the entropy.  
Solution:  
 a)  $\Delta S_{\text{sys}}$  **negative**, reaction involves a gaseous reactant and no gaseous products, so entropy decreases. The number of particles also decreases, indicating a decrease in entropy.  
 b)  $\Delta S_{\text{sys}}$  **negative**, gaseous reactants form solid product and number of particles decreases, so entropy decreases.  
 c)  $\Delta S_{\text{sys}}$  **positive**, when a solid salt dissolves in water, entropy generally increases since the entropy of the aqueous mixture has higher entropy than the solid.
- 20.13 a)  $\Delta S_{\text{sys}}$  **negative**    b)  $\Delta S_{\text{sys}}$  **negative**    c)  $\Delta S_{\text{sys}}$  **negative**
- 20.14 Plan:  $\Delta S_{\text{sys}}$  is the entropy of the products – the entropy of the reactants. Use the fact that  $S_{\text{gas}} > S_{\text{liquid}} > S_{\text{solid}}$ ; also, the greater the number of particles of a particular phase of matter, the higher the entropy.  
Solution:  
 a)  $\Delta S_{\text{sys}}$  **positive**, the reaction produces gaseous  $\text{CO}_2$  molecules that have greater entropy than the physical states of the reactants.  
 b)  $\Delta S_{\text{sys}}$  **negative**, the reaction produces a net decrease in the number of gaseous molecules, so the system's entropy decreases.  
 c)  $\Delta S_{\text{sys}}$  **positive**, the reaction produces a gas from a solid.

- 20.15 a)  $\Delta S_{\text{sys}}$  **negative**   b)  $\Delta S_{\text{sys}}$  **positive**   c)  $\Delta S_{\text{sys}}$  **negative**
- 20.16 Plan: Particles with more freedom of motion have higher entropy. In general the entropy of gases is greater than that of liquids, and the entropy of liquids is greater than that of solids. Entropy increases with temperature. For substances in the same phase, entropy increases with atomic size and molecular complexity. If the entropy of the products is greater than that of the reactants,  $\Delta S$  is positive.  
Solution:  
 a)  $\Delta S_{\text{sys}}$  **positive**, decreasing the pressure increases the volume available to the gas molecules so entropy of the system increases.  
 b)  $\Delta S_{\text{sys}}$  **negative**, gaseous nitrogen molecules have greater entropy (more possible states) than dissolved nitrogen molecules.  
 c)  $\Delta S_{\text{sys}}$  **positive**, dissolved oxygen molecules have lower entropy than gaseous oxygen molecules.
- 20.17 a)  $\Delta S_{\text{sys}}$  **negative**   b)  $\Delta S_{\text{sys}}$  **positive**   c)  $\Delta S_{\text{sys}}$  **negative**
- 20.18 Plan: Particles with more freedom of motion have higher entropy. In general the entropy of gases is greater than that of liquids, and the entropy of liquids is greater than that of solids. Entropy increases with temperature. For substances in the same phase, entropy increases with atomic size and molecular complexity.  
Solution:  
 a) **Butane** has the greater molar entropy because it has two additional C–H bonds that can vibrate and has greater rotational freedom around its bond. The presence of the double bond in 2-butene restricts rotation.  
 b) **Xe(g)** has the greater molar entropy because entropy increases with atomic size.  
 c) **CH<sub>4</sub>(g)** has the greater molar entropy because gases in general have greater entropy than liquids.
- 20.19 Plan: Particles with more freedom of motion have higher entropy. In general the entropy of gases is greater than that of liquids, and the entropy of liquids is greater than that of solids. Entropy increases with temperature. For substances in the same phase, entropy increases with atomic size and molecular complexity.  
Solution:  
 a) Ethanol, **C<sub>2</sub>H<sub>5</sub>OH(l)**, is a more complex molecule than methanol, CH<sub>3</sub>OH, and has the greater molar entropy.  
 b) When a salt dissolves, there is an increase in the number of possible states for the ions. Thus, **KClO<sub>3</sub>(aq)** has the greater molar entropy.  
 c) **K(s)** has greater molar entropy because K(s) has greater mass than Na(s).
- 20.20 Plan: Particles with more freedom of motion have higher entropy. In general the entropy of gases is greater than that of liquids, and the entropy of liquids is greater than that of solids. Entropy increases with temperature. For substances in the same phase, entropy increases with atomic size and molecular complexity.  
Solution:  
 a) **Diamond < graphite < charcoal**. Diamond has an ordered, three-dimensional crystalline shape, followed by graphite with an ordered two-dimensional structure, followed by the amorphous (disordered) structure of charcoal.  
 b) **Ice < liquid water < water vapor**. Entropy increases as a substance changes from solid to liquid to gas.  
 c) **O atoms < O<sub>2</sub> < O<sub>3</sub>**. Entropy increases with molecular complexity because there are more modes of movement (e.g., bond vibration) available to the complex molecules.
- 20.21 a) **Ribose < glucose < sucrose**; entropy increases with molecular complexity.  
 b) **CaCO<sub>3</sub>(s) < (CaO(s) + CO<sub>2</sub>(g)) < (Ca(s) + C(s) + 3/2O<sub>2</sub>(g))**; entropy increases with moles of gas particles.  
 c) **SF<sub>4</sub>(g) < SF<sub>6</sub>(g) < S<sub>2</sub>F<sub>10</sub>(g)**; entropy increases with molecular complexity.
- 20.22 Plan: Particles with more freedom of motion have higher entropy. In general the entropy of gases is greater than that of liquids, and the entropy of liquids is greater than that of solids. Entropy increases with temperature. For substances in the same phase, entropy increases with atomic size and molecular complexity.  
Solution:  
 a) **ClO<sub>4</sub><sup>-</sup>(aq) > ClO<sub>3</sub><sup>-</sup>(aq) > ClO<sub>2</sub><sup>-</sup>(aq)**. The decreasing order of molar entropy follows the order of decreasing molecular complexity.

- b)  $\text{NO}_2(\text{g}) > \text{NO}(\text{g}) > \text{N}_2(\text{g})$ .  $\text{N}_2$  has lower molar entropy than  $\text{NO}$  because  $\text{N}_2$  consists of two of the same atoms while  $\text{NO}$  consists of two different atoms.  $\text{NO}_2$  has greater molar entropy than  $\text{NO}$  because  $\text{NO}_2$  consists of three atoms while  $\text{NO}$  consists of only two.
- c)  $\text{Fe}_3\text{O}_4(\text{s}) > \text{Fe}_2\text{O}_3(\text{s}) > \text{Al}_2\text{O}_3(\text{s})$ .  $\text{Fe}_3\text{O}_4$  has greater molar entropy than  $\text{Fe}_2\text{O}_3$  because  $\text{Fe}_3\text{O}_4$  is more complex and more massive.  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  contain the same number of atoms but  $\text{Fe}_2\text{O}_3$  has greater molar entropy because iron atoms are more massive than aluminum atoms.
- 20.23 a)  $\text{Ba}(\text{s}) > \text{Ca}(\text{s}) > \text{Mg}(\text{s})$ ; entropy decreases with lower mass.  
 b)  $\text{C}_6\text{H}_{14} > \text{C}_6\text{H}_{12} > \text{C}_6\text{H}_6$ ; entropy decreases with lower molecular complexity and lower molecular flexibility.  
 c)  $\text{PF}_2\text{Cl}_3(\text{g}) > \text{PF}_5(\text{g}) > \text{PF}_3(\text{g})$ ; entropy decreases with lower molecular complexity.
- 20.24 a)  $\text{X}_2(\text{g}) + 3\text{Y}_2(\text{g}) \rightarrow 2\text{XY}_3(\text{g})$   
 b)  $\Delta S < 0$  since there are fewer moles of gas in the products than in the reactants.  
 c)  $\text{XY}_3$  is the most complex molecule and thus will have the highest molar entropy.
- 20.25 Entropy, like enthalpy, is a state function, which is a property of a system determined by the state of the system and not in the process by which it achieved that state.
- 20.26 A system at equilibrium does not spontaneously produce more products or more reactants. For either reaction direction, the entropy change of the system is exactly offset by the entropy change of the surroundings. Therefore, for system at equilibrium,  $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0$ . However, for a system moving to equilibrium,  $\Delta S_{\text{univ}} > 0$ , because the second law states that for any spontaneous process, the entropy of the universe increases.
- 20.27 Plan: Since entropy is a state function, the entropy changes can be found by summing the entropies of the products and subtracting the sum of the entropies of the reactants.  
Solution:  

$$\Delta S_{\text{rxn}}^\circ = [(2 \text{ mol HClO})(S^\circ \text{ of HClO})] - [(1 \text{ mol H}_2\text{O})(S^\circ \text{ of H}_2\text{O}) + (1 \text{ mol Cl}_2\text{O})(S^\circ \text{ of Cl}_2\text{O})]$$
 Rearranging this expression to solve for  $S^\circ$  of  $\text{Cl}_2\text{O}$  gives:  $S^\circ \text{ of Cl}_2\text{O} = 2(S^\circ \text{ of HClO}) - S^\circ \text{ of H}_2\text{O} - \Delta S_{\text{rxn}}^\circ$
- 20.28 Plan: To calculate the standard entropy change, use the relationship  $\Delta S_{\text{rxn}}^\circ = \sum m S_{\text{products}}^\circ - \sum n S_{\text{reactants}}^\circ$ .  
 To predict the sign of entropy recall that in general  $S_{\text{gas}} > S_{\text{liquid}} > S_{\text{solid}}$ , and entropy increases as the number of particles of a particular phase of matter increases, and with increasing atomic size and molecular complexity.  
Solution:  
 a) Prediction:  $\Delta S^\circ$  **negative** because number of moles of ( $\Delta n$ ) gas decreases.  

$$\Delta S^\circ = [(1 \text{ mol N}_2\text{O})(S^\circ \text{ of N}_2\text{O}) + (1 \text{ mol NO}_2)(S^\circ \text{ of NO}_2)] - [(3 \text{ mol NO})(S^\circ \text{ of NO})]$$

$$\Delta S^\circ = [(1 \text{ mol})(219.7 \text{ J/mol}\cdot\text{K}) + (1 \text{ mol})(239.9 \text{ J/mol}\cdot\text{K})] - [(3 \text{ mol})(210.65 \text{ J/mol}\cdot\text{K})]$$

$$\Delta S^\circ = -172.35 = \mathbf{-172.4 \text{ J/K}}$$
  
 b) Prediction: Sign difficult to predict because  $\Delta n = 0$ , but **possibly  $\Delta S^\circ$  positive** because water vapor has greater complexity than  $\text{H}_2$  gas.  

$$\Delta S^\circ = [(2 \text{ mol Fe})(S^\circ \text{ of Fe}) + (3 \text{ mol H}_2\text{O})(S^\circ \text{ of H}_2\text{O})] - [(3 \text{ mol H}_2)(S^\circ \text{ of H}_2) + (1 \text{ mol Fe}_2\text{O}_3)(S^\circ \text{ of Fe}_2\text{O}_3)]$$

$$\Delta S^\circ = [(2 \text{ mol})(27.3 \text{ J/mol}\cdot\text{K}) + (3 \text{ mol})(188.72 \text{ J/mol}\cdot\text{K})] - [(3 \text{ mol})(130.6 \text{ J/mol}\cdot\text{K}) + (1 \text{ mol})(87.400 \text{ J/mol}\cdot\text{K})]$$

$$\Delta S^\circ = 141.56 = \mathbf{141.6 \text{ J/K}}$$
  
 c) Prediction:  $\Delta S^\circ$  **negative** because a gaseous reactant forms a solid product and also because the number of moles of gas ( $\Delta n$ ) decreases.  

$$\Delta S^\circ = [(1 \text{ mol P}_4\text{O}_{10})(S^\circ \text{ of P}_4\text{O}_{10})] - [(1 \text{ mol P}_4)(S^\circ \text{ of P}_4) + (5 \text{ mol O}_2)(S^\circ \text{ of O})]$$

$$\Delta S^\circ = [(1 \text{ mol})(229 \text{ J/mol}\cdot\text{K})] - [(1 \text{ mol})(41.1 \text{ J/mol}\cdot\text{K}) + (5 \text{ mol})(205.0 \text{ J/mol}\cdot\text{K})]$$

$$\Delta S^\circ = -837.1 = \mathbf{-837 \text{ J/K}}$$
- 20.29 a)  $3\text{NO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow 2\text{HNO}_3(\text{l}) + \text{NO}(\text{g})$   $\Delta S^\circ$  **negative**  

$$\Delta S^\circ = [(2 \text{ mol HNO}_3)(S^\circ \text{ of HNO}_3) + (1 \text{ mol NO})(S^\circ \text{ of NO})]$$

$$- [(3 \text{ mol NO}_2)(S^\circ \text{ of NO}_2) + (1 \text{ mol H}_2\text{O})(S^\circ \text{ of H}_2\text{O})]$$

$$\Delta S^\circ = [(2 \text{ mol})(155.6 \text{ J/K}\cdot\text{mol}) + (1 \text{ mol})(210.65 \text{ J/K}\cdot\text{mol})] \\ - [(3 \text{ mol})(239.9 \text{ J/K}\cdot\text{mol}) + (1 \text{ mol})(69.940 \text{ J/K}\cdot\text{mol})]$$

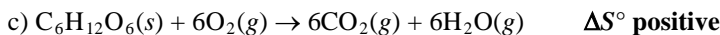
$$\Delta S^\circ = -267.79 = \mathbf{-267.8 \text{ J/K}}$$



$$\Delta S^\circ = [(2 \text{ mol NF}_3)(S^\circ \text{ of NF}_3)] - [(1 \text{ mol N}_2)(S^\circ \text{ of N}_2) + (3 \text{ mol F}_2)(S^\circ \text{ of F}_2)]$$

$$\Delta S^\circ = [(2 \text{ mol})(260.6 \text{ J/K}\cdot\text{mol})] - [(1 \text{ mol})(191.5 \text{ J/K}\cdot\text{mol}) + (3 \text{ mol})(202.7 \text{ J/K}\cdot\text{mol})]$$

$$\Delta S^\circ = \mathbf{-278.4 \text{ J/K}}$$



$$\Delta S^\circ = [(6 \text{ mol CO}_2)(S^\circ \text{ of CO}_2) + (6 \text{ mol H}_2\text{O})(S^\circ \text{ of H}_2\text{O})]$$

$$- [(1 \text{ mol C}_6\text{H}_{12}\text{O}_6)(S^\circ \text{ of C}_6\text{H}_{12}\text{O}_6) + (6 \text{ mol O}_2)(S^\circ \text{ of O}_2)]$$

$$\Delta S^\circ = [(6 \text{ mol})(213.7 \text{ J/K}\cdot\text{mol}) + (6 \text{ mol H}_2\text{O})(188.72 \text{ J/K}\cdot\text{mol})]$$

$$- [(1 \text{ mol})(212.1 \text{ J/K}\cdot\text{mol}) + (6 \text{ mol})(205.0 \text{ J/K}\cdot\text{mol})]$$

$$\Delta S^\circ = 972.42 = \mathbf{972.4 \text{ J/K}}$$

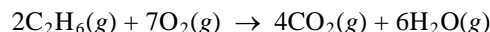
20.30 **Plan:** Write the balanced equation. To calculate the standard entropy change, use the relationship

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

To predict the sign of entropy recall that in general  $S_{\text{gas}} > S_{\text{liquid}} > S_{\text{solid}}$ , entropy increases as the number of particles of a particular phase of matter increases, and entropy increases with increasing atomic size and molecular complexity.

**Solution:**

The balanced combustion reaction is:



$$\Delta S^\circ = [(4 \text{ mol CO}_2)(S^\circ \text{ of CO}_2) + (6 \text{ mol H}_2\text{O})(S^\circ \text{ of H}_2\text{O})] - [(2 \text{ mol C}_2\text{H}_6)(S^\circ \text{ of C}_2\text{H}_6) + (7 \text{ mol O}_2)(S^\circ \text{ of O}_2)]$$

$$\Delta S^\circ = [(4 \text{ mol})(213.7 \text{ J/mol}\cdot\text{K}) + (6 \text{ mol})(188.72 \text{ J/mol}\cdot\text{K})] - [(2 \text{ mol})(229.5 \text{ J/mol}\cdot\text{K}) + (7 \text{ mol})(205.0 \text{ J/mol}\cdot\text{K})]$$

$$\Delta S^\circ = 93.12 = \mathbf{93.1 \text{ J/K}}$$

The entropy value is not per mole of  $\text{C}_2\text{H}_6$  but per two moles. Divide the calculated value by two to obtain entropy per mole of  $\text{C}_2\text{H}_6$ .

**Yes**, the positive sign of  $\Delta S^\circ$  is expected because there is a net increase in the number of gas molecules from nine moles as reactants to ten moles as products.

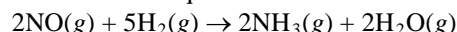
20.31 **Plan:** Write the balanced equation. To calculate the standard entropy change, use the relationship

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

To predict the sign of entropy recall that in general  $S_{\text{gas}} > S_{\text{liquid}} > S_{\text{solid}}$ , entropy increases as the number of particles of a particular phase of matter increases, and entropy increases with increasing atomic size and molecular complexity.

**Solution:**

The balanced chemical equation for the described reaction is:



Because the number of moles of gas decreases, i.e.,  $\Delta n = 4 - 7 = -3$ , the entropy is expected to decrease.

$$\Delta S^\circ = [(2 \text{ mol NH}_3)(S^\circ \text{ of NH}_3) + (2 \text{ mol H}_2\text{O})(S^\circ \text{ of H}_2\text{O})] - [(2 \text{ mol NO})(S^\circ \text{ of NO}) + (5 \text{ mol H}_2)(S^\circ \text{ of H}_2)]$$

$$\Delta S^\circ = [(2 \text{ mol})(193 \text{ J/mol}\cdot\text{K}) + (2 \text{ mol})(188.72 \text{ J/mol}\cdot\text{K})] - [(2 \text{ mol})(210.65 \text{ J/mol}\cdot\text{K}) + (5 \text{ mol})(130.6 \text{ J/mol}\cdot\text{K})]$$

$$\Delta S^\circ = -310.86 = \mathbf{-311 \text{ J/K}}$$

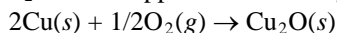
**Yes**, the calculated entropy matches the predicted decrease.

20.32 **Plan:** Write the balanced equation. To calculate the standard entropy change, use the relationship

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

**Solution:**

The reaction for forming  $\text{Cu}_2\text{O}$  from copper metal and oxygen gas is



$$\Delta S^\circ = [(1 \text{ mol Cu}_2\text{O})(S^\circ \text{ of Cu}_2\text{O})] - [(2 \text{ mol Cu})(S^\circ \text{ of Cu}) + (1/2 \text{ mol O}_2)(S^\circ \text{ of O}_2)]$$

$$\Delta S^\circ = [(1 \text{ mol})(93.1 \text{ J/mol}\cdot\text{K})] - [(2 \text{ mol})(33.1 \text{ J/mol}\cdot\text{K}) + (1/2 \text{ mol})(205.0 \text{ J/mol}\cdot\text{K})]$$

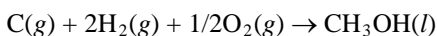
$$\Delta S^\circ = \mathbf{-75.6 \text{ J/K}}$$

20.33 Plan: Write the balanced equation. To calculate the standard entropy change, use the relationship

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

Solution:

One mole of methanol is formed from its elements in their standard states according to the following equation:



$$\Delta S^{\circ} = [(1 \text{ mol CH}_3\text{OH})(S^{\circ} \text{ of CH}_3\text{OH})] - [(1 \text{ mol C})(S^{\circ} \text{ of C}) + (2 \text{ mol H}_2)(S^{\circ} \text{ of H}_2) + (1/2 \text{ mol O}_2)(S^{\circ} \text{ of O}_2)]$$

$$\Delta S^{\circ} = [(1 \text{ mol})(127 \text{ J/mol}\cdot\text{K})] - [(1 \text{ mol})(5.686 \text{ J/mol}\cdot\text{K}) + (2 \text{ mol})(130.6 \text{ J/mol}\cdot\text{K}) + (1/2 \text{ mol})(205.0 \text{ J/mol}\cdot\text{K})]$$

$$\Delta S^{\circ} = -242.386 = \mathbf{-242 \text{ J/K}}$$

20.34  $\text{SO}_2(g) + \text{Ca}(\text{OH})_2(s) \rightarrow \text{CaSO}_3(s) + \text{H}_2\text{O}(l)$

$$\Delta S^{\circ} = [(1 \text{ mol CaSO}_3)(S^{\circ} \text{ of CaSO}_3) + (1 \text{ mol H}_2\text{O})(S^{\circ} \text{ of H}_2\text{O})]$$

$$- [(1 \text{ mol SO}_2)(S^{\circ} \text{ of SO}_2) + (1 \text{ mol Ca}(\text{OH})_2)(S^{\circ} \text{ of Ca}(\text{OH})_2)]$$

$$\Delta S^{\circ} = [1 \text{ mol})(101.4 \text{ J/K}\cdot\text{mol}) + (1 \text{ mol})(69.940 \text{ J/K}\cdot\text{mol})] - [(1 \text{ mol})(248.1 \text{ J/K}\cdot\text{mol}) + (1 \text{ mol})(83.39 \text{ J/K}\cdot\text{mol})]$$

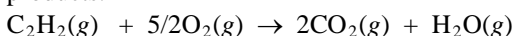
$$\Delta S^{\circ} = -160.15 = \mathbf{-160.2 \text{ J/K}}$$

20.35 Plan: Write the balanced equation. To calculate the standard entropy change, use the relationship

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

Solution:

Complete combustion of a hydrocarbon includes oxygen as a reactant and carbon dioxide and water as the products.



$\Delta S^{\circ} = [(2 \text{ mol CO}_2)(S^{\circ} \text{ of CO}_2) + (1 \text{ mol H}_2\text{O})(S^{\circ} \text{ of H}_2\text{O})] - [(1 \text{ mol C}_2\text{H}_2)(S^{\circ} \text{ of C}_2\text{H}_2) + (5/2 \text{ mol O}_2)(S^{\circ} \text{ of O}_2)]$

$$\Delta S^{\circ} = [(2 \text{ mol})(213.7 \text{ J/mol}\cdot\text{K}) + (1 \text{ mol})(188.72 \text{ J/mol}\cdot\text{K})]$$

$$- [(1 \text{ mol})(200.85 \text{ J/mol}\cdot\text{K}) + (5/2 \text{ mol})(205.0 \text{ J/mol}\cdot\text{K})]$$

$$\Delta S^{\circ} = -97.23 = \mathbf{-97.2 \text{ J/K}}$$

20.36 Reaction spontaneity may now be predicted from the value of only one variable ( $\Delta G_{\text{sys}}$ ) rather than two ( $\Delta S_{\text{sys}}$  and  $\Delta S_{\text{surr}}$ ).

20.37 A spontaneous process has  $\Delta S_{\text{univ}} > 0$ . Since the Kelvin temperature is always positive,  $\Delta G_{\text{sys}}$  must be negative ( $\Delta G_{\text{sys}} < 0$ ) for a spontaneous process.

20.38 a)  $\Delta G = \Delta H - T\Delta S$ . Since  $T\Delta S > \Delta H$  for an endothermic reaction to be spontaneous, the reaction is more likely to be spontaneous at **higher temperatures**.

b) The change depicted is the phase change of a solid converting to a gas (sublimation).

1. Energy must be absorbed to overcome intermolecular forces to convert a substance in the solid phase to the gas phase. This is an endothermic process and  **$\Delta H$  is positive**.

2. Since gases have higher entropy values than solids, the process results in an increase in entropy and  **$\Delta S$  is positive**.

3. This is an endothermic process so the surroundings lose energy to the system.  **$\Delta S_{\text{surr}}$  is negative**.

4.  $\Delta G = \Delta H - T\Delta S$ . Both  $\Delta H$  and  $\Delta S$  are positive. At low temperature, the  $\Delta H$  term will predominate and  $\Delta G$  will be positive; at high temperatures, the  $T\Delta S$  term will predominate and  $\Delta G$  will be negative.

20.39  **$\Delta H^{\circ}$  is positive and  $\Delta S^{\circ}$  is positive**. The reaction is endothermic ( $\Delta H^{\circ} > 0$ ) and requires a lot of heat from its surroundings to be spontaneous. The removal of heat from the surroundings results in  $\Delta S^{\circ} < 0$ . The only way an endothermic reaction can proceed spontaneously is if  $\Delta S^{\circ} > 0$ , effectively offsetting the decrease in surroundings entropy. In summary, the values of  $\Delta H^{\circ}$  and  $\Delta S^{\circ}$  are both positive for this reaction. Melting is an example.

20.40 Plan:  $\Delta G^\circ$  can be calculated with the relationship  $\sum m \Delta G_f^\circ(\text{products}) - \sum n \Delta G_f^\circ(\text{reactants})$ .

Solution:

$$\text{a) } \Delta G^\circ = [(2 \text{ mol MgO})(\Delta G_f^\circ \text{ of MgO})] - [(2 \text{ mol Mg})(\Delta G_f^\circ \text{ of Mg}) + (1 \text{ mol O}_2)(\Delta G_f^\circ \text{ of O}_2)]$$

Both Mg(s) and O<sub>2</sub>(g) are the standard-state forms of their respective elements, so their  $\Delta G_f^\circ$  values are zero.

$$\Delta G^\circ = [(2 \text{ mol})(-569.0 \text{ kJ/mol})] - [(2 \text{ mol})(0) + (1 \text{ mol})(0)] = \mathbf{-1138.0 \text{ kJ}}$$

$$\text{b) } \Delta G^\circ = [(2 \text{ mol CO}_2)(\Delta G_f^\circ \text{ of CO}_2) + (4 \text{ mol H}_2\text{O})(\Delta G_f^\circ \text{ of H}_2\text{O})]$$

$$- [(2 \text{ mol CH}_3\text{OH})(\Delta G_f^\circ \text{ of CH}_3\text{OH}) + (3 \text{ mol O}_2)(\Delta G_f^\circ \text{ of O}_2)]$$

$$\Delta G^\circ = [(2 \text{ mol})(-394.4 \text{ kJ/mol}) + (4 \text{ mol})(-228.60 \text{ kJ/mol})] - [(2 \text{ mol})(-161.9 \text{ kJ/mol}) + (3 \text{ mol})(0)]$$

$$\Delta G^\circ = \mathbf{-1379.4 \text{ kJ}}$$

$$\text{c) } \Delta G^\circ = [(1 \text{ mol BaCO}_3)(\Delta G_f^\circ \text{ of BaCO}_3)] - [(1 \text{ mol BaO})(\Delta G_f^\circ \text{ of BaO}) + (1 \text{ mol CO}_2)(\Delta G_f^\circ \text{ of CO}_2)]$$

$$\Delta G^\circ = [(1 \text{ mol})(-1139 \text{ kJ/mol})] - [(1 \text{ mol})(-520.4 \text{ kJ/mol}) + (1 \text{ mol})(-394.4 \text{ kJ/mol})]$$

$$\Delta G^\circ = -224.2 = \mathbf{-224 \text{ kJ}}$$

20.41 a)  $\text{H}_2(\text{g}) + \text{I}_2(\text{s}) \rightarrow 2\text{HI}(\text{g})$

$$\Delta G^\circ = [(2 \text{ mol HI})(\Delta G_f^\circ \text{ of HI})] - [(1 \text{ mol H}_2)(\Delta G_f^\circ \text{ of H}_2) + (1 \text{ mol I}_2)(\Delta G_f^\circ \text{ of I}_2)]$$

$$\Delta G^\circ = [(2 \text{ mol})(1.3 \text{ kJ/mol})] - [(1 \text{ mol})(0 \text{ kJ/mol}) + (1 \text{ mol})(0 \text{ kJ/mol})]$$

$$\Delta G^\circ = \mathbf{2.6 \text{ kJ}}$$

b)  $\text{MnO}_2(\text{s}) + 2\text{CO}(\text{g}) \rightarrow \text{Mn}(\text{s}) + 2\text{CO}_2(\text{g})$

$$\Delta G^\circ = [(1 \text{ mol Mn})(\Delta G_f^\circ \text{ of Mn}) + (2 \text{ mol CO}_2)(\Delta G_f^\circ \text{ of CO}_2)]$$

$$- [(1 \text{ mol MnO}_2)(\Delta G_f^\circ \text{ of MnO}_2) + (2 \text{ mol CO})(\Delta G_f^\circ \text{ of CO})]$$

$$\Delta G^\circ = [(1 \text{ mol})(0 \text{ kJ/mol}) + (2 \text{ mol})(-394.4 \text{ kJ/mol})]$$

$$- [(1 \text{ mol})(-466.1 \text{ kJ/mol}) + (2 \text{ mol})(-137.2 \text{ kJ/mol})]$$

$$\Delta G^\circ = \mathbf{-48.3 \text{ kJ}}$$

c)  $\text{NH}_4\text{Cl}(\text{s}) \rightarrow \text{NH}_3(\text{g}) + \text{HCl}(\text{g})$

$$\Delta G^\circ = [(1 \text{ mol NH}_3)(\Delta G_f^\circ \text{ of NH}_3) + (1 \text{ mol HCl})(\Delta G_f^\circ \text{ of HCl})] - [(1 \text{ mol NH}_4\text{Cl})(\Delta G_f^\circ \text{ of NH}_4\text{Cl})]$$

$$\Delta G^\circ = [(1 \text{ mol})(-16 \text{ kJ/mol}) + (1 \text{ mol})(-95.30 \text{ kJ/mol})] - [1 \text{ mol})(-203.0 \text{ kJ/mol})]$$

$$\Delta G^\circ = 91.7 = \mathbf{92 \text{ kJ}}$$

20.42 Plan:  $\Delta H_{\text{rxn}}^\circ$  can be calculated from the individual  $\Delta H_f^\circ$  values of the reactants and products by using the relationship  $\Delta H_{\text{rxn}}^\circ = \sum m \Delta H_f^\circ(\text{products}) - \sum n \Delta H_f^\circ(\text{reactants})$ .  $\Delta S_{\text{rxn}}^\circ$  can be calculated from the individual  $S^\circ$  values of the reactants and products by using the relationship  $\Delta S_{\text{rxn}}^\circ = \sum m S_{\text{products}}^\circ - \sum n S_{\text{reactants}}^\circ$ . Once  $\Delta H_{\text{rxn}}^\circ$  and  $\Delta S_{\text{rxn}}^\circ$  are known,  $\Delta G^\circ$  can be calculated with the relationship  $\Delta G_{\text{rxn}}^\circ = \Delta H_{\text{rxn}}^\circ - T\Delta S_{\text{rxn}}^\circ$ .  $\Delta S_{\text{rxn}}^\circ$  values in J/K must be converted to units of kJ/K to match the units of  $\Delta H_{\text{rxn}}^\circ$ .

Solution:

$$\text{a) } \Delta H_{\text{rxn}}^\circ = [(2 \text{ mol MgO})(\Delta H_f^\circ \text{ of MgO})] - [(2 \text{ mol Mg})(\Delta H_f^\circ \text{ of Mg}) + (1 \text{ mol O}_2)(\Delta H_f^\circ \text{ of O}_2)]$$

$$\Delta H_{\text{rxn}}^\circ = [(2 \text{ mol})(-601.2 \text{ kJ/mol})] - [(2 \text{ mol})(0 \text{ kJ/mol}) + (1 \text{ mol})(0 \text{ kJ/mol})]$$

$$\Delta H_{\text{rxn}}^\circ = -1202.4 \text{ kJ}$$

$$\Delta S_{\text{rxn}}^\circ = [(2 \text{ mol MgO})(S^\circ \text{ of MgO})] - [(2 \text{ mol Mg})(S^\circ \text{ of Mg}) + (1 \text{ mol O}_2)(S^\circ \text{ of O}_2)]$$

$$\Delta S_{\text{rxn}}^\circ = [(2 \text{ mol})(26.9 \text{ J/mol}\cdot\text{K})] - [(2 \text{ mol})(32.69 \text{ J/mol}\cdot\text{K}) + (1 \text{ mol})(205.0 \text{ J/mol}\cdot\text{K})]$$

$$\Delta S_{\text{rxn}}^\circ = -216.58 \text{ J/K}$$

$$\Delta G_{\text{rxn}}^\circ = \Delta H_{\text{rxn}}^\circ - T\Delta S_{\text{rxn}}^\circ = -1202.4 \text{ kJ} - [(298 \text{ K})(-216.58 \text{ J/K})(1 \text{ kJ}/10^3 \text{ J})] = -1137.859 = \mathbf{-1138 \text{ kJ}}$$

$$\begin{aligned} \text{b) } \Delta H_{\text{rxn}}^{\circ} &= [(2 \text{ mol CO}_2)(\Delta H_{\text{f}}^{\circ} \text{ of CO}_2) + (4 \text{ mol H}_2\text{O})(\Delta H_{\text{f}}^{\circ} \text{ of H}_2\text{O})] \\ &\quad - [(2 \text{ mol CH}_3\text{OH})(\Delta H_{\text{f}}^{\circ} \text{ of CH}_3\text{OH}) + (3 \text{ mol O}_2)(\Delta H_{\text{f}}^{\circ} \text{ of O}_2)] \\ \Delta H_{\text{rxn}}^{\circ} &= [(2 \text{ mol})(-393.5 \text{ kJ/mol}) + (4 \text{ mol})(-241.826 \text{ kJ/mol})] - [(2 \text{ mol})(-201.2 \text{ kJ/mol}) + (3 \text{ mol})(0 \text{ kJ/mol})] \\ \Delta H_{\text{rxn}}^{\circ} &= -1351.904 \text{ kJ} \\ \Delta S_{\text{rxn}}^{\circ} &= [(2 \text{ mol CO}_2)(S^{\circ} \text{ of CO}_2) + (4 \text{ mol H}_2\text{O})(S^{\circ} \text{ of H}_2\text{O})] \\ &\quad - [(2 \text{ mol CH}_3\text{OH})(S^{\circ} \text{ of CH}_3\text{OH}) + (3 \text{ mol O}_2)(S^{\circ} \text{ of O}_2)] \\ \Delta S_{\text{rxn}}^{\circ} &= [(2 \text{ mol})(213.7 \text{ J/mol}\cdot\text{K}) + (4 \text{ mol})(188.72 \text{ J/mol}\cdot\text{K})] \\ &\quad - [(2 \text{ mol})(238 \text{ J/mol}\cdot\text{K}) + (3 \text{ mol})(205.0 \text{ J/mol}\cdot\text{K})] = 91.28 \text{ J/K} \end{aligned}$$

$$\Delta G_{\text{rxn}}^{\circ} = \Delta H_{\text{rxn}}^{\circ} - T\Delta S_{\text{rxn}}^{\circ} = -1351.904 \text{ kJ} - [(298 \text{ K})(91.28 \text{ J/K})(1 \text{ kJ}/10^3 \text{ J})] = -1379.105 = \mathbf{-1379 \text{ kJ}}$$

$$\begin{aligned} \text{c) } \Delta H_{\text{rxn}}^{\circ} &= [(1 \text{ mol BaCO}_3)(\Delta H_{\text{f}}^{\circ} \text{ of BaCO}_3)] - [(1 \text{ mol BaO})(\Delta H_{\text{f}}^{\circ} \text{ of BaO}) + (1 \text{ mol CO}_2)(\Delta H_{\text{f}}^{\circ} \text{ of CO}_2)] \\ \Delta H_{\text{rxn}}^{\circ} &= [(1 \text{ mol})(-1219 \text{ kJ/mol})] - [(1 \text{ mol})(-548.1 \text{ kJ/mol}) + (1 \text{ mol})(-393.5 \text{ kJ/mol})] \\ \Delta H_{\text{rxn}}^{\circ} &= -277.4 \text{ kJ} \\ \Delta S_{\text{rxn}}^{\circ} &= [(1 \text{ mol BaCO}_3)(S^{\circ} \text{ of BaCO}_3)] - [(1 \text{ mol BaO})(S^{\circ} \text{ of BaO}) + (1 \text{ mol CO}_2)(S^{\circ} \text{ of CO}_2)] \\ \Delta S_{\text{rxn}}^{\circ} &= [(1 \text{ mol})(112 \text{ J/mol}\cdot\text{K})] - [(1 \text{ mol})(72.07 \text{ J/mol}\cdot\text{K}) + (1 \text{ mol})(213.7 \text{ J/mol}\cdot\text{K})] \\ \Delta S_{\text{rxn}}^{\circ} &= -173.77 \text{ J/K} \\ \Delta G_{\text{rxn}}^{\circ} &= \Delta H_{\text{rxn}}^{\circ} - T\Delta S_{\text{rxn}}^{\circ} = -277.4 \text{ kJ} - [(298 \text{ K})(-173.77 \text{ J/K})(1 \text{ kJ}/10^3 \text{ J})] = -225.6265 = \mathbf{-226 \text{ kJ}} \end{aligned}$$

$$\begin{aligned} 20.43 \text{ a) } \Delta H_{\text{rxn}}^{\circ} &= [(2 \text{ mol HI})(25.9 \text{ kJ/mol})] - [(1 \text{ mol H}_2)(0 \text{ kJ/mol}) + (1 \text{ mol I}_2)(0 \text{ kJ/mol})] \\ \Delta H_{\text{rxn}}^{\circ} &= 51.8 \text{ kJ} \\ \Delta S_{\text{rxn}}^{\circ} &= [(2 \text{ mol HI})(206.33 \text{ J/K}\cdot\text{mol})] - [(1 \text{ mol H}_2)(130.6 \text{ J/K}\cdot\text{mol}) + (1 \text{ mol I}_2)(116.14 \text{ J/K}\cdot\text{mol})] \\ \Delta S_{\text{rxn}}^{\circ} &= 165.92 \text{ J/K} \\ \Delta G_{\text{rxn}}^{\circ} &= \Delta H_{\text{rxn}}^{\circ} - T\Delta S_{\text{rxn}}^{\circ} = 51.8 \text{ kJ} - [(298 \text{ K})(165.92 \text{ J/K})(1 \text{ kJ}/10^3 \text{ J})] = 2.3558 = \mathbf{2.4 \text{ kJ}} \end{aligned}$$

$$\begin{aligned} \text{b) } \Delta H_{\text{rxn}}^{\circ} &= [(1 \text{ mol Mn})(0 \text{ kJ/mol}) + (2 \text{ mol CO}_2)(-393.5 \text{ kJ/mol})] \\ &\quad - [(1 \text{ mol MnO}_2)(-520.9 \text{ kJ/mol}) + (2 \text{ mol CO})(-110.5 \text{ kJ/mol})] \\ \Delta H_{\text{rxn}}^{\circ} &= -45.1 \text{ kJ} \\ \Delta S_{\text{rxn}}^{\circ} &= [(1 \text{ mol Mn})(31.8 \text{ J/K}\cdot\text{mol}) + (2 \text{ mol CO}_2)(213.7 \text{ J/K}\cdot\text{mol})] \\ &\quad - [(1 \text{ mol MnO}_2)(53.1 \text{ J/K}\cdot\text{mol}) + (2 \text{ mol CO})(197.5 \text{ J/K}\cdot\text{mol})] \\ \Delta S_{\text{rxn}}^{\circ} &= 11.1 \text{ J/K} \\ \Delta G_{\text{rxn}}^{\circ} &= \Delta H_{\text{rxn}}^{\circ} - T\Delta S_{\text{rxn}}^{\circ} = -45.1 \text{ kJ} - [(298 \text{ K})(11.1 \text{ J/K})(1 \text{ kJ}/10^3 \text{ J})] = -48.4078 = \mathbf{-48.4 \text{ kJ}} \\ \text{c) } \Delta H_{\text{rxn}}^{\circ} &= [(1 \text{ mol NH}_3)(-45.9 \text{ kJ/mol}) + (1 \text{ mol HCl})(-92.3 \text{ kJ/mol})] - [(1 \text{ mol NH}_4\text{Cl})(-314.4 \text{ kJ/mol})] \\ \Delta H_{\text{rxn}}^{\circ} &= 176.2 \text{ kJ} \\ \Delta S_{\text{rxn}}^{\circ} &= [(1 \text{ mol NH}_3)(193 \text{ J/K}\cdot\text{mol}) + (1 \text{ mol HCl})(186.79 \text{ J/K}\cdot\text{mol})] - [(1 \text{ mol NH}_4\text{Cl})(94.6 \text{ J/K}\cdot\text{mol})] \\ \Delta S_{\text{rxn}}^{\circ} &= 285.19 \text{ J/K} \\ \Delta G_{\text{rxn}}^{\circ} &= \Delta H_{\text{rxn}}^{\circ} - T\Delta S_{\text{rxn}}^{\circ} = 176.2 \text{ kJ} - [(298 \text{ K})(285.19 \text{ J/K})(1 \text{ kJ}/10^3 \text{ J})] = 91.213 = \mathbf{91.2 \text{ kJ}} \end{aligned}$$

20.44 Plan:  $\Delta G_{\text{rxn}}^{\circ}$  can be calculated with the relationship  $\sum m \Delta G_{\text{f}}^{\circ}(\text{products}) - \sum n \Delta G_{\text{f}}^{\circ}(\text{reactants})$ . Alternatively,  $\Delta G_{\text{rxn}}^{\circ}$  can be calculated with the relationship  $\Delta G_{\text{rxn}}^{\circ} = \Delta H_{\text{rxn}}^{\circ} - T\Delta S_{\text{rxn}}^{\circ}$ . Entropy decreases (is negative) when there are fewer moles of gaseous products than there are of gaseous reactants.



**Solution:**

a) Entropy decreases ( $\Delta S^\circ$  **negative**) because the number of moles of gas decreases from reactants (1 1/2 mol) to products (1 mole). The oxidation (combustion) of CO requires initial energy input to start the reaction, but then releases energy (exothermic,  $\Delta H^\circ$  **negative**) which is typical of all combustion reactions.

b) Method 1: Calculate  $\Delta G_{\text{rxn}}^\circ$  from  $\Delta G_f^\circ$  values of products and reactants.

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

$$\Delta G_{\text{rxn}}^\circ = [(1 \text{ mol CO}_2)(\Delta G_f^\circ \text{ of CO}_2)] - [(1 \text{ mol CO})(\Delta G_f^\circ \text{ of CO}) + (1/2 \text{ mol})(\Delta G_f^\circ \text{ of O}_2)]$$

$$\Delta G_{\text{rxn}}^\circ = [(1 \text{ mol})(-394.4 \text{ kJ/mol})] - [(1 \text{ mol})(-137.2 \text{ kJ/mol}) + (1/2 \text{ mol})(0 \text{ kJ/mol})] = \mathbf{-257.2 \text{ kJ}}$$

Method 2: Calculate  $\Delta G_{\text{rxn}}^\circ$  from  $\Delta H_{\text{rxn}}^\circ$  and  $\Delta S_{\text{rxn}}^\circ$  at 298 K (the degree superscript indicates a reaction at standard state, given in the Appendix at 25°C).

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

$$\Delta H_{\text{rxn}}^\circ = [(1 \text{ mol CO}_2)(\Delta H_f^\circ \text{ of CO}_2)] - [(1 \text{ mol CO})(\Delta H_f^\circ \text{ of CO}) + (1/2 \text{ mol})(\Delta H_f^\circ \text{ of O}_2)]$$

$$\Delta H_{\text{rxn}}^\circ = [(1 \text{ mol})(-393.5 \text{ kJ/mol})] - [(1 \text{ mol})(-110.5 \text{ kJ/mol}) + (1/2 \text{ mol})(0 \text{ kJ/mol})] = -283.0 \text{ kJ}$$

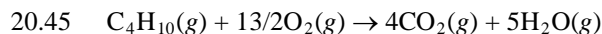
$$\Delta S_{\text{rxn}}^\circ = \sum m S_{\text{products}}^\circ - \sum n S_{\text{reactants}}^\circ$$

$$\Delta S_{\text{rxn}}^\circ = [(1 \text{ mol CO}_2)(S^\circ \text{ of CO}_2)] - [(1 \text{ mol CO})(S^\circ \text{ of CO}) + (1/2 \text{ mol})(S^\circ \text{ of O}_2)]$$

$$\Delta S_{\text{rxn}}^\circ = [(1 \text{ mol})(213.7 \text{ J/mol}\cdot\text{K})] - [(1 \text{ mol})(197.5 \text{ J/mol}\cdot\text{K}) + (1/2 \text{ mol})(205.0 \text{ J/mol}\cdot\text{K})]$$

$$\Delta S_{\text{rxn}}^\circ = -86.3 \text{ J/K}$$

$$\Delta G_{\text{rxn}}^\circ = \Delta H_{\text{rxn}}^\circ - T\Delta S_{\text{rxn}}^\circ = (-283.0 \text{ kJ}) - [(298 \text{ K})(-86.3 \text{ J/K})(1 \text{ kJ}/10^3 \text{ J})] = -257.2826 = \mathbf{-257.3 \text{ kJ}}$$



a) An increase in the number of moles of gas should result in a **positive**  $\Delta S^\circ$  value. The combustion of  $\text{C}_4\text{H}_{10}(\text{g})$  will result in a release of energy or a **negative**  $\Delta H^\circ$  value.

b)  $\Delta H_{\text{rxn}}^\circ = \sum m \Delta H_f^\circ(\text{products}) - \sum n \Delta H_f^\circ(\text{reactants})$

$$\Delta H_{\text{rxn}}^\circ = [(4 \text{ mol CO}_2)(-393.5 \text{ kJ/mol}) + (5 \text{ mol H}_2\text{O})(-241.826 \text{ kJ/mol})] \\ - [(1 \text{ mol C}_4\text{H}_{10})(-126 \text{ kJ/mol}) + (13/2 \text{ mol O}_2)(0 \text{ kJ/mol})]$$

$$\Delta H_{\text{rxn}}^\circ = -2657.13 \text{ kJ}$$

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

$$\Delta S_{\text{rxn}}^\circ = [(4 \text{ mol CO}_2)(213.7 \text{ J/K}\cdot\text{mol}) + (5 \text{ mol H}_2\text{O})(188.72 \text{ J/K}\cdot\text{mol})] \\ - [(1 \text{ mol C}_4\text{H}_{10})(310 \text{ J/K}\cdot\text{mol}) + (13/2 \text{ mol O}_2)(205.0 \text{ J/K}\cdot\text{mol})]$$

$$\Delta S_{\text{rxn}}^\circ = 155.9 \text{ J/K}$$

$$\Delta G_{\text{rxn}}^\circ = \Delta H_{\text{rxn}}^\circ - T\Delta S_{\text{rxn}}^\circ = -2657.13 \text{ kJ} - [(298 \text{ K})(155.9 \text{ J/K})(1 \text{ kJ}/10^3 \text{ J})] = -2703.588 = \mathbf{-2704 \text{ kJ}}$$

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

$$\Delta G_{\text{rxn}}^\circ = [(4 \text{ mol CO}_2)(-394.4 \text{ kJ/mol}) + (5 \text{ mol H}_2\text{O})(-228.60 \text{ kJ/mol})] \\ - [(1 \text{ mol C}_4\text{H}_{10})(-16.7 \text{ kJ/mol}) + (13/2 \text{ mol O}_2)(0 \text{ kJ/mol})]$$

$$\Delta G_{\text{rxn}}^\circ = \mathbf{-2703.9 \text{ kJ}}$$

20.46 Plan:  $\Delta H_{\text{rxn}}^{\circ}$  can be calculated from the individual  $\Delta H_f^{\circ}$  values of the reactants and products by using the relationship  $\Delta H_{\text{rxn}}^{\circ} = \sum m \Delta H_f^{\circ}(\text{products}) - \sum n \Delta H_f^{\circ}(\text{reactants})$ .  $\Delta S_{\text{rxn}}^{\circ}$  can be calculated from the individual  $S^{\circ}$  values of the reactants and products by using the relationship  $\Delta S_{\text{rxn}}^{\circ} = \sum m S_{\text{products}}^{\circ} - \sum n S_{\text{reactants}}^{\circ}$ . Once  $\Delta H_{\text{rxn}}^{\circ}$  and  $\Delta S_{\text{rxn}}^{\circ}$  are known,  $\Delta G^{\circ}$  can be calculated with the relationship  $\Delta G_{\text{rxn}}^{\circ} = \Delta H_{\text{rxn}}^{\circ} - T \Delta S_{\text{rxn}}^{\circ}$ .  $\Delta S_{\text{rxn}}^{\circ}$  values in J/K must be converted to units of kJ/K to match the units of  $\Delta H_{\text{rxn}}^{\circ}$ .

Solution:

$$\text{a) } \Delta H_{\text{rxn}}^{\circ} = [(1 \text{ mol CO})(\Delta H_f^{\circ} \text{ of CO}) + (2 \text{ mol H}_2)(\Delta H_f^{\circ} \text{ of H}_2)] - [(1 \text{ mol CH}_3\text{OH})(\Delta H_f^{\circ} \text{ of CH}_3\text{OH})]$$

$$\Delta H_{\text{rxn}}^{\circ} = [(1 \text{ mol})(-110.5 \text{ kJ/mol}) + (2 \text{ mol})(0 \text{ kJ/mol})] - [(1 \text{ mol})(-201.2 \text{ kJ/mol})]$$

$$\Delta H_{\text{rxn}}^{\circ} = \mathbf{90.7 \text{ kJ}}$$

$$\Delta S_{\text{rxn}}^{\circ} = [(1 \text{ mol CO})(S^{\circ} \text{ of CO}) + (2 \text{ mol H}_2)(S^{\circ} \text{ of H}_2)] - [(1 \text{ mol CH}_3\text{OH})(S^{\circ} \text{ of CH}_3\text{OH})]$$

$$\Delta S_{\text{rxn}}^{\circ} = [(1 \text{ mol})(197.5 \text{ J/mol}\cdot\text{K}) + (2 \text{ mol})(130.6 \text{ J/mol}\cdot\text{K})] - [(1 \text{ mol})(238 \text{ J/mol}\cdot\text{K})]$$

$$\Delta S_{\text{rxn}}^{\circ} = 220.7 = \mathbf{221 \text{ J/K}}$$

$$\text{b) } \Delta G_{\text{rxn}}^{\circ} = \Delta H_{\text{rxn}}^{\circ} - T \Delta S_{\text{rxn}}^{\circ}$$

$$T_1 = 28 + 273 = 301 \text{ K} \quad \Delta G^{\circ} = 90.7 \text{ kJ} - [(301 \text{ K})(220.7 \text{ J/K})(1 \text{ kJ}/10^3 \text{ J})] = 24.2693 = \mathbf{24.3 \text{ kJ}}$$

$$T_2 = 128 + 273 = 401 \text{ K} \quad \Delta G^{\circ} = 90.7 \text{ kJ} - [(401 \text{ K})(220.7 \text{ J/K})(1 \text{ kJ}/10^3 \text{ J})] = 2.1993 = \mathbf{2.2 \text{ kJ}}$$

$$T_3 = 228 + 273 = 501 \text{ K} \quad \Delta G^{\circ} = 90.7 \text{ kJ} - [(501 \text{ K})(220.7 \text{ J/K})(1 \text{ kJ}/10^3 \text{ J})] = -19.8707 = \mathbf{-19.9 \text{ kJ}}$$

c) For the substances in their standard states, the reaction is nonspontaneous at 28°C, near equilibrium at 128°C, and spontaneous at 228°C. Reactions with positive values of  $\Delta H_{\text{rxn}}^{\circ}$  and  $\Delta S_{\text{rxn}}^{\circ}$  become spontaneous at high temperatures.

20.47 a)  $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$

$$\Delta H_{\text{rxn}}^{\circ} = [(2 \text{ mol NO})(90.29 \text{ kJ/mol})] - [(1 \text{ mol N}_2)(0 \text{ kJ/mol}) + (1 \text{ mol O}_2)(0 \text{ kJ/mol})]$$

$$\Delta H_{\text{rxn}}^{\circ} = \mathbf{180.58 \text{ kJ}}$$

$$\Delta S_{\text{rxn}}^{\circ} = [(2 \text{ mol NO})(210.65 \text{ J/K}\cdot\text{mol})] - [(1 \text{ mol N}_2)(191.5 \text{ J/K}\cdot\text{mol}) + (1 \text{ mol O}_2)(205.0 \text{ J/K}\cdot\text{mol})]$$

$$\Delta S_{\text{rxn}}^{\circ} = \mathbf{24.8 \text{ J/K}}$$

$$\begin{aligned} \text{b) } \Delta G_{373}^{\circ} &= \Delta H^{\circ} - ((273 + 100.)\text{K})(\Delta S^{\circ}) \\ &= 180.58 \text{ kJ} - [(373 \text{ K})(24.8 \text{ J/K})(1 \text{ kJ}/10^3 \text{ J})] \\ &= 171.3296 = \mathbf{171.33 \text{ kJ}} \end{aligned}$$

$$\begin{aligned} \Delta G_{2833}^{\circ} &= \Delta H^{\circ} - ((273 + 2560.)\text{K})(\Delta S^{\circ}) \\ &= 180.58 \text{ kJ} - [(2833 \text{ K})(24.8 \text{ J/K})(1 \text{ kJ}/10^3 \text{ J})] \\ &= 110.3216 = \mathbf{110.3 \text{ kJ}} \end{aligned}$$

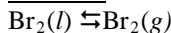
$$\begin{aligned} \Delta G_{3813}^{\circ} &= \Delta H^{\circ} - ((273 + 3540.)\text{K})(\Delta S^{\circ}) \\ &= 180.58 \text{ kJ} - [(3813 \text{ K})(24.8 \text{ J/K})(1 \text{ kJ}/10^3 \text{ J})] \\ &= 86.0176 = \mathbf{86.0 \text{ kJ}} \end{aligned}$$

c) The values of  $\Delta G$  became smaller at higher temperatures. The reaction is not spontaneous at any of these temperatures; however, the reaction becomes **less** nonspontaneous as the temperature increases.

20.48 Plan: At the normal boiling point, defined as the temperature at which the vapor pressure of the liquid equals 1 atm, the phase change from liquid to gas is at equilibrium. For a system at equilibrium, the change in Gibbs free energy is zero. Since the gas is at 1 atm and the liquid assumed to be pure, the system is at standard state and  $\Delta G^{\circ} = 0$ . The temperature at which this occurs can be found from  $\Delta G_{\text{rxn}}^{\circ} = 0 = \Delta H_{\text{rxn}}^{\circ} - T \Delta S_{\text{rxn}}^{\circ}$ .  $\Delta H_{\text{rxn}}^{\circ}$  can be calculated from the individual  $\Delta H_f^{\circ}$  values of the reactants and products by using the relationship

$\Delta H_{\text{rxn}}^{\circ} = \sum m \Delta H_{\text{f}}^{\circ}(\text{products}) - \sum n \Delta H_{\text{f}}^{\circ}(\text{reactants})$ .  $\Delta S_{\text{rxn}}^{\circ}$  can be calculated from the individual  $S^{\circ}$  values of the reactants and products by using the relationship  $\Delta S_{\text{rxn}}^{\circ} = \sum m S_{\text{products}}^{\circ} - \sum n S_{\text{reactants}}^{\circ}$ .

Solution:



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

$$\Delta H_{\text{rxn}}^{\circ} = [(1 \text{ mol Br}_2)(\Delta H_{\text{f}}^{\circ} \text{ of Br}_2(g))] - [(1 \text{ mol Br}_2)(\Delta H_{\text{f}}^{\circ} \text{ of Br}_2(l))]$$

$$\Delta H_{\text{rxn}}^{\circ} = [(1 \text{ mol})(30.91 \text{ kJ/mol})] - [(1 \text{ mol})(0 \text{ kJ/mol})] = 30.91 \text{ kJ}$$

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

$$\Delta S_{\text{rxn}}^{\circ} = [(1 \text{ mol Br}_2)(S^{\circ} \text{ of Br}_2(g))] - [(1 \text{ mol Br}_2)(S^{\circ} \text{ of Br}_2(l))]$$

$$\Delta S_{\text{rxn}}^{\circ} = [(1 \text{ mol})(245.38 \text{ J/K}\cdot\text{mol})] - [(1 \text{ mol})(152.23 \text{ J/K}\cdot\text{mol})] = 93.15 \text{ J/K} = 0.09315 \text{ kJ/K}$$

$$\Delta G_{\text{rxn}}^{\circ} = 0 = \Delta H_{\text{rxn}}^{\circ} - T \Delta S_{\text{rxn}}^{\circ}$$

$$\Delta H_{\text{rxn}}^{\circ} = T \Delta S_{\text{rxn}}^{\circ}$$

$$T = \frac{\Delta H^{\circ}}{\Delta S^{\circ}} = \frac{30.91 \text{ kJ}}{0.09315 \text{ kJ/K}} = 331.830 = \mathbf{331.8 \text{ K}}$$

20.49  $\text{S}(\text{rhombic}) \rightleftharpoons \text{S}(\text{monoclinic})$

$$\Delta H_{\text{rxn}}^{\circ} = [1 \text{ mol S(monoclinic)}(0.30 \text{ kJ/mol})] - [1 \text{ mol S(rhombic)}(0 \text{ kJ/mol})] = 0.30 \text{ kJ}$$

$$\Delta S_{\text{rxn}}^{\circ} = [1 \text{ mol S(monoclinic)}(32.6 \text{ J/K}\cdot\text{mol})] - [1 \text{ mol S(rhombic)}(31.9 \text{ J/K}\cdot\text{mol})] = 0.7 \text{ J/K} = 0.0007 \text{ kJ/K}$$

$$\Delta G_{\text{rxn}}^{\circ} = 0 = \Delta H_{\text{rxn}}^{\circ} - T \Delta S_{\text{rxn}}^{\circ}$$

$$\Delta H_{\text{rxn}}^{\circ} = T \Delta S_{\text{rxn}}^{\circ}$$

$$T = \frac{\Delta H^{\circ}}{\Delta S^{\circ}} = \frac{30.91 \text{ kJ}}{0.09315 \text{ kJ/K}} = 428.571 = \mathbf{4 \times 10^2 \text{ K}}$$

20.50 Plan:  $\Delta H_{\text{rxn}}^{\circ}$  can be calculated from the individual  $\Delta H_{\text{f}}^{\circ}$  values of the reactants and products by using the relationship  $\Delta H_{\text{rxn}}^{\circ} = \sum m \Delta H_{\text{f}}^{\circ}(\text{products}) - \sum n \Delta H_{\text{f}}^{\circ}(\text{reactants})$ .  $\Delta S_{\text{rxn}}^{\circ}$  can be calculated from the individual  $S^{\circ}$  values of the reactants and products by using the relationship  $\Delta S_{\text{rxn}}^{\circ} = \sum m S_{\text{products}}^{\circ} - \sum n S_{\text{reactants}}^{\circ}$ . Once  $\Delta H_{\text{rxn}}^{\circ}$  and  $\Delta S_{\text{rxn}}^{\circ}$  are known,  $\Delta G^{\circ}$  can be calculated with the relationship  $\Delta G_{\text{rxn}}^{\circ} = \Delta H_{\text{rxn}}^{\circ} - T \Delta S_{\text{rxn}}^{\circ}$ .  $\Delta S_{\text{rxn}}^{\circ}$  values in J/K must be converted to units of kJ/K to match the units of  $\Delta H_{\text{rxn}}^{\circ}$ . To find the temperature at which the reaction becomes spontaneous, use  $\Delta G_{\text{rxn}}^{\circ} = 0 = \Delta H_{\text{rxn}}^{\circ} - T \Delta S_{\text{rxn}}^{\circ}$  and solve for temperature.

Solution:

a) The reaction for this process is  $\text{H}_2(g) + 1/2\text{O}_2(g) \rightarrow \text{H}_2\text{O}(g)$ . The coefficients are written this way (instead of  $2\text{H}_2(g) + \text{O}_2(g) \rightarrow 2\text{H}_2\text{O}(g)$ ) because the problem specifies thermodynamic values “per (1) mol  $\text{H}_2$ ,” not per 2 mol  $\text{H}_2$ .

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

$$\Delta H_{\text{rxn}}^{\circ} = [(1 \text{ mol H}_2\text{O})(\Delta H_{\text{f}}^{\circ} \text{ of H}_2\text{O})] - [(1 \text{ mol H}_2)(\Delta H_{\text{f}}^{\circ} \text{ of H}_2) + (1/2 \text{ mol O}_2)(\Delta H_{\text{f}}^{\circ} \text{ of O}_2)]$$

$$\Delta H_{\text{rxn}}^{\circ} = [(1 \text{ mol H}_2\text{O})(-241.826 \text{ kJ/mol})] - [(1 \text{ mol H}_2)(0 \text{ kJ/mol}) + (1/2 \text{ mol O}_2)(0 \text{ kJ/mol})]$$

$$\Delta H_{\text{rxn}}^{\circ} = \mathbf{-241.826 \text{ kJ}}$$

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

$$\Delta S_{\text{rxn}}^{\circ} = [(1 \text{ mol H}_2\text{O})(S^{\circ} \text{ of H}_2\text{O})] - [(1 \text{ mol H}_2)(S^{\circ} \text{ of H}_2) + (1/2 \text{ mol O}_2)(S^{\circ} \text{ of O}_2)]$$

$$\Delta S_{\text{rxn}}^{\circ} = [(1 \text{ mol})(188.72 \text{ J/mol}\cdot\text{K})] - [(1 \text{ mol})(130.6 \text{ J/mol}\cdot\text{K}) + (1/2 \text{ mol})(205.0 \text{ J/mol}\cdot\text{K})]$$

$$\Delta S_{\text{rxn}}^{\circ} = -44.38 = \mathbf{-44.4 \text{ J/K} = -0.0444 \text{ kJ/K}}$$

$$\Delta G_{\text{rxn}}^{\circ} = \Delta H_{\text{rxn}}^{\circ} - T\Delta S_{\text{rxn}}^{\circ}$$

$$\Delta G_{\text{rxn}}^{\circ} = -241.826 \text{ kJ} - [(298 \text{ K})(-0.0444 \text{ kJ/K})]$$

$$\Delta G_{\text{rxn}}^{\circ} = \mathbf{-228.6 \text{ kJ}}$$

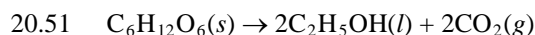
b) Because  $\Delta H < 0$  and  $\Delta S < 0$ , the reaction will become nonspontaneous at higher temperatures because the positive ( $-T\Delta S$ ) term becomes larger than the negative  $\Delta H$  term.

c) The reaction becomes spontaneous below the temperature where  $\Delta G_{\text{rxn}}^{\circ} = 0$

$$\Delta G_{\text{rxn}}^{\circ} = 0 = \Delta H_{\text{rxn}}^{\circ} - T\Delta S_{\text{rxn}}^{\circ}$$

$$\Delta H_{\text{rxn}}^{\circ} = T\Delta S_{\text{rxn}}^{\circ}$$

$$T = \frac{\Delta H^{\circ}}{\Delta S^{\circ}} = \frac{-241.826 \text{ kJ}}{-0.0444 \text{ kJ/K}} = 5446.53 = \mathbf{5.45 \times 10^3 \text{ K}}$$



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

$$\Delta H_{\text{rxn}}^{\circ} = [(2 \text{ mol C}_2\text{H}_5\text{OH})(-277.63 \text{ kJ/mol}) + (2 \text{ mol CO}_2)(-393.5 \text{ kJ/mol})] - [1 \text{ mol C}_6\text{H}_{12}\text{O}_6(-1273.3 \text{ kJ/mol})]$$

$$\Delta H_{\text{rxn}}^{\circ} = -68.96 \text{ kJ} = \mathbf{-69.0 \text{ kJ}}$$

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

$$\Delta S_{\text{rxn}}^{\circ} = [(2 \text{ mol C}_2\text{H}_5\text{OH})(161 \text{ J/K}\cdot\text{mol}) + (2 \text{ mol CO}_2)(213.7 \text{ J/K}\cdot\text{mol})] - [(1 \text{ mol C}_6\text{H}_{12}\text{O}_6)(212.1 \text{ K}\cdot\text{mol})]$$

$$\Delta S_{\text{rxn}}^{\circ} = 537.3 \text{ J/K} = \mathbf{537 \text{ J/K}}$$

$$\Delta G_{\text{rxn}}^{\circ} = \Delta H_{\text{rxn}}^{\circ} - T\Delta S_{\text{rxn}}^{\circ}$$

$$\Delta G_{\text{rxn}}^{\circ} = -68.96 \text{ kJ} - [(298 \text{ K})(0.5373 \text{ kJ/K})]$$

$$\Delta G_{\text{rxn}}^{\circ} = -229.0754 \text{ kJ/mol} = \mathbf{-229.1 \text{ kJ/mol}}$$

**No**, a reaction with a negative value for  $\Delta H$  and a positive value for  $\Delta S$  is spontaneous at all temperatures.

20.52 a) An equilibrium constant that is much less than one indicates that very little product is made to reach equilibrium. The reaction, thus, is not spontaneous in the forward direction and  $\Delta G^{\circ}$  is a relatively large positive value.

b) A large negative  $\Delta G^{\circ}$  indicates that the reaction is quite spontaneous and goes almost to completion. At equilibrium, much more product is present than reactant so  $K > 1$ .  $Q$  depends on initial conditions, not equilibrium conditions, so its value cannot be predicted from  $\Delta G^{\circ}$ .

20.53 For a spontaneous process,  $\Delta G$  is the maximum useful work obtainable from the system. In reality, the actual amount of useful work is less due to energy lost as heat. If the process is run in a slower or more controlled fashion, the actual amount of available work approaches  $\Delta G$ .

20.54 a) Point x represents the difference between  $G_{\text{reactants}}$  and  $G_{\text{products}}$  or  $\Delta G^{\circ}$ , the standard free energy change for the reaction.

b) **Scene A** corresponds to Point 1 on the graph. This point corresponds to the pure substances, not a mixture.

c) **Scene C** corresponds to Point 2 on the graph. Point 2 represents equilibrium; for this reaction, products dominate at equilibrium (the minimum in the curve is close to the XY side of the graph).

20.55 The standard free energy change,  $\Delta G^\circ$ , occurs when all components of the system are in their standard states. Standard state is defined as 1 atm for gases, 1 M for solutes, and pure solids and liquids. Standard state does not specify a temperature because standard state can occur at any temperature.  $\Delta G^\circ = \Delta G$  when all concentrations equal 1 M and all partial pressures equal 1 atm. This occurs because the value of  $Q = 1$  and  $\ln Q = 0$  in the equation  $\Delta G = \Delta G^\circ + RT \ln Q$ .

20.56 Plan: For each reaction, first find  $\Delta G^\circ$ , then calculate  $K$  from  $\Delta G^\circ = -RT \ln K$ . Calculate  $\Delta G_{\text{rxn}}^\circ$  using  $\Delta G_f^\circ$  values in the relationship  $\Delta G_{\text{rxn}}^\circ = \sum m \Delta G_f^\circ(\text{products}) - \sum n \Delta G_f^\circ(\text{reactants})$ .

Solution:

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

$$\Delta G_{\text{rxn}}^\circ = [(1 \text{ mol NO}_2)(\Delta G_f^\circ \text{ of NO}_2)] - [(1 \text{ mol NO})(\Delta G_f^\circ \text{ of NO}) + (1/2 \text{ mol O}_2)(\Delta G_f^\circ \text{ of O}_2)]$$

$$\Delta G_{\text{rxn}}^\circ = [(1 \text{ mol})(51 \text{ kJ/mol})] - [(1 \text{ mol})(86.60 \text{ kJ/mol}) + (1/2 \text{ mol})(0 \text{ kJ/mol})] = -35.6 \text{ kJ}$$

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

$$\ln K = \frac{\Delta G^\circ}{-RT} = \left( \frac{-35.6 \text{ kJ/mol}}{-(8.314 \text{ J/mol}\cdot\text{K})(298 \text{ K})} \right) \left( \frac{10^3 \text{ J}}{1 \text{ kJ}} \right) = 14.3689$$

$$K = e^{14.3689} = 1.7391377 \times 10^6 = \mathbf{1.7 \times 10^6}$$

$$\text{b) } \Delta G_{\text{rxn}}^\circ = [(1 \text{ mol H}_2)(\Delta G_f^\circ \text{ of H}_2) + (1 \text{ mol Cl}_2)(\Delta G_f^\circ \text{ of Cl}_2)] - [(2 \text{ mol HCl})(\Delta G_f^\circ \text{ of HCl})]$$

$$\Delta G_{\text{rxn}}^\circ = [(1 \text{ mol})(0 \text{ kJ/mol}) + (1 \text{ mol})(0 \text{ kJ/mol})] - [(2 \text{ mol})(-95.30 \text{ kJ/mol})] = 190.60 \text{ kJ}$$

$$\ln K = \frac{\Delta G^\circ}{-RT} = \left( \frac{190.60 \text{ kJ/mol}}{-(8.314 \text{ J/mol}\cdot\text{K})(298 \text{ K})} \right) \left( \frac{10^3 \text{ J}}{1 \text{ kJ}} \right) = -76.930$$

$$K = e^{-76.930} = 3.88799 \times 10^{-34} = \mathbf{3.89 \times 10^{-34}}$$

$$\text{c) } \Delta G_{\text{rxn}}^\circ = [(2 \text{ mol CO})(\Delta G_f^\circ \text{ of CO})] - [(2 \text{ mol C})(\Delta G_f^\circ \text{ of C}) + (1 \text{ mol O}_2)(\Delta G_f^\circ \text{ of O}_2)]$$

$$\Delta G_{\text{rxn}}^\circ = [(2 \text{ mol})(-137.2 \text{ kJ/mol})] - [(2 \text{ mol})(0 \text{ kJ/mol}) + (1 \text{ mol})(0 \text{ kJ/mol})] = 274.4 \text{ kJ}$$

$$\ln K = \frac{\Delta G^\circ}{-RT} = \left( \frac{-274.4 \text{ kJ/mol}}{-(8.314 \text{ J/mol}\cdot\text{K})(298 \text{ K})} \right) \left( \frac{10^3 \text{ J}}{1 \text{ kJ}} \right) = 110.75359$$

$$K = e^{110.75359} = 1.2579778 \times 10^{48} = \mathbf{1.26 \times 10^{48}}$$

Note: You may get a different answer depending on how you rounded in earlier calculations.

20.57 Plan: For each reaction, first find  $\Delta G^\circ$ , then calculate  $K$  from  $\Delta G^\circ = -RT \ln K$ . Calculate  $\Delta G^\circ$  using  $\Delta G_f^\circ$  values in the relationship  $\Delta G_{\text{rxn}}^\circ = \sum m \Delta G_f^\circ(\text{products}) - \sum n \Delta G_f^\circ(\text{reactants})$ .

Solution:

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

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

$$- [(2 \text{ mol H}_2\text{S})(\Delta G_f^\circ \text{ of H}_2\text{S}) + (3 \text{ mol O}_2)(\Delta G_f^\circ \text{ of O}_2)]$$

$$\Delta G_{\text{rxn}}^\circ = [(2 \text{ mol})(-228.60 \text{ kJ/mol}) + (2 \text{ mol})(-300.2 \text{ kJ/mol})] - [(2 \text{ mol})(-33 \text{ kJ/mol}) + (3 \text{ mol})(0 \text{ kJ/mol})]$$

$$\Delta G_{\text{rxn}}^\circ = -991.6 \text{ kJ}$$

$$\ln K = \frac{\Delta G^\circ}{-RT} = \left( \frac{-991.6 \text{ kJ/mol}}{-(8.314 \text{ J/mol}\cdot\text{K})(298 \text{ K})} \right) \left( \frac{10^3 \text{ J}}{1 \text{ kJ}} \right) = 400.2305$$

$$K = e^{400.2305} = 6.571696 \times 10^{173} = \mathbf{6.57 \times 10^{173}}$$

Comment: Depending on how you round  $\Delta G_{\text{rxn}}^{\circ}$ , the value for  $K$  can vary by a factor of 2 or 3 because the inverse natural log varies greatly with small changes in  $\Delta G_{\text{rxn}}^{\circ}$ . Your calculator might register “error” when trying to calculate  $e^{400}$  because it cannot calculate exponents greater than 99. In this case, divide 400.2305 by 2 (= 200.115), and calculate  $e^{200.115}e^{200.115} = (8.1066 \times 10^{86})^2 = (8.1066)^2 \times 10^{86 \times 2} = 65.71696 \times 10^{172} = 6.5 \times 10^{173}$ , which equals the first answer with rounding errors.

$$\text{b) } \Delta G_{\text{rxn}}^{\circ} = [(1 \text{ mol H}_2\text{O})(\Delta G_{\text{f}}^{\circ} \text{ of H}_2\text{O}) + (1 \text{ mol SO}_3)(\Delta G_{\text{f}}^{\circ} \text{ of SO}_3)] - [(1 \text{ mol H}_2\text{SO}_4)(\Delta G_{\text{f}}^{\circ} \text{ of H}_2\text{SO}_4)]$$

$$\Delta G_{\text{rxn}}^{\circ} = [(1 \text{ mol})(-237.192 \text{ kJ/mol}) + (1 \text{ mol})(-371 \text{ kJ/mol})] - [(1 \text{ mol})(-690.059 \text{ kJ/mol})]$$

$$\Delta G_{\text{rxn}}^{\circ} = 81.867 \text{ kJ}$$

$$\ln K = \frac{\Delta G^{\circ}}{-RT} = \left( \frac{81.867 \text{ kJ/mol}}{-(8.314 \text{ J/mol}\cdot\text{K})(298 \text{ K})} \right) \left( \frac{10^3 \text{ J}}{1 \text{ kJ}} \right) = -33.0432$$

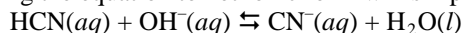
$$K = e^{-33.0432} = 4.4619 \times 10^{-15} = \mathbf{4.46 \times 10^{-15}}$$

$$\text{c) } \Delta G_{\text{rxn}}^{\circ} = [(1 \text{ mol NaCN})(\Delta G_{\text{f}}^{\circ} \text{ of NaCN}) + (1 \text{ mol H}_2\text{O})(\Delta G_{\text{f}}^{\circ} \text{ of H}_2\text{O})]$$

$$- [(1 \text{ mol HCN})(\Delta G_{\text{f}}^{\circ} \text{ of HCN}) + (1 \text{ mol NaOH})(\Delta G_{\text{f}}^{\circ} \text{ of NaOH})]$$

NaCN(aq) and NaOH(aq) are not listed in Appendix B.

Converting the equation to net ionic form will simplify the problem:



$$\Delta G_{\text{rxn}}^{\circ} = [(1 \text{ mol CN}^-)(\Delta G_{\text{f}}^{\circ} \text{ of CN}^-) + (1 \text{ mol H}_2\text{O})(\Delta G_{\text{f}}^{\circ} \text{ of H}_2\text{O})]$$

$$- [(1 \text{ mol HCN})(\Delta G_{\text{f}}^{\circ} \text{ of HCN}) + (1 \text{ mol OH}^-)(\Delta G_{\text{f}}^{\circ} \text{ of OH}^-)]$$

$$\Delta G_{\text{rxn}}^{\circ} = [(1 \text{ mol})(166 \text{ kJ/mol}) + (1 \text{ mol})(-237.192 \text{ kJ/mol})]$$

$$- [(1 \text{ mol})(112 \text{ kJ/mol}) + (1 \text{ mol})(-157.30 \text{ kJ/mol})]$$

$$\Delta G_{\text{rxn}}^{\circ} = -25.892 \text{ kJ}$$

$$\ln K = \frac{\Delta G^{\circ}}{-RT} = \left( \frac{-25.892 \text{ kJ/mol}}{-(8.314 \text{ J/mol}\cdot\text{K})(298 \text{ K})} \right) \left( \frac{10^3 \text{ J}}{1 \text{ kJ}} \right) = 10.45055$$

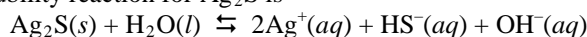
$$K = e^{10.45055} = 3.4563 \times 10^4 = \mathbf{3.46 \times 10^4}$$

20.58 Plan: Write the balanced equation. First find  $\Delta G^{\circ}$ , then calculate  $K$  from  $\Delta G^{\circ} = -RT \ln K$ . Calculate  $\Delta G^{\circ}$  using

$$\Delta G_{\text{rxn}}^{\circ} \text{ values in the relationship } \Delta G_{\text{rxn}}^{\circ} = \sum m \Delta G_{\text{f}}^{\circ}(\text{products}) - \sum n \Delta G_{\text{f}}^{\circ}(\text{reactants}) .$$

Solution:

The solubility reaction for  $\text{Ag}_2\text{S}$  is



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

$$\Delta G_{\text{rxn}}^{\circ} = [(2 \text{ mol Ag}^+)(\Delta G_{\text{f}}^{\circ} \text{ of Ag}^+) + (1 \text{ mol HS}^-)(\Delta G_{\text{f}}^{\circ} \text{ of HS}^-) + (1 \text{ mol OH}^-)(\Delta G_{\text{f}}^{\circ} \text{ of OH}^-)]$$

$$- [(1 \text{ mol Ag}_2\text{S})(\Delta G_{\text{f}}^{\circ} \text{ of Ag}_2\text{S}) + (1 \text{ mol H}_2\text{O})(\Delta G_{\text{f}}^{\circ} \text{ of H}_2\text{O})]$$

$$\Delta G_{\text{rxn}}^{\circ} = [(2 \text{ mol})(77.111 \text{ kJ/mol}) + (1 \text{ mol})(12.6 \text{ kJ/mol}) + (1 \text{ mol})(-157.30 \text{ kJ/mol})]$$

$$- [(1 \text{ mol})(-40.3 \text{ kJ/mol}) + (1 \text{ mol})(-237.192 \text{ kJ/mol})]$$

$$\Delta G_{\text{rxn}}^{\circ} = 287.014 \text{ kJ}$$

$$\ln K = \frac{\Delta G^{\circ}}{-RT} = \left( \frac{287.014 \text{ kJ/mol}}{-(8.314 \text{ J/mol}\cdot\text{K})(298 \text{ K})} \right) \left( \frac{10^3 \text{ J}}{1 \text{ kJ}} \right) = -115.8448675$$

$$K = e^{-115.8448675} = 4.8889241 \times 10^{-51} = \mathbf{4.89 \times 10^{-51}}$$

20.59  $\text{CaF}_2(s) \rightleftharpoons \text{Ca}^{2+}(aq) + 2\text{F}^{-}(aq)$   
 $\Delta G_{\text{rxn}}^{\circ} = [(1 \text{ mol Ca}^{2+})(-553.04 \text{ kJ/mol}) + (2 \text{ mol F}^{-})(-276.5 \text{ kJ/mol})] - [(1 \text{ mol CaF}_2)(-1162 \text{ kJ/mol})]$   
 $\Delta G_{\text{rxn}}^{\circ} = 55.96 \text{ kJ}$   
 $\ln K = \frac{\Delta G^{\circ}}{-RT} = \left( \frac{55.96 \text{ kJ/mol}}{-(8.314 \text{ J/mol}\cdot\text{K})(298 \text{ K})} \right) \left( \frac{10^3 \text{ J}}{1 \text{ kJ}} \right) = -22.586629$   
 $K = e^{-22.586629} = 1.5514995 \times 10^{-10} = \mathbf{1.55 \times 10^{-10}}$

20.60 **Plan:** First find  $\Delta G^{\circ}$ , then calculate  $K$  from  $\Delta G^{\circ} = -RT \ln K$ . Calculate  $\Delta G^{\circ}$  using  $\Delta G_{\text{f}}^{\circ}$  values in the relationship

$$\Delta G_{\text{rxn}}^{\circ} = \sum m \Delta G_{\text{f}}^{\circ}(\text{products}) - \sum n \Delta G_{\text{f}}^{\circ}(\text{reactants}) \cdot \text{Recognize that } \text{I}_2(s), \text{ not } \text{I}_2(g), \text{ is the standard state for iodine.}$$

**Solution:**

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

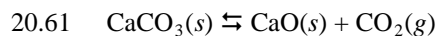
$$\Delta G_{\text{rxn}}^{\circ} = [(2 \text{ mol ICl})(\Delta G_{\text{f}}^{\circ} \text{ of ICl})] - [(1 \text{ mol I}_2)(\Delta G_{\text{f}}^{\circ} \text{ of I}_2) + (1 \text{ mol Cl}_2)(\Delta G_{\text{f}}^{\circ} \text{ of Cl}_2)]$$

$$\Delta G_{\text{rxn}}^{\circ} = [(2 \text{ mol})(-6.075 \text{ kJ/mol})] - [(1 \text{ mol})(19.38 \text{ kJ/mol}) + (1 \text{ mol})(0 \text{ kJ/mol})]$$

$$\Delta G_{\text{rxn}}^{\circ} = -31.53 \text{ kJ}$$

$$\ln K_{\text{p}} = \frac{\Delta G^{\circ}}{-RT} = \left( \frac{-31.53 \text{ kJ/mol}}{-(8.314 \text{ J/mol}\cdot\text{K})(298 \text{ K})} \right) \left( \frac{10^3 \text{ J}}{1 \text{ kJ}} \right) = 12.726169$$

$$K_{\text{p}} = e^{12.726169} = 3.3643794 \times 10^5 = \mathbf{3.36 \times 10^5}$$



$$K_{\text{p}} = P_{\text{CO}_2}$$

$$\Delta G_{\text{rxn}}^{\circ} = [(1 \text{ mol CaO})(-603.5 \text{ kJ/mol}) + (1 \text{ mol CO}_2)(-394.4 \text{ kJ/mol})] - [(1 \text{ mol CaCO}_3)(-1128.8 \text{ kJ/mol})]$$

$$\Delta G_{\text{rxn}}^{\circ} = 130.9 \text{ kJ}$$

$$\ln K_{\text{p}} = \frac{\Delta G^{\circ}}{-RT} = \left( \frac{130.9 \text{ kJ/mol}}{-(8.314 \text{ J/mol}\cdot\text{K})(298 \text{ K})} \right) \left( \frac{10^3 \text{ J}}{1 \text{ kJ}} \right) = -52.83398$$

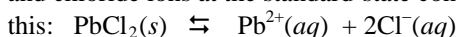
$$K_{\text{p}} = e^{-52.83398} = 1.1336892 \times 10^{-23} = \mathbf{1.13 \times 10^{-23} \text{ atm}} = P_{\text{CO}_2}$$

20.62 **Plan:** The equilibrium constant,  $K$ , is related to  $\Delta G^{\circ}$  through the equation  $\Delta G^{\circ} = -RT \ln K$ .

**Solution:**

$$\Delta G^{\circ} = -RT \ln K = -(8.314 \text{ J/mol}\cdot\text{K})(298 \text{ K}) \ln (1.7 \times 10^{-5}) = 2.72094 \times 10^4 \text{ J/mol} = \mathbf{2.7 \times 10^4 \text{ J/mol}}$$

The large positive  $\Delta G^{\circ}$  indicates that it would not be possible to prepare a solution with the concentrations of lead and chloride ions at the standard-state concentration of 1  $M$ . A  $Q$  calculation using 1  $M$  solutions will confirm



$$\begin{aligned} Q &= [\text{Pb}^{2+}][\text{Cl}^{-}]^2 \\ &= (1 \text{ M})(1 \text{ M})^2 \\ &= 1 \end{aligned}$$

Since  $Q > K_{\text{sp}}$ , it is impossible to prepare a standard-state solution of  $\text{Pb}^{2+}(aq)$  and  $\text{Cl}^{-}(aq)$ .

20.63  $\Delta G^{\circ} = -RT \ln K = -(8.314 \text{ J/mol}\cdot\text{K})(298 \text{ K}) \ln (3.0 \times 10^{-2}) = 8.6877 \times 10^3 \text{ J/mol} = \mathbf{8.7 \times 10^3 \text{ J/mol}}$

The large positive  $\Delta G^{\circ}$  indicates that it would not be possible to prepare a solution with the concentrations of zinc and fluoride ions at the standard-state concentration of 1  $M$ . A  $Q$  calculation using 1  $M$  solutions will confirm this:

$$\begin{aligned} Q &= [\text{Zn}^{2+}][\text{F}^{-}]^2 \\ &= (1 \text{ M})(1 \text{ M})^2 \\ &= 1 \end{aligned}$$

Since  $Q > K_{\text{sp}}$ , it is impossible to prepare a standard state solution of  $\text{ZnF}_2$ .

20.64 Plan: The equilibrium constant,  $K$ , is related to  $\Delta G^\circ$  through the equation  $\Delta G^\circ = -RT \ln K$ .  $\Delta G$  is found by using the relationship  $\Delta G = \Delta G^\circ + RT \ln Q$ .

Solution:

a)  $\Delta G^\circ = -RT \ln K = -(8.314 \text{ J/mol}\cdot\text{K})(298 \text{ K}) \ln (9.1 \times 10^{-6}) = 2.875776 \times 10^4 = \mathbf{2.9 \times 10^4 \text{ J/mol}}$

b) Since  $\Delta G_{\text{rxn}}^\circ$  is positive, the reaction direction as written is nonspontaneous. The reverse direction, formation of reactants, is spontaneous, so the reaction proceeds to the **left**.

c) Calculate the value for  $Q$  and then use it to find  $\Delta G$ .

$$Q = \frac{[\text{Fe}^{2+}]^2 [\text{Hg}^{2+}]^2}{[\text{Fe}^{3+}]^2 [\text{Hg}_2^{2+}]} = \frac{[0.010]^2 [0.025]^2}{[0.20]^2 [0.010]} = 1.5625 \times 10^{-4}$$

$$\Delta G = \Delta G^\circ + RT \ln Q = 2.875776 \times 10^4 \text{ J/mol} + (8.314 \text{ J/mol}\cdot\text{K})(298) \ln (1.5625 \times 10^{-4}) \\ = 7.044187 \times 10^3 = \mathbf{7.0 \times 10^3 \text{ J/mol}}$$

Because  $\Delta G_{298} > 0$  and  $Q > K$ , the reaction proceeds to the **left** to reach equilibrium.

20.65 a)  $\Delta G^\circ = -RT \ln K = -(8.314 \text{ J/mol}\cdot\text{K})(273 + 25) \text{ K}) \ln (5.6 \times 10^{-8}) = -4.9906841 \times 10^4 = \mathbf{-5.0 \times 10^4 \text{ J/mol}}$

b) Since  $\Delta G_{\text{rxn}}^\circ$  is negative, the reaction direction as written is spontaneous. The reaction proceeds to the right.

c) Calculate the value for  $Q$  and then use it to find  $\Delta G$ .

$$Q = \frac{[\text{Ni}(\text{NH}_3)_6^{2+}]}{[\text{Ni}^{2+}][\text{NH}_3]^6} = \frac{[0.010]}{[0.0010][0.0050]^6} = 6.4 \times 10^{14}$$

$$\Delta G = \Delta G^\circ + RT \ln Q = -4.9906841 \times 10^4 \text{ J/mol} + (8.314 \text{ J/mol}\cdot\text{K})(298) \ln (6.4 \times 10^{14}) \\ = 3.4559756 \times 10^4 = \mathbf{3.5 \times 10^4 \text{ J/mol}}$$

Because  $\Delta G_{298} > 0$  and  $Q > K$ , the reaction proceeds to the left to equilibrium.

20.66 Plan: To decide when production of ozone is favored, both the signs of  $\Delta H_{\text{rxn}}^\circ$  and  $\Delta S_{\text{rxn}}^\circ$  for ozone are needed.

The values of  $\Delta H_f^\circ$  and  $S^\circ$  can be used. Once  $\Delta H_{\text{rxn}}^\circ$  and  $\Delta S_{\text{rxn}}^\circ$  are known,  $\Delta G^\circ$  can be calculated with the relationship  $\Delta G_{\text{rxn}}^\circ = \Delta H_{\text{rxn}}^\circ - T\Delta S_{\text{rxn}}^\circ$ .  $\Delta S_{\text{rxn}}^\circ$  values in J/K must be converted to units of kJ/K to match the units of  $\Delta H_{\text{rxn}}^\circ$ .  $\Delta G$  is found by using the relationship  $\Delta G = \Delta G^\circ + RT \ln Q$ .

Solution:

a) Formation of  $\text{O}_3$  from  $\text{O}_2$ :  $3\text{O}_2(\text{g}) \rightleftharpoons 2\text{O}_3(\text{g})$  or per mole of ozone:  $3/2\text{O}_2(\text{g}) \rightleftharpoons \text{O}_3(\text{g})$ .

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

$$\Delta H_{\text{rxn}}^\circ = [(1 \text{ mol O}_3)(\Delta H_f^\circ \text{ of O}_3)] - [(3/2 \text{ mol O}_2)(\Delta H_f^\circ \text{ of O}_2)]$$

$$\Delta H_{\text{rxn}}^\circ = [(1 \text{ mol})(143 \text{ kJ/mol})] - [(3/2 \text{ mol})(0 \text{ kJ/mol})] = 143 \text{ kJ}$$

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

$$\Delta S_{\text{rxn}}^\circ = [(1 \text{ mol O}_3)(S^\circ \text{ of O}_3)] - [(3/2 \text{ mol O}_2)(S^\circ \text{ of O}_2)]$$

$$\Delta S_{\text{rxn}}^\circ = [(1 \text{ mol})(238.82 \text{ J/mol}\cdot\text{K})] - [(3/2 \text{ mol})(205.0 \text{ J/mol}\cdot\text{K})] = -68.68 \text{ J/K} = -0.06868 \text{ kJ/K}$$

The positive sign for  $\Delta H_{\text{rxn}}^\circ$  and the negative sign for  $\Delta S_{\text{rxn}}^\circ$  indicates the formation of ozone is favored at **no temperature**. The reaction is nonspontaneous at all temperatures.

b)  $\Delta G_{\text{rxn}}^\circ = \Delta H_{\text{rxn}}^\circ - T\Delta S_{\text{rxn}}^\circ$

$$\Delta G_{\text{rxn}}^\circ = 143 \text{ kJ} - [(298 \text{ K})(-0.06868 \text{ kJ/K})] = 163.46664 = \mathbf{163 \text{ kJ}}$$
 for the formation of one mole of  $\text{O}_3$ .

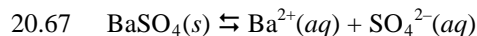
c) Calculate the value for  $Q$  and then use to find  $\Delta G$ .

$$Q = \frac{[\text{O}_3]}{[\text{O}_2]^{3/2}} = \frac{[5 \times 10^{-7} \text{ atm}]}{[0.21 \text{ atm}]^{3/2}} = 5.195664 \times 10^{-6}$$



$$\Delta G = \Delta G^\circ + RT \ln Q = 163 \text{ kJ/mol} + (8.314 \text{ J/mol}\cdot\text{K})(298)(1 \text{ kJ}/10^3 \text{ J}) \ln (5.195664 \times 10^{-6})$$

$$= 132.85368 = \mathbf{1 \times 10^2 \text{ kJ/mol}}$$



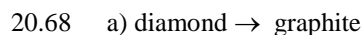
The equilibrium constant,  $K$ , is related to  $\Delta G^\circ$  through the equation  $\Delta G^\circ = -RT \ln K$ .

$$\ln K_p = \frac{\Delta G^\circ}{-RT} = \left( \frac{59.1 \text{ kJ/mol}}{-(8.314 \text{ J/mol}\cdot\text{K})(273 + 37)\text{K}} \right) \left( \frac{10^3 \text{ J}}{1 \text{ kJ}} \right) = -22.930618$$

$$K = e^{-22.930618} = 1.099915 \times 10^{-10} = 1.10 \times 10^{-10}$$

$$K_{\text{sp}} = [\text{Ba}^{2+}][\text{SO}_4^{2-}] = 1.099915 \times 10^{-10} = S^2$$

$$S = \sqrt{1.099915 \times 10^{-10}} = 1.0487683 \times 10^{-5} = \mathbf{1.05 \times 10^{-5} \text{ M Ba}^{2+}}$$

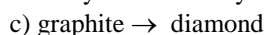


$$\Delta H_{\text{rxn}}^\circ = [(1 \text{ mol graphite})(0 \text{ kJ/mol})] - [(1 \text{ mol diamond})(1.896 \text{ kJ/mol})] = \mathbf{-1.896 \text{ kJ/mol}}$$

$$\Delta S_{\text{rxn}}^\circ = [(1 \text{ mol graphite})(5.686 \text{ J/K}\cdot\text{mol})] - [(1 \text{ mol diamond})(2.439 \text{ kJ/mol})] = \mathbf{3.247 \text{ J/K}}$$

$$\Delta G_{\text{rxn}}^\circ = [(1 \text{ mol graphite})(0 \text{ kJ/mol})] - [(1 \text{ mol diamond})(2.866 \text{ kJ/mol})] = \mathbf{-2.866 \text{ kJ/mol}}$$

b) Since  $\Delta G^\circ$  is negative, the reaction diamond  $\rightarrow$  graphite is spontaneous at room temperature. However, this does not give any information about the rate of reaction, which is very slow. Therefore, diamonds are not forever, but they are for a very long time.



For this process, the signs of  $\Delta H$  and  $\Delta S$  are, like the reaction, reversed. A process with  $\Delta H$  positive and  $\Delta S$  negative is nonspontaneous at all temperatures. Thus, something other than a change in temperature is necessary. That is why diamonds also require a change in pressure.

d) Graphite cannot be converted to diamond spontaneously at 1 atm.

At all temperatures  $\Delta G^\circ > 0$  (nonspontaneous).

20.69

|     | $\Delta S_{\text{rxn}}$ | $\Delta H_{\text{rxn}}$ | $\Delta G_{\text{rxn}}$ | Comment                |
|-----|-------------------------|-------------------------|-------------------------|------------------------|
| (a) | +                       | -                       | -                       | <b>Spontaneous</b>     |
| (b) | (+)                     | 0                       | -                       | Spontaneous            |
| (c) | -                       | +                       | (+)                     | Not spontaneous        |
| (d) | 0                       | (-)                     | -                       | Spontaneous            |
| (e) | (-)                     | 0                       | +                       | <b>Not spontaneous</b> |
| (f) | +                       | +                       | (-)                     | $T\Delta S > \Delta H$ |

a) The reaction is always spontaneous when  $\Delta G_{\text{rxn}} < 0$ , so there is no need to look at the other values other than to check the answer.

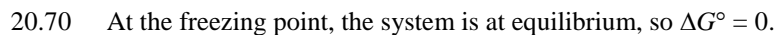
b) Because  $\Delta G_{\text{rxn}} = \Delta H - T\Delta S = -T\Delta S$ ,  $\Delta S$  must be positive for  $\Delta G_{\text{rxn}}$  to be negative.

c) The reaction is always nonspontaneous when  $\Delta G_{\text{rxn}} > 0$ , so there is no need to look at the other values other than to check the answer.

d) Because  $\Delta G_{\text{rxn}} = \Delta H - T\Delta S = \Delta H$ ,  $\Delta H$  must be negative for  $\Delta G_{\text{rxn}}$  to be negative.

e) Because  $\Delta G_{\text{rxn}} = \Delta H - T\Delta S = -T\Delta S$ ,  $\Delta S$  must be negative for  $\Delta G_{\text{rxn}}$  to be positive.

f) Because  $T\Delta S > \Delta H$ , the subtraction of a larger positive term causes  $\Delta G_{\text{rxn}}$  to be negative.



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

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

$$\Delta S^\circ = \Delta H^\circ/T = (2.39 \text{ kJ/mol})/((273.2 + 63.7)\text{K}) = 7.0940932 \times 10^{-3} \text{ kJ/mol}\cdot\text{K}$$

$$\Delta S^\circ = (0.200 \text{ mol})(7.0940932 \times 10^{-3} \text{ kJ/mol}\cdot\text{K}) = 1.4188 \times 10^{-3} = \mathbf{1.42 \times 10^{-3} \text{ kJ/K}}$$

20.71 Plan: Write the equilibrium expression for the reaction. The equilibrium constant,  $K$ , is related to  $\Delta G^\circ$  through the equation  $\Delta G^\circ = -RT \ln K$ . Once  $K$  is known, the ratio of the two species is known.

Solution:

a) For the reaction,  $K = \frac{[\text{Hb}\cdot\text{CO}][\text{O}_2]}{[\text{Hb}\cdot\text{O}_2][\text{CO}]}$  since the problem states that  $[\text{O}_2] = [\text{CO}]$ ; the  $K$  expression simplifies to:

$$K = \frac{[\text{Hb}\cdot\text{CO}]}{[\text{Hb}\cdot\text{O}_2]}$$

$$\ln K_p = \frac{\Delta G^\circ}{-RT} = \left( \frac{-14 \text{ kJ/mol}}{-(8.314 \text{ J/mol}\cdot\text{K})(273 + 37)\text{K}} \right) \left( \frac{10^3 \text{ J}}{1 \text{ kJ}} \right) = 5.431956979$$

$$K = e^{5.431956979} = 228.596 = \mathbf{2.3 \times 10^2} = \frac{[\text{Hb}\cdot\text{CO}]}{[\text{Hb}\cdot\text{O}_2]}$$

b) By increasing the concentration of oxygen, the equilibrium can be shifted in the direction of  $\text{Hb}\cdot\text{O}_2$ . Administer oxygen-rich air to counteract the CO poisoning.

20.72 a)  $\text{MgCO}_3(s) \rightleftharpoons \text{MgO}(s) + \text{CO}_2(g)$

b) Locate the thermodynamic values.

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

$$\Delta H_{\text{rxn}}^\circ = [(1 \text{ mol MgO})(-601.2 \text{ kJ/mol}) + (1 \text{ mol CO}_2)(-393.5 \text{ kJ/mol})] - [(1 \text{ mol MgCO}_3)(-1112 \text{ kJ/mol})] \\ = 117.3 \text{ kJ}$$

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

$$\Delta S_{\text{rxn}}^\circ = [(1 \text{ mol MgO})(26.9 \text{ J/K}\cdot\text{mol}) + (1 \text{ mol CO}_2)(213.7 \text{ J/K}\cdot\text{mol})] - [(1 \text{ mol MgCO}_3)(65.86 \text{ J/K}\cdot\text{mol})] \\ = 174.74 \text{ J/K}$$

$$\Delta G_{\text{rxn}}^\circ = \Delta H_{\text{rxn}}^\circ - T \Delta S_{\text{rxn}}^\circ = 117.3 \text{ kJ} - (298 \text{ K})(174.74 \text{ J/K})(1 \text{ kJ}/10^3 \text{ J}) = 65.22748 = \mathbf{65.2 \text{ kJ}}$$

c)  $\Delta G_{\text{rxn}}^\circ = 0 = \Delta H_{\text{rxn}}^\circ - T \Delta S_{\text{rxn}}^\circ$

$$\Delta H_{\text{rxn}}^\circ = T \Delta S_{\text{rxn}}^\circ$$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{117.3 \text{ kJ}}{0.17474 \text{ kJ/K}} = \mathbf{671 \text{ K}}$$

d)  $K_p = P_{\text{CO}_2}$  and  $\Delta G^\circ = -RT \ln K$  are necessary.

$$\ln K = \frac{\Delta G^\circ}{-RT} = \left( \frac{65.22748 \text{ kJ/mol}}{-(8.314 \text{ J/mol}\cdot\text{K})(298 \text{ K})} \right) \left( \frac{10^3 \text{ J}}{1 \text{ kJ}} \right) = -26.327178$$

$$K = e^{-26.327178} = 3.6834253 \times 10^{-12} = \mathbf{3.68 \times 10^{-12} \text{ atm}} = P_{\text{CO}_2}$$

e) This is similar to part d) except a new  $\Delta G^\circ$  must be determined at 1200 K.

$$\Delta G_{\text{rxn}}^\circ = \Delta H_{\text{rxn}}^\circ - T \Delta S_{\text{rxn}}^\circ = 117.3 \text{ kJ} - (1200 \text{ K})(174.74 \text{ J/K})(1 \text{ kJ}/10^3 \text{ J}) = -92.388 \text{ kJ}$$

$$\ln K = \frac{\Delta G^\circ}{-RT} = \left( \frac{-92.388 \text{ kJ/mol}}{-(8.314 \text{ J/mol}\cdot\text{K})(1200 \text{ K})} \right) \left( \frac{10^3 \text{ J}}{1 \text{ kJ}} \right) = 9.26028$$

$$K = e^{9.26028} = 1.0512 \times 10^4 = \mathbf{1.05 \times 10^4 \text{ atm}} = P_{\text{CO}_2}$$

20.73  $\text{CO}(g) + 2\text{H}_2(g) \rightarrow \text{CH}_3\text{OH}(l)$

$$\text{a) } \Delta H_{\text{rxn}}^\circ = [(1 \text{ mol CH}_3\text{OH})(-238.6 \text{ kJ/mol})] - [(1 \text{ mol CO})(-110.5 \text{ kJ/mol}) + (2 \text{ mol H}_2)(0 \text{ kJ/mol})] \\ = -128.1 \text{ kJ}$$

$$\Delta S_{\text{rxn}}^\circ = [(1 \text{ mol CH}_3\text{OH})(127 \text{ J/K}\cdot\text{mol})] - [(1 \text{ mol CO})(197.5 \text{ J/K}\cdot\text{mol}) + (2 \text{ mol H}_2)(130.6 \text{ J/K}\cdot\text{mol})] \\ = -331.7 \text{ J/K}$$

$$\Delta G_{\text{rxn}}^{\circ} = \Delta H_{\text{rxn}}^{\circ} - T\Delta S_{\text{rxn}}^{\circ} = -128.1 \text{ kJ} - [(298 \text{ K})(-331.7 \text{ J/K})(1 \text{ kJ}/10^3 \text{ J})] = -29.2534 = -29.2 \text{ kJ}$$

The negative value of  $\Delta G^{\circ}$  indicates that the reaction is spontaneous (feasible).

b)  $\Delta H^{\circ}$  negative and  $\Delta S^{\circ}$  negative means the reaction is favored at low temperature.

c)  $\text{CH}_3\text{OH}(g) + 1/2\text{O}_2(g) \rightarrow \text{CH}_2\text{O}(g) + \text{H}_2\text{O}(g)$

$$\begin{aligned}\Delta H_{\text{rxn}}^{\circ} &= [(1 \text{ mol CH}_2\text{O})(-116 \text{ kJ/mol}) + (1 \text{ mol H}_2\text{O})(-241.826 \text{ kJ/mol})] \\ &\quad - [(1 \text{ mol CH}_3\text{OH})(-201.2 \text{ kJ/mol}) + (1/2 \text{ mol O}_2)(0 \text{ kJ/mol})] \\ &= -156.626 \text{ kJ}\end{aligned}$$

$$\begin{aligned}\Delta S_{\text{rxn}}^{\circ} &= [(1 \text{ mol CH}_2\text{O})(219 \text{ J/K}\cdot\text{mol}) + (1 \text{ mol H}_2\text{O})(188.72 \text{ J/K}\cdot\text{mol})] \\ &\quad - [(1 \text{ mol CH}_3\text{OH})(238 \text{ J/K}\cdot\text{mol}) + (1/2 \text{ mol O}_2)(205.0 \text{ J/K}\cdot\text{mol})] \\ &= 67.22 \text{ J/K}\end{aligned}$$

$$\Delta G_{\text{rxn}}^{\circ} = \Delta H_{\text{rxn}}^{\circ} - T\Delta S_{\text{rxn}}^{\circ} = -156.626 \text{ kJ} - [(273 + 100.)\text{K})(67.22 \text{ J/K})(1 \text{ kJ}/10^3 \text{ J})] = -181.699 = \mathbf{-182 \text{ kJ}}$$

20.74 Plan:  $\Delta G_{\text{rxn}}^{\circ}$  can be calculated with the relationship  $\sum m \Delta G_{\text{f}}^{\circ}(\text{products}) - \sum n \Delta G_{\text{f}}^{\circ}(\text{reactants})$ .  $\Delta G$  is found by using the relationship  $\Delta G = \Delta G^{\circ} + RT \ln Q$ .

Solution:

a)  $2\text{N}_2\text{O}_5(g) + 6\text{F}_2(g) \rightarrow 4\text{NF}_3(g) + 5\text{O}_2(g)$

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

$$\begin{aligned}\Delta G_{\text{rxn}}^{\circ} &= [(4 \text{ mol NF}_3)(\Delta G_{\text{f}}^{\circ} \text{ of NF}_3) + (5 \text{ mol O}_2)(\Delta G_{\text{f}}^{\circ} \text{ of O}_2)] \\ &\quad - [(2 \text{ mol N}_2\text{O}_5)(\Delta G_{\text{f}}^{\circ} \text{ of N}_2\text{O}_5) + (6 \text{ mol F}_2)(\Delta G_{\text{f}}^{\circ} \text{ of F}_2)]\end{aligned}$$

$$\Delta G_{\text{rxn}}^{\circ} = [(4 \text{ mol})(-83.3 \text{ kJ/mol}) + (5 \text{ mol})(0 \text{ kJ/mol})] - [(2 \text{ mol})(118 \text{ kJ/mol}) + (6 \text{ mol})(0 \text{ kJ/mol})]$$

$$\Delta G_{\text{rxn}}^{\circ} = -569.2 = \mathbf{-569 \text{ kJ}}$$

c) Calculate the value for  $Q$  and then use to find  $\Delta G$ .

$$Q = \frac{[\text{NF}_3]^4 [\text{O}_2]^5}{[\text{N}_2\text{O}_5]^2 [\text{F}_2]^6} = \frac{[0.25 \text{ atm}]^4 [0.50 \text{ atm}]^5}{[0.20 \text{ atm}]^2 [0.20 \text{ atm}]^6} = 47.6837$$

$$\begin{aligned}\Delta G &= \Delta G^{\circ} + RT \ln Q = -569.2 \text{ kJ/mol} + (1 \text{ kJ}/10^3 \text{ J})(8.314 \text{ J/mol}\cdot\text{K})(298) \ln (47.6837) \\ &= -559.625 = \mathbf{-5.60 \times 10^2 \text{ kJ/mol}}\end{aligned}$$

20.75 a)  $\Delta S_{\text{rxn}}^{\circ} = [(2 \text{ mol NO})(210.65 \text{ J/K}\cdot\text{mol}) + (1 \text{ mol Br}_2)(245.38 \text{ J/K}\cdot\text{mol})] - [(2 \text{ mol NOBr})(272.6 \text{ J/mol}\cdot\text{K})]$   
 $\Delta S_{\text{rxn}}^{\circ} = 121.48 = \mathbf{121.5 \text{ J/K}}$

b)  $\Delta G_{\text{rxn}}^{\circ} = -RT \ln K = -(8.314 \text{ J/mol}\cdot\text{K})(373 \text{ K}) \ln (0.42) = 2690.225 = \mathbf{2.7 \times 10^3 \text{ J/mol}}$

c)  $\Delta G_{\text{rxn}}^{\circ} = \Delta H_{\text{rxn}}^{\circ} - T\Delta S_{\text{rxn}}^{\circ}$

$$\Delta H_{\text{rxn}}^{\circ} = \Delta G_{\text{rxn}}^{\circ} + T\Delta S_{\text{rxn}}^{\circ} = 2690.225 \text{ J/mol} + (373)(121.48 \text{ J/K}) = 4.8002265 \times 10^4 = \mathbf{4.80 \times 10^4 \text{ J/mol}}$$

d)  $\Delta H_{\text{rxn}}^{\circ} = [(2 \text{ mol NO})(90.29 \text{ kJ/mol}) + (1 \text{ mol Br}_2)(30.91 \text{ kJ/mol})] - [(2 \text{ mol NOBr})(\Delta H_{\text{f}}^{\circ} \text{ of NOBr})]$   
 $(2 \text{ mol NOBr})(\Delta H_{\text{f}}^{\circ} \text{ of NOBr}) = [(2 \text{ mol})(90.29 \text{ kJ}) + (1 \text{ mol})(30.91 \text{ kJ})] - (4.8002265 \times 10^4 \text{ J})(1 \text{ kJ}/10^3 \text{ J})$

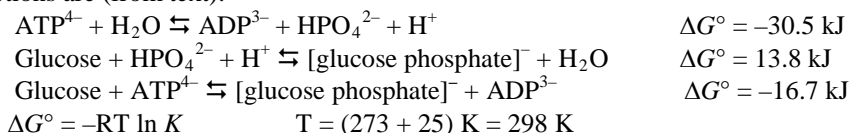
$$\Delta H_{\text{f}}^{\circ} \text{ of NOBr} = 81.7438675 = \mathbf{81.7 \text{ kJ/mol}}$$

e)  $\Delta G_{\text{rxn}}^{\circ} = \Delta H_{\text{rxn}}^{\circ} - T\Delta S_{\text{rxn}}^{\circ} = 4.8002265 \times 10^4 \text{ J/mol} - (298 \text{ K})(121.48 \text{ J/mol}\cdot\text{K})$   
 $= 1.1801225 \times 10^4 = \mathbf{1.18 \times 10^4 \text{ J/mol}}$

f)  $\Delta G_{\text{rxn}}^{\circ} = [(2 \text{ mol NO})(86.60 \text{ kJ/mol}) + (1 \text{ mol Br}_2)(3.13 \text{ kJ/mol})] - [(2 \text{ mol NOBr})(\Delta G_{\text{f}}^{\circ} \text{ of NOBr})]$   
 $(2 \text{ mol NOBr})(\Delta G_{\text{f}}^{\circ} \text{ of NOBr}) = [(2 \text{ mol})(86.60 \text{ kJ}) + (1 \text{ mol})(3.13 \text{ kJ})] - (1.1801225 \times 10^4 \text{ J})(1 \text{ kJ}/10^3 \text{ J})$

$$\Delta G_{\text{f}}^{\circ} \text{ of NOBr} = 82.264 = \mathbf{82.3 \text{ kJ/mol}}$$

20.76 The reactions are (from text):



$$\begin{aligned} \text{a) } \ln K &= \frac{\Delta G^\circ}{-RT} = \left( \frac{-30.5 \text{ kJ/mol}}{-(8.314 \text{ J/mol}\cdot\text{K})(298 \text{ K})} \right) \left( \frac{10^3 \text{ J}}{1 \text{ kJ}} \right) = 12.3104 \\ K &= e^{12.3104} = 2.2199 \times 10^5 = \mathbf{2.22 \times 10^5} \end{aligned}$$

$$\begin{aligned} \text{b) } \ln K &= \frac{\Delta G^\circ}{-RT} = \left( \frac{13.8 \text{ kJ/mol}}{-(8.314 \text{ J/mol}\cdot\text{K})(298 \text{ K})} \right) \left( \frac{10^3 \text{ J}}{1 \text{ kJ}} \right) = -5.569969 \\ K &= e^{-5.569969} = 3.8105985 \times 10^{-3} = \mathbf{3.81 \times 10^{-3}} \end{aligned}$$

$$\begin{aligned} \text{c) } \ln K &= \frac{\Delta G^\circ}{-RT} = \left( \frac{-16.7 \text{ kJ/mol}}{-(8.314 \text{ J/mol}\cdot\text{K})(298 \text{ K})} \right) \left( \frac{10^3 \text{ J}}{1 \text{ kJ}} \right) = 6.74047 \\ K &= e^{6.74047} = 8.45958 \times 10^2 = \mathbf{8.46 \times 10^2} \end{aligned}$$

d) Repeat the calculations at the new temperature.  $T = (273 + 37) = 310. \text{ K}$

$$\begin{aligned} \ln K &= \frac{\Delta G^\circ}{-RT} = \left( \frac{-30.5 \text{ kJ/mol}}{-(8.314 \text{ J/mol}\cdot\text{K})(310. \text{ K})} \right) \left( \frac{10^3 \text{ J}}{1 \text{ kJ}} \right) = 11.8339 \\ K &= e^{11.8339} = 1.37847 \times 10^5 = \mathbf{1.38 \times 10^5} \end{aligned}$$

$$\begin{aligned} \ln K &= \frac{\Delta G^\circ}{-RT} = \left( \frac{13.8 \text{ kJ/mol}}{-(8.314 \text{ J/mol}\cdot\text{K})(310. \text{ K})} \right) \left( \frac{10^3 \text{ J}}{1 \text{ kJ}} \right) = -5.3543576 \\ K &= e^{-5.3543576} = 4.7275 \times 10^{-3} = \mathbf{4.73 \times 10^{-3}} \end{aligned}$$

$$\begin{aligned} \ln K &= \frac{\Delta G^\circ}{-RT} = \left( \frac{-16.7 \text{ kJ/mol}}{-(8.314 \text{ J/mol}\cdot\text{K})(310. \text{ K})} \right) \left( \frac{10^3 \text{ J}}{1 \text{ kJ}} \right) = 6.4795 \\ K &= e^{6.4795} = 6.51645 \times 10^2 = \mathbf{6.52 \times 10^2} \end{aligned}$$

20.77  $2\text{HF}(g) \rightleftharpoons \text{H}_2(g) + \text{F}_2(g)$

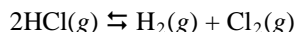
$$\Delta G^\circ = [(1 \text{ mol H}_2)(\Delta G_f^\circ \text{ of H}_2) + (1 \text{ mol F}_2)(\Delta G_f^\circ \text{ of F}_2)] - [(2 \text{ mol HF})(\Delta G_f^\circ \text{ of HF})]$$

$$\Delta G^\circ = [(1 \text{ mol})(0 \text{ kJ/mol}) + (1 \text{ mol})(0 \text{ kJ/mol})] - [(2 \text{ mol})(-275 \text{ kJ/mol})] = 550. \text{ kJ}$$

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

$$\ln K = \frac{\Delta G^\circ}{-RT} = \left( \frac{550. \text{ kJ/mol}}{-(8.314 \text{ J/mol}\cdot\text{K})(298 \text{ K})} \right) \left( \frac{10^3 \text{ J}}{1 \text{ kJ}} \right) = -221.9915$$

$$K = e^{-221.9915} = 3.8932879 \times 10^{-97} = \mathbf{4 \times 10^{-97}}$$



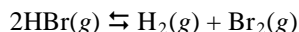
$$\Delta G^\circ = [(1 \text{ mol H}_2)(\Delta G_f^\circ \text{ of H}_2) + (1 \text{ mol Cl}_2)(\Delta G_f^\circ \text{ of Cl}_2)] - [(2 \text{ mol HCl})(\Delta G_f^\circ \text{ of HCl})]$$

$$\Delta G^\circ = [(1 \text{ mol})(0 \text{ kJ/mol}) + (1 \text{ mol})(0 \text{ kJ/mol})] - [(2 \text{ mol})(-95.30 \text{ kJ/mol})] = 190.60 \text{ kJ}$$

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

$$\ln K = \frac{\Delta G^\circ}{-RT} = \left( \frac{190.60 \text{ kJ/mol}}{-(8.314 \text{ J/mol}\cdot\text{K})(298 \text{ K})} \right) \left( \frac{10^3 \text{ J}}{1 \text{ kJ}} \right) = -76.930$$

$$K = e^{-76.930} = 3.88799 \times 10^{-34} = \mathbf{4 \times 10^{-34}}$$



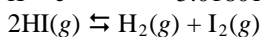
$$\Delta G^\circ = [(1 \text{ mol H}_2)(\Delta G_f^\circ \text{ of H}_2) + (1 \text{ mol Br}_2)(\Delta G_f^\circ \text{ of Cl}_2)] - [(2 \text{ mol HBr})(\Delta G_f^\circ \text{ of HBr})]$$

$$\Delta G^\circ = [(1 \text{ mol})(0 \text{ kJ/mol}) + (1 \text{ mol})(3.13 \text{ kJ/mol})] - [(2 \text{ mol})(-53.6 \text{ kJ/mol})] = 110.1 \text{ kJ}$$

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

$$\ln K = \frac{\Delta G^\circ}{-RT} = \left( \frac{110.1 \text{ kJ/mol}}{-(8.314 \text{ J/mol}\cdot\text{K})(298 \text{ K})} \right) \left( \frac{10^3 \text{ J}}{1 \text{ kJ}} \right) = -44.438668$$

$$K = e^{-44.438668} = 5.01801 \times 10^{-20} = \mathbf{5 \times 10^{-20}}$$



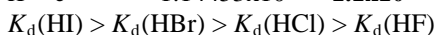
$$\Delta G^\circ = [(1 \text{ mol H}_2)(\Delta G_f^\circ \text{ of H}_2) + (1 \text{ mol I}_2)(\Delta G_f^\circ \text{ of I}_2)] - [(2 \text{ mol HI})(\Delta G_f^\circ \text{ of HI})]$$

$$\Delta G^\circ = [(1 \text{ mol})(0 \text{ kJ/mol}) + (1 \text{ mol})(19.38 \text{ kJ/mol})] - [(2 \text{ mol})(1.3 \text{ kJ/mol})] = 16.78 \text{ kJ}$$

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

$$\ln K = \frac{\Delta G^\circ}{-RT} = \left( \frac{16.78 \text{ kJ/mol}}{-(8.314 \text{ J/mol}\cdot\text{K})(298 \text{ K})} \right) \left( \frac{10^3 \text{ J}}{1 \text{ kJ}} \right) = -6.77276$$

$$K = e^{-6.77276} = 1.14453 \times 10^{-3} = \mathbf{1.1 \times 10^{-3}}$$



Hydrogen iodide is the most easily decomposed of all the hydrogen halides. The hydrogen halide bond energy decreases down the halogen group as the atomic radius of the halogen increases.

- 20.78 Plan:  $\Delta H_{\text{rxn}}^\circ$  can be calculated from the individual  $\Delta H_f^\circ$  values of the reactants and products by using the relationship  $\Delta H_{\text{rxn}}^\circ = \sum m \Delta H_f^\circ(\text{products}) - \sum n \Delta H_f^\circ(\text{reactants})$ .  $\Delta S_{\text{rxn}}^\circ$  can be calculated from the individual  $S^\circ$  values of the reactants and products by using the relationship  $\Delta S_{\text{rxn}}^\circ = \sum m S_{\text{products}}^\circ - \sum n S_{\text{reactants}}^\circ$ . Once  $\Delta H_{\text{rxn}}^\circ$  and  $\Delta S_{\text{rxn}}^\circ$  are known,  $\Delta G^\circ$  can be calculated with the relationship  $\Delta G_{\text{rxn}}^\circ = \Delta H_{\text{rxn}}^\circ - T \Delta S_{\text{rxn}}^\circ$ .  $\Delta S_{\text{rxn}}^\circ$  values in J/K must be converted to units of kJ/K to match the units of  $\Delta H_{\text{rxn}}^\circ$ . To find the temperature at which the reaction becomes spontaneous, use  $\Delta G_{\text{rxn}}^\circ = 0 = \Delta H_{\text{rxn}}^\circ - T \Delta S_{\text{rxn}}^\circ$  and solve for temperature.

Solution:

a) The chemical equation for this process is  $3\text{C}(s) + 2\text{Fe}_2\text{O}_3(s) \rightarrow 3\text{CO}_2(g) + 4\text{Fe}(s)$

$$\Delta H_{\text{rxn}}^\circ = [(3 \text{ mol CO}_2)(\Delta H_f^\circ \text{ of CO}_2) + (4 \text{ mol Fe})(\Delta H_f^\circ \text{ of Fe})] - [(3 \text{ mol C})(\Delta H_f^\circ \text{ of C}) + (2 \text{ mol Fe}_2\text{O}_3)(\Delta H_f^\circ \text{ of Fe}_2\text{O}_3)]$$

$$\Delta H_{\text{rxn}}^\circ = [(3 \text{ mol})(-393.5 \text{ kJ/mol}) + (4 \text{ mol})(0 \text{ kJ/mol})] - [(3 \text{ mol})(0 \text{ kJ/mol}) + (2 \text{ mol})(-825.5 \text{ kJ/mol})]$$

$$\Delta H_{\text{rxn}}^\circ = \mathbf{470.5 \text{ kJ}}$$

$$\Delta S_{\text{rxn}}^\circ = [(3 \text{ mol CO}_2)(S^\circ \text{ of CO}_2) + (4 \text{ mol Fe})(S^\circ \text{ of Fe})] - [(3 \text{ mol C})(S^\circ \text{ of C}) + (2 \text{ mol Fe}_2\text{O}_3)(S^\circ \text{ of Fe}_2\text{O}_3)]$$

$$\Delta S_{\text{rxn}}^\circ = [(3 \text{ mol})(213.7 \text{ J/mol}\cdot\text{K}) + (4 \text{ mol})(27.3 \text{ J/mol}\cdot\text{K})] - [(3 \text{ mol})(5.686 \text{ J/mol}\cdot\text{K}) + (2 \text{ mol})(87.400 \text{ J/mol}\cdot\text{K})]$$

$$\Delta S_{\text{rxn}}^\circ = 558.442 = \mathbf{558.4 \text{ J/K}}$$

b) The reaction will be spontaneous at higher temperatures, where the  $-T\Delta S$  term will be larger in magnitude than  $\Delta H$ .

$$\text{c) } \Delta G_{\text{rxn}}^\circ = \Delta H_{\text{rxn}}^\circ - T \Delta S_{\text{rxn}}^\circ = 470.5 \text{ kJ} - [(298 \text{ K})(558.442 \text{ J/K})(1 \text{ kJ}/10^3 \text{ J})] = 304.084 = 304.1 \text{ kJ}$$

Because  $\Delta G$  is positive, the reaction is **not spontaneous**.

d) The temperature at which the reaction becomes spontaneous is found by calculating

$$\Delta G_{\text{rxn}}^\circ = 0 = \Delta H_{\text{rxn}}^\circ - T \Delta S_{\text{rxn}}^\circ$$

$$\Delta H_{\text{rxn}}^\circ = T \Delta S_{\text{rxn}}^\circ$$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{470.5 \text{ kJ}}{558.442 \text{ J/K}} \left( \frac{10^3 \text{ J}}{1 \text{ kJ}} \right) = 842.5225896 = \mathbf{842.5 \text{ K}}$$

20.79 Use the given reaction:  $\text{Cl}_2(g) + \text{Br}_2(g) \rightarrow 2\text{BrCl}(g)$  and the appendix to determine the desired values.

$$\Delta H_{\text{rxn}}^{\circ} = [(2 \text{ mol BrCl})(\Delta H_f^{\circ} \text{ of BrCl})] - [(1 \text{ mol Cl}_2)(\Delta H_f^{\circ} \text{ of Cl}_2) + (1 \text{ mol Br}_2)(\Delta H_f^{\circ} \text{ of Br}_2)]$$

$$-1.35 \text{ kJ/mol} = [(2 \text{ mol})(\Delta H_f^{\circ} \text{ of BrCl})] - [(1 \text{ mol})(0 \text{ kJ/mol}) + (1 \text{ mol})(30.91 \text{ kJ/mol})]$$

$$-1.35 \text{ kJ/mol} = [(2 \text{ mol})(\Delta H_f^{\circ} \text{ of BrCl})] - [(1 \text{ mol})(30.91 \text{ kJ/mol})]$$

$$-1.35 \text{ kJ/mol} + [(1 \text{ mol})(30.91 \text{ kJ/mol})] = [(2 \text{ mol})(\Delta H_f^{\circ} \text{ of BrCl})]$$

$$29.56 \text{ kJ/mol} = [(2 \text{ mol})(\Delta H_f^{\circ} \text{ of BrCl})]$$

$$\Delta H_f^{\circ} \text{ of BrCl} = \mathbf{14.78 \text{ kJ/mol}}$$

$$\Delta G_{\text{rxn}}^{\circ} = -0.88 \text{ kJ/mol} = \Delta H_{\text{rxn}}^{\circ} - T\Delta S_{\text{rxn}}^{\circ}$$

$$-0.88 \text{ kJ/mol} = -1.35 \text{ kJ/mol} - (298 \text{ K})\Delta S_{\text{rxn}}^{\circ}$$

$$0.88 \text{ kJ/mol} - 1.35 \text{ kJ/mol} = -0.47 \text{ kJ/mol} = (298 \text{ K})\Delta S_{\text{rxn}}^{\circ}$$

$$(-0.47 \text{ kJ/mol})/(298 \text{ K}) = \Delta S_{\text{rxn}}^{\circ}$$

$$\Delta S_{\text{rxn}}^{\circ} = (-0.001577181 \text{ kJ/mol}\cdot\text{K})(10^3 \text{ J/1 kJ}) = -1.577181 \text{ J/mol}\cdot\text{K}$$

$$\Delta S_{\text{rxn}}^{\circ} = [(2 \text{ mol BrCl})(S^{\circ} \text{ of BrCl})] - [(1 \text{ mol Cl}_2)(S^{\circ} \text{ of Cl}_2) + (1 \text{ mol Br}_2)(S^{\circ} \text{ of Br}_2)]$$

$$-1.577181 \text{ J/mol}\cdot\text{K} = [(2 \text{ mol})(S^{\circ} \text{ of BrCl})] - [(1 \text{ mol})(223.0 \text{ J/mol}\cdot\text{K}) + (1 \text{ mol})(245.38 \text{ J/mol}\cdot\text{K})]$$

$$-1.577181 \text{ J/mol}\cdot\text{K} = [(2 \text{ mol})(S^{\circ} \text{ of BrCl})] - [468.38 \text{ J/mol}\cdot\text{K}]$$

$$466.802819 \text{ J/mol}\cdot\text{K} = [(2 \text{ mol})(S^{\circ} \text{ of BrCl})]$$

$$S^{\circ} \text{ of BrCl} = 233.4014 = \mathbf{233.4 \text{ J/mol}\cdot\text{K}}$$

20.80 Plan: To determine if the reactions in parts a and b are spontaneous or not, calculate  $\Delta G^{\circ}$  for the reaction and see if the value is positive or negative.  $\Delta G^{\circ}$  can be calculated with the relationship  $\sum m \Delta G_f^{\circ}(\text{products}) -$

$\sum n \Delta G_f^{\circ}(\text{reactants})$ .  $\Delta H_{\text{rxn}}^{\circ}$  can be calculated from the individual  $\Delta H_f^{\circ}$  values of the reactants and products by using

the relationship  $\Delta H_{\text{rxn}}^{\circ} = \sum m \Delta H_f^{\circ}(\text{products}) - \sum n \Delta H_f^{\circ}(\text{reactants})$ .  $\Delta S_{\text{rxn}}^{\circ}$  can be calculated from the individual

$S^{\circ}$  values of the reactants and products by using the relationship  $\Delta S_{\text{rxn}}^{\circ} = \sum m S^{\circ}_{\text{products}} - \sum n S^{\circ}_{\text{reactants}}$ . To find

the temperature at which the reactions in part b and c become spontaneous, use  $\Delta G_{\text{rxn}}^{\circ} = 0 = \Delta H_{\text{rxn}}^{\circ} - T\Delta S_{\text{rxn}}^{\circ}$  and solve for temperature.

Solution:

a) The balanced chemical equation is  $\text{N}_2\text{O}_5(s) + \text{H}_2\text{O}(l) \rightarrow 2\text{HNO}_3(l)$

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

$$\Delta G^{\circ} = [(2 \text{ mol HNO}_3)(\Delta G_f^{\circ} \text{ of HNO}_3)] - [(1 \text{ mol N}_2\text{O}_5)(\Delta G_f^{\circ} \text{ of N}_2\text{O}_5) + (1 \text{ mol H}_2\text{O})(\Delta G_f^{\circ} \text{ of H}_2\text{O})]$$

$$\Delta G^{\circ} = [(2 \text{ mol})(-79.914 \text{ kJ/mol})] - [(1 \text{ mol})(114 \text{ kJ/mol}) + (1 \text{ mol})(-237.192 \text{ kJ/mol})] = -36.636 = -37 \text{ kJ}$$

**Yes**, the reaction is spontaneous because the value of  $\Delta G^{\circ}$  is negative.

b) The balanced chemical equation is  $2\text{N}_2\text{O}_5(s) \rightarrow 4\text{NO}_2(g) + \text{O}_2(g)$

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

$$\Delta G^{\circ} = [(4 \text{ mol NO}_2)(\Delta G_f^{\circ} \text{ of NO}_2) + (1 \text{ mol O}_2)(\Delta G_f^{\circ} \text{ of O}_2)] - [(2 \text{ mol N}_2\text{O}_5)(\Delta G_f^{\circ} \text{ of N}_2\text{O}_5)]$$

$$\Delta G^{\circ} = [(4 \text{ mol})(51 \text{ kJ/mol}) + (1 \text{ mol})(0 \text{ kJ/mol})] - [(2 \text{ mol})(114 \text{ kJ/mol})] = -24 \text{ kJ}$$

**Yes**, the reaction is spontaneous because the value of  $\Delta G^{\circ}$  is negative.

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

$$\Delta H_{\text{rxn}}^{\circ} = [(4 \text{ mol NO}_2)(\Delta H_{\text{f}}^{\circ} \text{ of NO}_2) + (1 \text{ mol O}_2)(\Delta H_{\text{f}}^{\circ} \text{ of O}_2)] - [(2 \text{ mol N}_2\text{O}_5)(\Delta H_{\text{f}}^{\circ} \text{ of N}_2\text{O}_5)]$$

$$\Delta H_{\text{rxn}}^{\circ} = [(4 \text{ mol NO}_2)(33.2 \text{ kJ/mol}) + (1 \text{ mol O}_2)(0 \text{ kJ/mol})] - [(2 \text{ mol N}_2\text{O}_5)(-43.1 \text{ kJ/mol})]$$

$$\Delta H_{\text{rxn}}^{\circ} = 219.0 \text{ kJ}$$

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

$$\Delta S_{\text{rxn}}^{\circ} = [(4 \text{ mol NO}_2)(S^{\circ} \text{ of NO}_2) + (1 \text{ mol O}_2)(S^{\circ} \text{ of O}_2)] - [(2 \text{ mol N}_2\text{O}_5)(S^{\circ} \text{ of N}_2\text{O}_5)]$$

$$\Delta S_{\text{rxn}}^{\circ} = [(4 \text{ mol})(239.9 \text{ J/mol}\cdot\text{K}) + (1 \text{ mol})(205.0 \text{ J/mol}\cdot\text{K})] - [(2 \text{ mol})(178 \text{ J/mol}\cdot\text{K})]$$

$$\Delta S_{\text{rxn}}^{\circ} = 808.6 \text{ J/K} = 0.808 \text{ kJ/K}$$

$$\Delta G_{\text{rxn}}^{\circ} = 0 = \Delta H_{\text{rxn}}^{\circ} - T \Delta S_{\text{rxn}}^{\circ}$$

$$\Delta H_{\text{rxn}}^{\circ} = T \Delta S_{\text{rxn}}^{\circ}$$

$$T = \frac{\Delta H^{\circ}}{\Delta S^{\circ}} = \frac{219 \text{ kJ}}{0.808 \text{ kJ/K}} = 270.838 = \mathbf{270.8 \text{ K}}$$

c) The balanced chemical equation is  $2\text{N}_2\text{O}_5(\text{g}) \rightarrow 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$

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

$$\Delta H_{\text{rxn}}^{\circ} = [(4 \text{ mol NO}_2)(\Delta H_{\text{f}}^{\circ} \text{ of NO}_2) + (1 \text{ mol O}_2)(\Delta H_{\text{f}}^{\circ} \text{ of O}_2)] - [(2 \text{ mol N}_2\text{O}_5)(\Delta H_{\text{f}}^{\circ} \text{ of N}_2\text{O}_5)]$$

$$\Delta H_{\text{rxn}}^{\circ} = [(4 \text{ mol NO}_2)(33.2 \text{ kJ/mol}) + (1 \text{ mol O}_2)(0 \text{ kJ/mol})] - [(2 \text{ mol N}_2\text{O}_5)(11 \text{ kJ/mol})]$$

$$\Delta H_{\text{rxn}}^{\circ} = 110.8 = 111 \text{ kJ}$$

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

$$\Delta S_{\text{rxn}}^{\circ} = [(4 \text{ mol NO}_2)(S^{\circ} \text{ of NO}_2) + (1 \text{ mol O}_2)(S^{\circ} \text{ of O}_2)] - [(2 \text{ mol N}_2\text{O}_5)(S^{\circ} \text{ of N}_2\text{O}_5)]$$

$$\Delta S_{\text{rxn}}^{\circ} = [(4 \text{ mol})(239.9 \text{ J/mol}\cdot\text{K}) + (1 \text{ mol})(205.0 \text{ J/mol}\cdot\text{K})] - [(2 \text{ mol})(346 \text{ J/mol}\cdot\text{K})]$$

$$\Delta S_{\text{rxn}}^{\circ} = 472.6 = 0.4726 \text{ kJ/K}$$

$$\Delta G_{\text{rxn}}^{\circ} = 0 = \Delta H_{\text{rxn}}^{\circ} - T \Delta S_{\text{rxn}}^{\circ}$$

$$\Delta H_{\text{rxn}}^{\circ} = T \Delta S_{\text{rxn}}^{\circ}$$

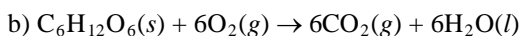
$$T = \frac{\Delta H^{\circ}}{\Delta S^{\circ}} = \frac{110.8 \text{ kJ}}{0.4726 \text{ kJ/K}} = 234.4477 = \mathbf{234 \text{ K}}$$

The temperature is different because the values for  $\text{N}_2\text{O}_5$  vary with physical state.

20.81 a)  $\text{ATP}^{4+} + \text{H}_2\text{O} \rightleftharpoons \text{ADP}^{3+} + \text{HPO}_4^{2-} + \text{H}^+ \quad \Delta G^{\circ} = -30.5 \text{ kJ}$

$$\ln K = \frac{\Delta G^{\circ}}{-RT} = \left( \frac{-30.5 \text{ kJ/mol}}{-(8.314 \text{ J/mol}\cdot\text{K})(310. \text{ K})} \right) \left( \frac{10^3 \text{ J}}{1 \text{ kJ}} \right) = 11.8339$$

$$K = e^{11.8339} = 1.37847 \times 10^5 = \mathbf{1.38 \times 10^5}$$



$$\Delta G_{\text{rxn}}^{\circ} = [(6 \text{ mol CO}_2)(\Delta G_{\text{f}}^{\circ} \text{ of CO}_2) + (6 \text{ mol H}_2\text{O})(\Delta G_{\text{f}}^{\circ} \text{ of H}_2\text{O})]$$

$$- [(1 \text{ mol C}_6\text{H}_{12}\text{O}_6)(\Delta G_{\text{f}}^{\circ} \text{ of C}_6\text{H}_{12}\text{O}_6) + (6 \text{ mol O}_2)(\Delta G_{\text{f}}^{\circ} \text{ of O}_2)]$$

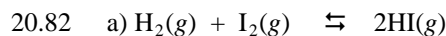
$$\Delta G_{\text{rxn}}^{\circ} = [(6 \text{ mol})(-394.4 \text{ kJ/mol}) + (6 \text{ mol})(-237.192 \text{ kJ/mol})] - [(1 \text{ mol})(-910.56 \text{ kJ/mol}) + (6 \text{ mol})(0 \text{ kJ/mol})]$$

$$\Delta G_{\text{rxn}}^{\circ} = -2878.992 = \mathbf{-2879.0 \text{ kJ}}$$

c)  $\left( \frac{1 \text{ mol ATP}}{-30.5 \text{ kJ}} \right) \left( \frac{-2878.992 \text{ kJ}}{1 \text{ mol glucose}} \right) = 94.39318 = \mathbf{94.4 \text{ mol ATP/mol glucose}}$

d) The actual yield is 36 moles ATP (this is assumed to be an exact value). The percent yield is:

$$\left( \frac{36 \text{ mol ATP}}{94.39318 \text{ mol ATP}} \right) \times 100\% = 38.1383 = \mathbf{38.1\%}$$



$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{[0.10]^2}{[0.010][0.020]} = 50 \quad K_c > 1$$

b)  $K_p = K_c(RT)^{\Delta n_{\text{gas}}}$

$$K_p = 50[(0.0821 \text{ Latm/molK})(733 \text{ K})]^0$$

$$K_p = \mathbf{50 = K_c}$$

c)  $\Delta G^\circ = -RT \ln K = -(8.314 \text{ J/mol}\cdot\text{K})(733 \text{ K}) \ln(50) = 2.38405 \times 10^4 = \mathbf{2.4 \times 10^4 \text{ J/mol}}$

d)  $K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{[0.10]^2}{[0.020][0.010]} = 50$

The value of  $K_c$  is 50 in this situation as in a) so  $\Delta G^\circ$  does not change.

20.83 a) **Graph D** depicts how  $G_{\text{sys}}$  changes for the chemical reaction.  $G$  decreases as the reaction proceeds from either pure reactant or pure product until it reaches the minimum at equilibrium. Beyond that in either direction the reaction is nonspontaneous.

b) **Graph A** depicts how  $G_{\text{sys}}$  changes as ice melts at  $1^\circ\text{C}$ .  $1^\circ\text{C}$  is higher than the melting point of water, therefore the system is not at equilibrium. Melting is spontaneous at  $1^\circ\text{C}$  and 1 atm, and the  $G_{\text{sys}}$  will decrease until the system reaches equilibrium.

20.84 Plan: First calculate  $\Delta H^\circ$  and  $\Delta S^\circ$ . According to the relationship  $\ln K = \frac{\Delta G^\circ}{-RT}$ , since  $\ln K_p = 0$  when  $K_p = 1.00$ ,

$\Delta G^\circ = 0$ . Use the relationship  $\Delta G^\circ = 0 = \Delta H^\circ - T\Delta S^\circ$  to find the temperature. For part b), calculate  $\Delta G^\circ$  at the

higher temperature with the relationship  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$  and then calculate  $K$  with  $\ln K = \frac{\Delta G^\circ}{-RT}$ .

Solution:

a)  $\Delta H^\circ = \sum m \Delta H_f^\circ(\text{products}) - \sum n \Delta H_f^\circ(\text{reactants})$

$$\Delta H^\circ = [(2 \text{ mol NH}_3)(\Delta H_f^\circ \text{ of NH}_3)] - [(1 \text{ mol N}_2)(\Delta H_f^\circ \text{ of N}_2) + (3 \text{ mol H}_2)(\Delta H_f^\circ \text{ of H}_2)]$$

$$\Delta H^\circ = [(2 \text{ mol})(-45.9 \text{ kJ/mol})] - [(1 \text{ mol})(0 \text{ kJ/mol}) + (3 \text{ mol})(0 \text{ kJ/mol})] = -91.8 \text{ kJ}$$

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

$$\Delta S^\circ = [(2 \text{ mol NH}_3)(S^\circ \text{ of NH}_3)] - [(1 \text{ mol N}_2)(S^\circ \text{ of N}_2) + (3 \text{ mol H}_2)(S^\circ \text{ of H}_2)]$$

$$\Delta S^\circ = [(2 \text{ mol})(193 \text{ J/mol}\cdot\text{K})] - [(1 \text{ mol})(191.50 \text{ J/mol}\cdot\text{K}) + (3 \text{ mol})(130.6 \text{ J/mol}\cdot\text{K})]$$

$$\Delta S^\circ = -197.3 \text{ J/K}$$

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

Since  $\ln K_p = 0$  when  $K_p = 1.00$ ,  $\Delta G^\circ = 0$ .

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

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

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{-91.8 \text{ kJ}}{-197.3 \text{ J/K}} \left( \frac{10^3 \text{ J}}{1 \text{ kJ}} \right) = 465.281 = \mathbf{465 \text{ K}}$$

b)  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = (-91.8 \text{ kJ})(10^3 \text{ J/1 kJ}) - (673 \text{ K})(-197.3 \text{ J/K}) = 4.09829 \times 10^4 \text{ J}$



$$\ln K = \frac{\Delta G^\circ}{-RT} = \left( \frac{4.09829 \times 10^4 \text{ J/mol}}{-(8.314 \text{ J/mol}\cdot\text{K})(673 \text{ K})} \right) = -7.32449$$
$$K = e^{-7.32449} = 6.591958 \times 10^{-4} = \mathbf{6.59 \times 10^{-4}}$$

c) The reaction rate is higher at the higher temperature. The time required (kinetics) overshadows the lower yield (thermodynamics).