

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

- 20.1 Spontaneous processes proceed without outside intervention. The fact that a process is spontaneous does not mean that it will occur instantaneously 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° 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 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 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 a) ΔS_{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) ΔS_{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) ΔS_{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 a) ΔS_{sys} **positive**, the process described is liquid alcohol becoming gaseous alcohol. The gas molecules have greater entropy than the liquid molecules.
 b) ΔS_{sys} **positive**, the process described is a change from solid to gas, an increase in possible energy states for the system.
 c) ΔS_{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 a) ΔS_{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) ΔS_{sys} **negative**, gaseous reactants form solid product and number of particles decreases, so entropy decreases.
 c) ΔS_{sys} **positive**, when salts dissolve in water, entropy generally increases.
- 20.13 a) ΔS_{sys} **negative** b) ΔS_{sys} **negative** c) ΔS_{sys} **negative**
- 20.14 a) ΔS_{sys} **positive**, the reaction produces gaseous CO_2 molecules that have greater entropy than the physical states of the reactants.
 b) ΔS_{sys} **negative**, the reaction produces a net decrease in the number of gaseous molecules, so the system's entropy decreases.
 c) ΔS_{sys} **positive**, the reaction produces a gas from a solid.
- 20.15 a) ΔS_{sys} **negative** b) ΔS_{sys} **positive** c) ΔS_{sys} **negative**
- 20.16 a) ΔS_{sys} **positive**, decreasing the pressure increases the volume available to the gas molecules so entropy of the system increases.
 b) ΔS_{sys} **negative**, gaseous nitrogen molecules have greater entropy (more possible states) than dissolved nitrogen molecules.
 c) ΔS_{sys} **positive**, dissolved oxygen molecules have lower entropy than gaseous oxygen molecules.
- 20.17 a) ΔS_{sys} **negative** b) ΔS_{sys} **positive** c) ΔS_{sys} **negative**
- 20.18 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) **CH₄(g)** has the greater molar entropy because gases in general have greater entropy than liquids.
- 20.19 a) Ethanol, **C₂H₅OH(l)**, is a more complex molecule than methanol, CH₃OH, and has the greater molar entropy.
 b) A salt dissolves, giving an increase in the number of possible states for the ions increases. Thus, **KClO₃(aq)** has the greater molar entropy.
 c) **K(s)** has greater molar entropy because K(s) has greater mass than Na(s).

- 20.20 a) **Diamond < graphite < charcoal.** Diamond has an ordered, 3-dimensional crystalline shape, followed by graphite with an ordered 2-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 < O₂ < O₃.** 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) **CaCO₃(s) < (CaO(s) + CO₂(g)) < (Ca(s) + C(s) + 3/2 O₂(g));** entropy increases with moles of gas particles.
 c) **SF₄(g) < SF₆(g) < S₂F₁₀(g);** entropy increases with molecular complexity.
- 20.22 a) **ClO₄⁻(aq) > ClO₃⁻(aq) > ClO₂⁻(aq).** The decreasing order of molar entropy follows the order of decreasing molecular complexity.
 b) **NO₂(g) > NO(g) > N₂(g).** N₂ has lower molar entropy than NO because N₂ consists of two of the same atoms while NO consists of two different atoms. NO₂ has greater molar entropy than NO because NO₂ consists of three atoms while NO consists of only two.
 c) **Fe₃O₄(s) > Fe₂O₃(s) > Al₂O₃(s).** Fe₃O₄ has greater molar entropy than Fe₂O₃ because Fe₃O₄ is more complex and more massive. Fe₂O₃ and Al₂O₃ contain the same number of atoms but Fe₂O₃ has greater molar entropy because iron atoms are more massive than aluminum atoms.
- 20.23 a) **Ba(s) > Ca(s) > Mg(s);** entropy decreases with lower mass.
 b) **C₆H₁₄ > C₆H₁₂ > C₆H₆;** entropy decreases with lower molecular complexity and lower molecular flexibility.
 c) **PF₂Cl₃(g) > PF₅(g) > PF₃(g);** entropy decreases with lower molecular complexity.
- 20.24 a) $X_2(g) + 3 Y_2(g) \rightarrow 2 XY_3(g)$
 b) $\Delta S < 0$ since there are fewer moles of gas in the products than in the reactants.
 c) XY₃ 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 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.
 For the given reaction $\Delta S_{\text{rxn}}^\circ = 2 S^\circ(\text{HClO}(g)) - (S^\circ(\text{H}_2\text{O}(g)) + S^\circ(\text{Cl}_2\text{O}(g)))$. Rearranging this expression to solve for $S^\circ(\text{Cl}_2\text{O}(g))$ gives $S^\circ(\text{Cl}_2\text{O}(g)) = 2 S^\circ(\text{HClO}(g)) - S^\circ(\text{H}_2\text{O}(g)) - \Delta S_{\text{rxn}}^\circ$
- 20.28 a) Prediction: **ΔS° negative** because number of moles of (Δn) gas decreases.

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

$$- [(3 \text{ mol NO}(g)) (S^\circ(\text{NO}))]$$

$$\Delta S^\circ = [(1 \text{ mol N}_2\text{O}(g)) (219.7 \text{ J/mol}\cdot\text{K}) + (1 \text{ mol NO}_2(g)) (239.9 \text{ J/mol}\cdot\text{K})]$$

$$- [(3 \text{ mol NO}(g)) (210.65 \text{ J/mol}\cdot\text{K})]$$

$$\Delta S^\circ = -172.35 = \mathbf{-172.4 \text{ J/K}}$$

 b) Prediction: Sign difficult to predict because $\Delta n = 0$, but **possibly ΔS° positive** because water vapor has greater complexity than H₂ gas.

$$\Delta S^\circ = [(2 \text{ mol Fe}(s)) (S^\circ(\text{Fe})) + (3 \text{ mol H}_2\text{O}(g)) (S^\circ(\text{H}_2\text{O}))]$$

$$- [(3 \text{ mol H}_2(g)) (S^\circ(\text{H}_2)) + (1 \text{ mol Fe}_2\text{O}_3(s)) (S^\circ(\text{Fe}_2\text{O}_3))]$$

$$\Delta S^\circ = [(2 \text{ mol Fe}(s)) (27.3 \text{ J/mol}\cdot\text{K}) + (3 \text{ mol H}_2\text{O}(g)) (188.72 \text{ J/mol}\cdot\text{K})]$$

$$- [(3 \text{ mol H}_2(g)) (130.6 \text{ J/mol}\cdot\text{K}) + (1 \text{ mol Fe}_2\text{O}_3(s)) (87.400 \text{ J/mol}\cdot\text{K})]$$

$$\Delta S^\circ = 141.56 = \mathbf{141.6 \text{ J/K}}$$

c) Prediction: $\Delta S_{\text{sys}}^\circ$ **negative** because a gaseous reactant forms a solid product and also because the number of moles of gas (Δn) decreases.

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

$$\Delta S^\circ = [(1 \text{ mol P}_4\text{O}_{10}(\text{s})) (229 \text{ J/mol}\cdot\text{K})] - [(1 \text{ mol P}_4(\text{s})) (41.1 \text{ J/mol}\cdot\text{K}) + (5 \text{ mol O}_2(\text{g})) (205.0 \text{ J/mol}\cdot\text{K})]$$

$$\Delta S^\circ = -837.1 = \mathbf{-837 \text{ J/K}}$$

20.29 a) $3 \text{ NO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow 2 \text{ HNO}_3(\text{l}) + \text{NO}(\text{g})$ ΔS negative

$$\begin{aligned}\Delta S_{\text{rxn}}^\circ &= [2 \text{ mol HNO}_3(\text{l}) (155.6 \text{ J/K}\cdot\text{mol}) + 1 \text{ mol NO}(\text{g}) (210.65 \text{ J/K}\cdot\text{mol})] \\ &\quad - [3 \text{ mol NO}_2(\text{g}) (239.9 \text{ J/K}\cdot\text{mol}) + 1 \text{ mol H}_2\text{O}(\text{l}) (69.940 \text{ J/K}\cdot\text{mol})] \\ &= -267.79 = \mathbf{-267.8 \text{ J/K}}\end{aligned}$$

b) $\text{N}_2(\text{g}) + 3 \text{ F}_2(\text{g}) \rightarrow 2 \text{ NF}_3(\text{g})$ ΔS negative

$$\begin{aligned}\Delta S_{\text{rxn}}^\circ &= [2 \text{ mol NF}_3(\text{g}) (260.6 \text{ J/K}\cdot\text{mol})] - [1 \text{ mol N}_2(\text{g}) (191.5 \text{ J/K}\cdot\text{mol}) + 3 \text{ mol F}_2(\text{g}) (202.7 \text{ J/K}\cdot\text{mol})] \\ &= \mathbf{-278.4 \text{ J/K}}\end{aligned}$$

c) $\text{C}_6\text{H}_{12}\text{O}_6(\text{s}) + 6 \text{ O}_2(\text{g}) \rightarrow 6 \text{ CO}_2(\text{g}) + 6 \text{ H}_2\text{O}(\text{g})$ ΔS positive

$$\begin{aligned}\Delta S_{\text{rxn}}^\circ &= [6 \text{ mol CO}_2(\text{g}) (213.7 \text{ J/K}\cdot\text{mol}) + 6 \text{ mol H}_2\text{O}(\text{g}) (188.72 \text{ J/K}\cdot\text{mol})] \\ &\quad - [1 \text{ mol C}_6\text{H}_{12}\text{O}_6(\text{s}) (212.1 \text{ J/K}\cdot\text{mol}) + 6 \text{ mol O}_2(\text{g}) (205.0 \text{ J/K}\cdot\text{mol})] = 972.42 = \mathbf{972.4 \text{ J/K}}\end{aligned}$$

20.30 The balanced combustion reaction is

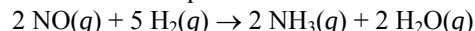


$$\begin{aligned}\Delta S_{\text{rxn}}^\circ &= [4 \text{ mol } (S^\circ(\text{CO}_2)) + 6 \text{ mol } (S^\circ(\text{H}_2\text{O}))] - [2 \text{ mol } (S^\circ(\text{C}_2\text{H}_6)) + 7 \text{ mol } (S^\circ(\text{O}_2))] \\ &= [4 \text{ mol } (213.7 \text{ J/mol}\cdot\text{K}) + 6 \text{ mol } (188.72 \text{ J/mol}\cdot\text{K})] \\ &\quad - [2 \text{ mol } (229.5 \text{ J/mol}\cdot\text{K}) + 7 \text{ mol } (205.0 \text{ J/mol}\cdot\text{K})] = 93.12 = \mathbf{93.1 \text{ J/K}}\end{aligned}$$

The entropy value is not per mole of C_2H_6 but per 2 moles. Divide the calculated value by 2 to obtain entropy per mole of C_2H_6 .

Yes, the positive sign of ΔS is expected because there is a net increase in the number of gas molecules from 9 moles as reactants to 10 moles as products.

20.31 The balanced chemical equation for the described reaction is:

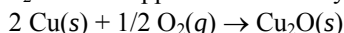


Because the number of moles of gas decreases, i.e., $\Delta n = 4 - 7 = -3$, the entropy is expected to decrease.

$$\begin{aligned}\Delta S^\circ &= \{(2 \text{ mol NH}_3) (193 \text{ J/mol}\cdot\text{K}) + (2 \text{ mol H}_2\text{O}) (188.72 \text{ J/mol}\cdot\text{K})\} \\ &\quad - \{(2 \text{ mol NO}) (210.65 \text{ J/mol}\cdot\text{K}) + (5 \text{ mol H}_2) (130.6 \text{ J/mol}\cdot\text{K})\} \\ \Delta S^\circ &= -310.86 = \mathbf{-311 \text{ J/K}}\end{aligned}$$

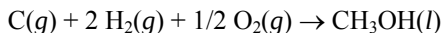
Yes, the calculated entropy matches the predicted decrease.

20.32 The reaction for forming Cu_2O from copper metal and oxygen gas is



$$\begin{aligned}\Delta S_{\text{rxn}}^\circ &= [1 \text{ mol } (S^\circ(\text{Cu}_2\text{O}))] - [2 \text{ mol } (S^\circ(\text{Cu})) + 1/2 \text{ mol } (S^\circ(\text{O}_2))] \\ &= [1 \text{ mol } (93.1 \text{ J/mol}\cdot\text{K})] - [2 \text{ mol } (33.1 \text{ J/mol}\cdot\text{K}) + 1/2 \text{ mol } (205.0 \text{ J/mol}\cdot\text{K})] \\ &= \mathbf{-75.6 \text{ J/K}}\end{aligned}$$

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



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

$$\begin{aligned}\Delta S^\circ &= [(1 \text{ mol CH}_3\text{OH}) (127 \text{ J/mol}\cdot\text{K})] \\ &\quad - [(1 \text{ mol C}) (5.686 \text{ J/mol}\cdot\text{K}) + (2 \text{ mol H}_2) (130.6 \text{ J/mol}\cdot\text{K}) + (1/2 \text{ mol O}_2) (205.0 \text{ J/mol}\cdot\text{K})] \\ \Delta S^\circ &= -242.386 = \mathbf{-242 \text{ J/K}}\end{aligned}$$

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

$$\Delta S^\circ_{\text{rxn}} = [1 \text{ mol CaSO}_3(s) (101.4 \text{ J/K}\cdot\text{mol}) + 1 \text{ mol H}_2\text{O}(l) (69.940 \text{ J/K}\cdot\text{mol})]$$

$$- [1 \text{ mol SO}_2(g) (248.1 \text{ J/K}\cdot\text{mol}) + 1 \text{ mol Ca}(\text{OH})_2(s) (83.39 \text{ J/K}\cdot\text{mol})]$$

$$= -160.15 = \mathbf{-160.2 \text{ J/K}}$$
- 20.35 Complete combustion of a hydrocarbon includes oxygen as a reactant and carbon dioxide and water as the products.

$$\text{C}_2\text{H}_2(g) + 5/2 \text{ O}_2(g) \rightarrow 2 \text{ CO}_2(g) + \text{H}_2\text{O}(g)$$

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

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

$$- [1 \text{ mol } (200.85 \text{ J/mol}\cdot\text{K}) + 5/2 \text{ mol } (205.0 \text{ J/mol}\cdot\text{K})] = -97.23 = \mathbf{-97.2 \text{ J/K}}$$
- 20.36 Reaction spontaneity may now be predicted from the value of only one variable (ΔG_{sys}) rather than two (ΔS_{sys} and ΔS_{surr}).
- 20.37 A spontaneous process has $\Delta S_{\text{univ}} > 0$. Since the Kelvin temperature is always positive, ΔG_{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 **ΔH is positive**.
 2. Since gases have higher entropy values than solids, the process results in an increase in entropy and **ΔS is positive**.
 3. This is an endothermic process so the surroundings loses energy to the system. **ΔS_{surr} is negative**.
 4. $\Delta G = \Delta H - T\Delta S$. Both ΔH and ΔS are positive. At low temperature, the ΔH term will predominate and ΔG will be positive; at high temperatures, the $T\Delta S$ term will predominate and ΔG will be negative.
- 20.39 **$\Delta H^\circ_{\text{rxn}}$ positive and $\Delta S^\circ_{\text{sys}}$ positive**. The reaction is endothermic ($\Delta H^\circ_{\text{rxn}} > 0$) and requires a lot of heat from its surroundings to be spontaneous. The removal of heat from the surroundings results in $\Delta S^\circ_{\text{surr}} < 0$. The only way an endothermic reaction can proceed spontaneously is if $\Delta S^\circ_{\text{sys}} \gg 0$, effectively offsetting the decrease in the entropy of the surroundings. In summary, the values of $\Delta H^\circ_{\text{rxn}}$ and $\Delta S^\circ_{\text{sys}}$ are both positive for this reaction. Melting is an example.
- 20.40 The $\Delta G^\circ_{\text{rxn}}$ can be calculated from the individual ΔG°_f 's of the reactants and products found in Appendix B.

$$\Delta G^\circ_{\text{rxn}} = \Sigma[m \Delta G^\circ_f (\text{products})] - \Sigma[n \Delta G^\circ_f (\text{reactants})]$$
 a) $\Delta G^\circ_{\text{rxn}} = [(2 \text{ mol MgO}) (\Delta G^\circ_f \text{ MgO})] - [(2 \text{ mol Mg}) (\Delta G^\circ_f \text{ Mg}) + (1 \text{ mol O}_2) (\Delta G^\circ_f \text{ O}_2)]$
 Both Mg(s) and O₂(g) are the standard state forms of their respective elements, so their ΔG°_f 's are zero.

$$\Delta G^\circ_{\text{rxn}} = [(2 \text{ mol MgO}) (-569.0 \text{ kJ/mol})] - [(2 \text{ mol Mg}) (0) + (1 \text{ mol O}_2) (0)] = \mathbf{-1138.0 \text{ kJ}}$$
 b) $\Delta G^\circ_{\text{rxn}} = [(2 \text{ mol CO}_2) (\Delta G^\circ_f \text{ CO}_2) + (4 \text{ mol H}_2\text{O}) (\Delta G^\circ_f \text{ H}_2\text{O})]$

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

$$\Delta G^\circ_{\text{rxn}} = [(2 \text{ mol CO}_2) (-394.4 \text{ kJ/mol}) + (4 \text{ mol H}_2\text{O}) (-228.60 \text{ kJ/mol})]$$

$$- [(2 \text{ mol CH}_3\text{OH}) (-161.9 \text{ kJ/mol}) + (3 \text{ mol O}_2) (0)]$$

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

$$\begin{aligned} \text{c) } \Delta G_{\text{rxn}}^{\circ} &= [(1 \text{ mol BaCO}_3) (\Delta G_{\text{f}}^{\circ} \text{BaCO}_3)] - [(1 \text{ mol BaO}) (\Delta G_{\text{f}}^{\circ} \text{BaO}) + (1 \text{ mol CO}_2) (\Delta G_{\text{f}}^{\circ} \text{CO}_2)] \\ \Delta G_{\text{rxn}}^{\circ} &= [(1 \text{ mol BaCO}_3) (-1139 \text{ kJ/mol})] - [(1 \text{ mol BaO}) (-520.4 \text{ kJ/mol}) + (1 \text{ mol CO}_2) (-394.4 \text{ kJ/mol})] \\ \Delta G_{\text{rxn}}^{\circ} &= -224.2 = \mathbf{-224 \text{ kJ}} \end{aligned}$$

$$\begin{aligned} 20.41 \quad \text{a) } \text{H}_2(\text{g}) + \text{I}_2(\text{s}) &\rightarrow 2 \text{HI}(\text{g}) \\ \Delta G_{\text{rxn}}^{\circ} &= [2 \text{ mol HI}(\text{g}) (1.3 \text{ kJ/mol})] - [1 \text{ mol H}_2(\text{g}) (0 \text{ kJ/mol}) + 1 \text{ mol I}_2(\text{s}) (0 \text{ kJ/mol})] \\ &= \mathbf{2.6 \text{ kJ}} \end{aligned}$$

$$\begin{aligned} \text{b) } \text{MnO}_2(\text{s}) + 2 \text{CO}(\text{g}) &\rightarrow \text{Mn}(\text{s}) + 2 \text{CO}_2(\text{g}) \\ \Delta G_{\text{rxn}}^{\circ} &= [1 \text{ mol Mn}(\text{s}) (0 \text{ kJ/mol}) + 2 \text{ mol CO}_2(\text{g}) (-394.4 \text{ kJ/mol})] \\ &\quad - [1 \text{ mol MnO}_2(\text{s}) (-466.1 \text{ kJ/mol}) + 2 \text{ mol CO}(\text{g}) (-137.2 \text{ kJ/mol})] \\ &= \mathbf{-48.3 \text{ kJ}} \end{aligned}$$

$$\begin{aligned} \text{c) } \text{NH}_4\text{Cl}(\text{s}) &\rightarrow \text{NH}_3(\text{g}) + \text{HCl}(\text{g}) \\ \Delta G_{\text{rxn}}^{\circ} &= [1 \text{ mol NH}_3(\text{g}) (-16 \text{ kJ/mol}) + 1 \text{ mol HCl}(\text{g}) (-95.30 \text{ kJ/mol})] \\ &\quad - 1 \text{ mol NH}_4\text{Cl}(\text{s}) (-203.0 \text{ kJ/mol}) \\ &= 91.7 = \mathbf{92 \text{ kJ}} \end{aligned}$$

20.42 The $\Delta H_{\text{rxn}}^{\circ}$ can be calculated from the individual $\Delta H_{\text{f}}^{\circ}$'s of the reactants and products found in Appendix B.

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

The $\Delta S_{\text{rxn}}^{\circ}$ can be calculated from the individual S° 's of the reactants and products found in Appendix B.

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

$$\Delta G_{\text{rxn}}^{\circ} \text{ can be calculated using } \Delta G_{\text{rxn}}^{\circ} = \Delta H_{\text{rxn}}^{\circ} - T \Delta S_{\text{rxn}}^{\circ}$$

$$\begin{aligned} \text{a) } \Delta H_{\text{rxn}}^{\circ} &= [2 \text{ mol } (\Delta H_{\text{f}}^{\circ}(\text{MgO}))] - [2 \text{ mol } (\Delta H_{\text{f}}^{\circ}(\text{Mg})) + 1 \text{ mol } (\Delta H_{\text{f}}^{\circ}(\text{O}_2))] \\ &= [2 \text{ mol } (-601.2 \text{ kJ/mol})] - [2 \text{ mol } (0) + 1 \text{ mol } (0)] \\ &= -1202.4 \text{ kJ} \\ \Delta S_{\text{rxn}}^{\circ} &= [2 \text{ mol } (S^{\circ}(\text{MgO}))] - [2 \text{ mol } (S^{\circ}(\text{Mg})) + 1 \text{ mol } S^{\circ}(\text{O}_2)] \\ &= [2 \text{ mol } (26.9 \text{ J/mol}\cdot\text{K})] - [2 \text{ mol } (32.69 \text{ J/mol}\cdot\text{K}) + 1 \text{ mol } (205.0 \text{ J/mol}\cdot\text{K})] \\ &= -216.58 \text{ J/K (unrounded)} \\ \Delta G_{\text{rxn}}^{\circ} &= \Delta H_{\text{rxn}}^{\circ} - T \Delta S_{\text{rxn}}^{\circ} = -1202.4 \text{ kJ} - [(298 \text{ K}) (-216.58 \text{ J/K}) (1 \text{ kJ}/10^3 \text{ J})] = -1137.859 = \mathbf{-1138 \text{ kJ}} \end{aligned}$$

$$\begin{aligned} \text{b) } \Delta H_{\text{rxn}}^{\circ} &= [2 \text{ mol } (\Delta H_{\text{f}}^{\circ}(\text{CO}_2)) + 4 \text{ mol } (\Delta H_{\text{f}}^{\circ}(\text{H}_2\text{O}(\text{g}))) - [2 \text{ mol } (\Delta H_{\text{f}}^{\circ}(\text{CH}_3\text{OH})) + 3 \text{ mol } (\Delta H_{\text{f}}^{\circ}(\text{O}_2))] \\ &= [2 \text{ mol } (-393.5 \text{ kJ/mol}) + 4 \text{ mol } (-241.826 \text{ kJ/mol})] - [2 \text{ mol } (-201.2 \text{ kJ/mol}) + 3 \text{ mol } (0)] \\ &= -1351.904 \text{ kJ (unrounded)} \\ \Delta S_{\text{rxn}}^{\circ} &= [2 \text{ mol } (S^{\circ}(\text{CO}_2)) + 4 \text{ mol } (S^{\circ}(\text{H}_2\text{O}(\text{g}))) - [2 \text{ mol } (S^{\circ}(\text{CH}_3\text{OH})) + 3 \text{ mol } (S^{\circ}(\text{O}_2))] \\ &= [2 \text{ mol } (213.7 \text{ J/mol}\cdot\text{K}) + 4 \text{ mol } (188.72 \text{ J/mol}\cdot\text{K})] \\ &\quad - [2 \text{ mol } (238 \text{ J/mol}\cdot\text{K}) + 3 \text{ mol } (205.0 \text{ J/mol}\cdot\text{K})] \\ &= 91.28 \text{ J/K (unrounded)} \\ \Delta G_{\text{rxn}}^{\circ} &= \Delta H_{\text{rxn}}^{\circ} - T \Delta S_{\text{rxn}}^{\circ} = -1351.904 \text{ kJ} - [(298 \text{ K}) (91.28 \text{ J/K}) (1 \text{ kJ}/10^3 \text{ J})] = -1379.105 = \mathbf{-1379 \text{ kJ}} \end{aligned}$$

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

- 20.43 a) $\Delta H_{\text{rxn}}^{\circ} = [2 \text{ mol HI}(g) (25.9 \text{ kJ/mol})] - [1 \text{ mol H}_2(g) (0 \text{ kJ/mol}) + 1 \text{ mol I}_2(s) (0 \text{ kJ/mol})]$
 $= 51.8 \text{ kJ}$
 $\Delta S_{\text{rxn}}^{\circ} = [2 \text{ mol HI}(g) (206.33 \text{ J/K}\cdot\text{mol})] - [1 \text{ mol H}_2(g) (130.6 \text{ J/K}\cdot\text{mol}) + 1 \text{ mol I}_2(s) (116.14 \text{ J/K}\cdot\text{mol})]$
 $= 165.92 \text{ J/K (unrounded)}$
 $\Delta G_{\text{rxn}}^{\circ} = \Delta H_{\text{rxn}}^{\circ} - T \Delta S_{\text{rxn}}^{\circ} = 51.8 \text{ kJ} - [(298 \text{ K}) (165.92 \text{ J/K}) (1 \text{ kJ} / 10^3 \text{ J})] = 2.3558 = \mathbf{2.4 \text{ kJ}}$
- b) $\Delta H_{\text{rxn}}^{\circ} = [1 \text{ mol Mn}(s) (0 \text{ kJ/mol}) + 2 \text{ mol CO}_2(g) (-393.5 \text{ kJ/mol})]$
 $- [1 \text{ mol MnO}_2(s) (-520.9 \text{ kJ/mol}) + 2 \text{ mol CO}(g) (-110.5 \text{ kJ/mol})]$
 $= -45.1 \text{ kJ}$
 $\Delta S_{\text{rxn}}^{\circ} = [1 \text{ mol Mn}(s) (31.8 \text{ J/K}\cdot\text{mol}) + 2 \text{ mol CO}_2(g) (213.7 \text{ J/K}\cdot\text{mol})]$
 $- [1 \text{ mol MnO}_2(s) (53.1 \text{ J/K}\cdot\text{mol}) + 2 \text{ mol CO}(g) (197.5 \text{ J/K}\cdot\text{mol})]$
 $= 11.1 \text{ J/K}$
 $\Delta G_{\text{rxn}}^{\circ} = \Delta H_{\text{rxn}}^{\circ} - T \Delta S_{\text{rxn}}^{\circ} = -45.1 \text{ kJ} - [(298 \text{ K}) (11.1 \text{ J/K}) (1 \text{ kJ} / 10^3 \text{ J})] = -48.4078 = \mathbf{-48.4 \text{ kJ}}$
- c) $\Delta H_{\text{rxn}}^{\circ} = [1 \text{ mol NH}_3(g) (-45.9 \text{ kJ/mol}) + 1 \text{ mol HCl}(g) (-92.3 \text{ kJ/mol})] - [1 \text{ mol NH}_4\text{Cl}(s) (-314.4 \text{ kJ/mol})]$
 $= 176.2 \text{ kJ}$
 $\Delta S_{\text{rxn}}^{\circ} = [1 \text{ mol NH}_3(g) (193 \text{ J/K}\cdot\text{mol}) + 1 \text{ mol HCl}(g) (186.79 \text{ J/K}\cdot\text{mol})] - [1 \text{ mol NH}_4\text{Cl}(s) (94.6 \text{ J/K}\cdot\text{mol})]$
 $= 285.19 \text{ J/K (unrounded)}$
 $\Delta G_{\text{rxn}}^{\circ} = \Delta H_{\text{rxn}}^{\circ} - T \Delta S_{\text{rxn}}^{\circ} = 176.2 \text{ kJ} - [(298 \text{ K}) (285.19 \text{ J/K}) (1 \text{ kJ} / 10^3 \text{ J})] = 91.213 = \mathbf{91.2 \text{ kJ}}$
- 20.44 a) Entropy decreases (ΔS° **negative**) because the number of moles of gas decreases from reactants (1½ mol) to products (1 mole). The oxidation (combustion) of CO requires initial energy input to start the reaction, but then releases energy (exothermic, ΔH° **negative**) which is typical of all combustion reactions.
- b) Method 1: Calculate $\Delta G_{\text{rxn}}^{\circ}$ from ΔG_f° 's of products and reactants.
- $$\Delta G_{\text{rxn}}^{\circ} = \Sigma[m \Delta G_f^{\circ} (\text{products})] - \Sigma[n \Delta G_f^{\circ} (\text{reactants})]$$
- $$\Delta G_{\text{rxn}}^{\circ} = [(1 \text{ mol CO}_2) (\Delta G_f^{\circ} (\text{CO}_2))] - [(1 \text{ mol CO}) (\Delta G_f^{\circ} (\text{CO})) + (1/2 \text{ mol O}_2) (\Delta G_f^{\circ} (\text{O}_2))]$$
- $$\Delta G_{\text{rxn}}^{\circ} = [(1 \text{ mol CO}_2) (-394.4 \text{ kJ/mol})] - [(1 \text{ mol CO}) (-137.2 \text{ kJ/mol}) + (1/2 \text{ mol O}_2) (0)] = \mathbf{-257.2 \text{ kJ}}$$
- Method 2: Calculate $\Delta G_{\text{rxn}}^{\circ}$ from ΔH° and ΔS° at 298 K (the degree superscript indicates a reaction at standard state, given in the Appendix at 25°C).
- $$\Delta H_{\text{rxn}}^{\circ} = \Sigma[m \Delta H_f^{\circ} (\text{products})] - \Sigma[n \Delta H_f^{\circ} (\text{reactants})]$$
- $$\Delta H_{\text{rxn}}^{\circ} = [(1 \text{ mol CO}_2) (\Delta H_f^{\circ} (\text{CO}_2))] - [(1 \text{ mol CO}) (\Delta H_f^{\circ} (\text{CO})) + (1/2 \text{ mol O}_2) (\Delta H_f^{\circ} (\text{O}_2))]$$
- $$\Delta H_{\text{rxn}}^{\circ} = [(1 \text{ mol CO}_2) (-393.5 \text{ kJ/mol})] - [(1 \text{ mol CO}) (-110.5 \text{ kJ/mol}) + (1/2 \text{ mol O}_2) (0)] = -283.0 \text{ kJ}$$
- $$\Delta S_{\text{rxn}}^{\circ} = \Sigma[m S^{\circ}(\text{products})] - \Sigma[n S^{\circ}(\text{reactants})]$$
- $$\Delta S_{\text{rxn}}^{\circ} = [(1 \text{ mol CO}_2) (213.7 \text{ J/mol}\cdot\text{K})] - [(1 \text{ mol CO}) (197.5 \text{ J/mol}\cdot\text{K}) + (1/2 \text{ mol O}_2) (205.0 \text{ J/mol}\cdot\text{K})]$$
- $$= -86.3 \text{ J/K}$$
- $$\Delta G_{\text{rxn}}^{\circ} = \Delta H_{\text{rxn}}^{\circ} - T \Delta S_{\text{rxn}}^{\circ} = (-283.0 \text{ kJ}) - [(298 \text{ K}) (-86.3 \text{ J/K}) (1 \text{ kJ}/10^3 \text{ J})] = -257.2826 = \mathbf{-257.3 \text{ kJ}}$$
- 20.45 $\text{C}_4\text{H}_{10}(g) + 13/2 \text{ O}_2(g) \rightarrow 4 \text{ CO}_2(g) + 5 \text{ H}_2\text{O}(g)$
- a) An increase in the number of moles of gas should result in a **positive** ΔS° value. The combustion of $\text{C}_4\text{H}_{10}(g)$ will result in a release of energy or a **negative** ΔH° value.
- b) $\Delta H_{\text{rxn}}^{\circ} = [4 \text{ mol CO}_2(g) (-393.5 \text{ kJ/mol}) + 5 \text{ mol H}_2\text{O}(g) (-241.826 \text{ kJ/mol})]$
 $- [1 \text{ mol C}_4\text{H}_{10}(g) (-126 \text{ kJ/mol}) + 13/2 \text{ mol O}_2(g) (0 \text{ kJ/mol})]$
 $= -2657.13 \text{ kJ (unrounded)}$

$$\begin{aligned}\Delta S_{\text{rxn}}^{\circ} &= [4 \text{ mol CO}_2(g) (213.7 \text{ J/K}\cdot\text{mol}) + 5 \text{ mol H}_2\text{O}(g) (188.72 \text{ J/K}\cdot\text{mol})] \\ &\quad - [1 \text{ mol C}_4\text{H}_{10}(g) (310 \text{ J/K}\cdot\text{mol}) + 13/2 \text{ mol O}_2(g) (205.0 \text{ J/K}\cdot\text{mol})] \\ &= 155.9 \text{ J/K (unrounded)} \\ \Delta G_{\text{rxn}}^{\circ} &= \Delta H_{\text{rxn}}^{\circ} - T \Delta S_{\text{rxn}}^{\circ} = -2657.13 \text{ kJ} - [(298 \text{ K}) (155.9 \text{ J/K}) (1 \text{ kJ} / 10^3 \text{ J})] = -2703.588 = \mathbf{-2704 \text{ kJ}} \\ \Delta G_{\text{rxn}}^{\circ} &= [4 \text{ mol CO}_2(g) (-394.4 \text{ kJ/mol}) + 5 \text{ mol H}_2\text{O}(g) (-228.60 \text{ kJ/mol})] \\ &\quad - [1 \text{ mol C}_4\text{H}_{10}(g) (-16.7 \text{ kJ/mol}) + 13/2 \text{ mol O}_2(g) (0 \text{ kJ/mol})] \\ &= \mathbf{-2703.9 \text{ kJ}}\end{aligned}$$

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

$$\Delta H_{\text{rxn}}^{\circ} = [(1 \text{ mol CO}) (-110.5 \text{ kJ/mol}) + (2 \text{ mol H}_2) (0)] - [(1 \text{ mol CH}_3\text{OH}) (-201.2 \text{ kJ/mol})]$$

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

$$\begin{aligned}\Delta S_{\text{rxn}}^{\circ} &= [(1 \text{ mol CO}) (S_f^{\circ}(\text{CO})) + (2 \text{ mol H}_2) (S_f^{\circ}(\text{H}_2))] - [(1 \text{ mol CH}_3\text{OH}) (S_f^{\circ}(\text{CH}_3\text{OH}))] \\ \Delta S_{\text{rxn}}^{\circ} &= [(1 \text{ mol CO}) (197.5 \text{ J/mol}\cdot\text{K}) + (2 \text{ mol H}_2) (130.6 \text{ J/mol}\cdot\text{K})] \\ &\quad - [(1 \text{ mol CH}_3\text{OH}) (238 \text{ J/mol}\cdot\text{K})] \\ \Delta S_{\text{rxn}}^{\circ} &= 220.7 = \mathbf{221 \text{ J/K}}\end{aligned}$$

b) $T_1 = 28 + 273 = 301 \text{ K} \quad \Delta G^{\circ} = 90.7 \text{ kJ} - [(301 \text{ K}) (220.7 \text{ J/K}) (1 \text{ kJ}/10^3 \text{ J})] = 24.2693 = \mathbf{24.3 \text{ kJ}}$
 $T_2 = 128 + 273 = 401 \text{ K} \quad \Delta G^{\circ} = 90.7 \text{ kJ} - [(401 \text{ K}) (220.7 \text{ J/K}) (1 \text{ kJ}/10^3 \text{ J})] = 2.1993 = \mathbf{2.2 \text{ kJ}}$
 $T_3 = 228 + 273 = 501 \text{ K} \quad \Delta G^{\circ} = 90.7 \text{ kJ} - [(501 \text{ K}) (220.7 \text{ J/K}) (1 \text{ kJ}/10^3 \text{ J})] = -19.8707 = \mathbf{-19.9 \text{ kJ}}$

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

$$\begin{aligned}\Delta H_{\text{rxn}}^{\circ} &= [2 \text{ mol NO}(g) (90.29 \text{ kJ/mol})] - [1 \text{ mol N}_2(g) (0 \text{ kJ/mol}) + 1 \text{ mol O}_2(g) (0 \text{ kJ/mol})] \\ &= \mathbf{180.58 \text{ kJ}} \\ \Delta S_{\text{rxn}}^{\circ} &= [2 \text{ mol NO}(g) (210.65 \text{ J/K}\cdot\text{mol})] - [1 \text{ mol N}_2(g) (191.5 \text{ J/K}\cdot\text{mol}) + 1 \text{ mol O}_2(g) (205.0 \text{ J/K}\cdot\text{mol})] \\ &= \mathbf{24.8 \text{ J/K}}\end{aligned}$$

b) $\Delta G_{373}^{\circ} = \Delta H^{\circ} - ((273 + 100.)\text{K}) (\Delta S^{\circ})$
 $= 180.58 \text{ kJ} - [(373 \text{ K}) (24.8 \text{ J/K}) (1 \text{ kJ}/10^3 \text{ J})]$
 $= 171.3296 = \mathbf{171.33 \text{ kJ}}$
 $\Delta G_{2833}^{\circ} = \Delta H^{\circ} - ((273 + 2560.)\text{K}) (\Delta S^{\circ})$
 $= 180.58 \text{ kJ} - [(2833 \text{ K}) (24.8 \text{ J/K}) (1 \text{ kJ}/10^3 \text{ J})]$
 $= 110.3216 = \mathbf{110.3 \text{ kJ}}$
 $\Delta G_{3813}^{\circ} = \Delta H^{\circ} - ((273 + 3540.)\text{K}) (\Delta S^{\circ})$
 $= 180.58 \text{ kJ} - [(3813 \text{ K}) (24.8 \text{ J/K}) (1 \text{ kJ}/10^3 \text{ J})]$
 $= 86.0176 = \mathbf{86.0 \text{ kJ}}$

c) The values of ΔG 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 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 $\Delta G_{\text{rxn}}^{\circ} = 0 = \Delta H_{\text{rxn}}^{\circ} - T \Delta S_{\text{rxn}}^{\circ}$.

$$\begin{aligned}\Delta H_{\text{rxn}}^{\circ} &= T \Delta S_{\text{rxn}}^{\circ} \\ T_{\text{bpt}} &= \Delta H^{\circ} / \Delta S^{\circ}\end{aligned}$$

$$\Delta H^\circ = [1 \text{ mol } (\Delta H_f^\circ (\text{Br}_2(g)))] - [1 \text{ mol } (\Delta H_f^\circ (\text{Br}_2(l)))]$$

$$\Delta H^\circ = [1 \text{ mol } (30.91 \text{ kJ/mol})] - [1 \text{ mol } (\Delta H_f^\circ (0))] = \mathbf{30.91 \text{ kJ} = 30,910 \text{ J}}$$

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

$$\Delta S^\circ = [1 \text{ mol } (S^\circ (245.38 \text{ J/K}\cdot\text{mol}))] - [1 \text{ mol } (S^\circ (152.23 \text{ J/K}\cdot\text{mol}))] = \mathbf{93.15 \text{ J/K}}$$

$$T_{\text{bpt}} = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{30910 \text{ J}}{93.15 \text{ J/K}} = 331.830 = \mathbf{331.8 \text{ K}}$$

20.49 S(rhombic) $\rightleftharpoons$ S(monoclinic)

$$\Delta H_{\text{rxn}}^\circ = [1 \text{ mol S(monoclinic)} (0.30 \text{ kJ/mol})] - [1 \text{ mol S(rhombic)} (0 \text{ kJ/mol})] (10^3 \text{ J/1 kJ}) = 3.0 \times 10^2 \text{ J}$$

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

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

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

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

$$T = \Delta H^\circ / \Delta S^\circ = (3.0 \times 10^2 \text{ J}) / (0.7 \text{ J/K}) = 428.571 = \mathbf{4 \times 10^2 \text{ K}}$$

20.50 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 H_2 ,” not per 2 mol H_2 .

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

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

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

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

$$\Delta S_{\text{rxn}}^\circ = [(1 \text{ mol H}_2\text{O}) (188.72 \text{ J/mol}\cdot\text{K})]$$

$$- [(1 \text{ mol H}_2) (130.6 \text{ J/mol}\cdot\text{K}) + (1/2 \text{ mol O}_2) (205.0 \text{ J/mol}\cdot\text{K})]$$

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

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

$$\Delta G_{\text{rxn}}^\circ = [(1 \text{ mol H}_2\text{O}) (-228.60 \text{ kJ/mol})] - [(1 \text{ mol H}_2) (0) + (1/2 \text{ mol O}_2) (0)]$$

$$\Delta G_{\text{rxn}}^\circ = \mathbf{-228.60 \text{ kJ}}$$

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 ΔH term.

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

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

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

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

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{-241.826 \text{ kJ}}{-44.38 \text{ J/K}} \left(\frac{10^3 \text{ J}}{1 \text{ kJ}} \right) = 5448.986 = \mathbf{5.45 \times 10^3 \text{ K}}$$

- 20.51 $\text{C}_6\text{H}_{12}\text{O}_6(\text{s}) \rightarrow 2 \text{C}_2\text{H}_5\text{OH}(\text{l}) + 2 \text{CO}_2(\text{g})$

$$\Delta H_{\text{rxn}}^\circ = [2 \text{ mol C}_2\text{H}_5\text{OH}(\text{l}) (-277.63 \text{ kJ/mol}) + 2 \text{ mol CO}_2(\text{g}) (-393.5 \text{ kJ/mol})]$$

$$- [1 \text{ mol C}_6\text{H}_{12}\text{O}_6(\text{s}) (-1273.3 \text{ kJ/mol})]$$

$$= -68.96 \text{ kJ/mol} = \mathbf{-69.0 \text{ kJ/mol}}$$

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

$$= 537.3 \text{ J/K} = \mathbf{537 \text{ J/K}}$$

$$\Delta G_{\text{rxn}}^\circ = [2 \text{ mol C}_2\text{H}_5\text{OH}(\text{l}) (-174.8 \text{ kJ/mol}) + 2 \text{ mol CO}_2(\text{g}) (-394.4 \text{ kJ/mol})]$$

$$- [1 \text{ mol C}_6\text{H}_{12}\text{O}_6(\text{s}) (-910.56 \text{ kJ/mol})] = -227.84 \text{ kJ/mol} = \mathbf{-227.8 \text{ kJ/mol}}$$

No, a reaction with a negative value for ΔH and a positive value for ΔS is spontaneous at all temperatures.

20.52 a) An equilibrium constant that is much less than 1 indicates that very little product is made to reach equilibrium. The reaction, thus, is not spontaneous in the forward direction and ΔG° is a relatively large positive value.
 b) A large negative ΔG° 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 ΔG° .

20.53 a) Point x represents the difference between $G_{\text{reactants}}$ and G_{products} or ΔG° , 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. 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).

20.54 For a spontaneous process, ΔG 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 ΔG .

20.55 The standard free energy change, ΔG° , occurs when all components of the system are in their standard states (do not confuse this with ΔG_f° , the standard free energy of formation). 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 For each reaction, first find ΔG° , then calculate K from $\Delta G^\circ = -RT \ln K$. Calculate $\Delta G_{\text{rxn}}^\circ$ using the ΔG_f° values from Appendix B.

a) $\Delta G^\circ = [1 \text{ mol } (\Delta G_f^\circ (\text{NO}_2(\text{g}))) - [1 \text{ mol } (\Delta G_f^\circ (\text{NO}(\text{g}))) + \frac{1}{2} \text{ mol } (\Delta G_f^\circ (\text{O}_2(\text{g})))]$

$$= [1 \text{ mol } (51 \text{ kJ})] - [1 \text{ mol } (86.60 \text{ kJ}) + \frac{1}{2} \text{ mol } (0 \text{ kJ})] = -35.6 \text{ kJ} \text{ (unrounded)}$$

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

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

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

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

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

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

$$\begin{aligned} \text{c) } \Delta G^\circ &= [2 \text{ mol } (\Delta G_f^\circ (\text{CO}(g)))] - [2 \text{ mol } (\Delta G_f^\circ (\text{C}(\text{graphite}))) + 1 \text{ mol } (\Delta G_f^\circ (\text{O}_2(g)))] \\ &= [2 \text{ mol } (-137.2 \text{ kJ/mol})] - [2 \text{ mol } (0) + 1 \text{ mol } (0) \text{ kJ}] = -274.4 \text{ kJ} \\ \ln K &= \frac{\Delta G^\circ}{-RT} = \left(\frac{-274.4 \text{ kJ/mol}}{-(8.314 \text{ J/mol} \cdot \text{K})(298 \text{ K})} \right) \left(\frac{10^3 \text{ J}}{1 \text{ kJ}} \right) = 110.75359 \text{ (unrounded)} \\ K &= e^{110.75359} = 1.2579778 \times 10^{48} = \mathbf{1.26 \times 10^{48}} \end{aligned}$$

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

20.57 The equilibrium constant, K , is related to ΔG° through the equation $\Delta G^\circ = -RT \ln K$. Calculate $\Delta G_{\text{rxn}}^\circ$ using the ΔG_f° values from Appendix B.

$$\begin{aligned} \text{a) } \Delta G_{\text{rxn}}^\circ &= [(2 \text{ mol}) (\Delta G_f^\circ (\text{H}_2\text{O})) + (2 \text{ mol}) (\Delta G_f^\circ (\text{SO}_2))] - [(2 \text{ mol}) (\Delta G_f^\circ (\text{H}_2\text{S})) + (3 \text{ mol}) (\Delta G_f^\circ (\text{O}_2))] \\ \Delta G_{\text{rxn}}^\circ &= [(2 \text{ mol}) (-228.60 \text{ kJ/mol}) + (2 \text{ mol}) (-300.2 \text{ kJ/mol})] - [(2 \text{ mol}) (-33 \text{ kJ/mol}) + (3 \text{ mol}) (0)] \\ \Delta G_{\text{rxn}}^\circ &= -991.6 \text{ kJ (unrounded)} \\ \ln K &= \frac{\Delta G^\circ}{-RT} = \left(\frac{-991.6 \text{ kJ/mol}}{-(8.314 \text{ J/mol} \cdot \text{K})(298 \text{ K})} \right) \left(\frac{10^3 \text{ J}}{1 \text{ kJ}} \right) = 400.2305 \text{ (unrounded)} \\ K &= e^{400.2305} = 6.571696 \times 10^{173} = \mathbf{6.57 \times 10^{173}} \end{aligned}$$

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 $\Delta G_{\text{rxn}}^\circ$.

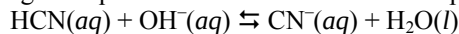
Your calculator might register “error” when trying to calculate e^{400} because it cannot calculate exponents greater than 99. In this case, divide 400.2305 by 2 (= 200.115), and calculate $e^{200.115} e^{200.115} = (8.1066 \times 10^{86})^2 = (8.1066)^2 \times 10^{86 \times 2} = 65.71696 \times 10^{172} = 6.57 \times 10^{173}$, which equals the first answer with rounding errors.

$$\begin{aligned} \text{b) } \Delta G_{\text{rxn}}^\circ &= [(1 \text{ mol}) (\Delta G_f^\circ (\text{H}_2\text{O})) + (1 \text{ mol}) (\Delta G_f^\circ (\text{SO}_3))] - [(1 \text{ mol}) (\Delta G_f^\circ (\text{H}_2\text{SO}_4))] \\ \Delta G_{\text{rxn}}^\circ &= [(1 \text{ mol}) (-237.192 \text{ kJ/mol}) + (1 \text{ mol}) (-371 \text{ kJ/mol})] - [(1 \text{ mol}) (-690.059 \text{ kJ/mol})] \\ \Delta G_{\text{rxn}}^\circ &= 81.867 \text{ kJ (unrounded)} \\ \ln K &= \frac{\Delta G^\circ}{-RT} = \left(\frac{81.867 \text{ kJ/mol}}{-(8.314 \text{ J/mol} \cdot \text{K})(298 \text{ K})} \right) \left(\frac{10^3 \text{ J}}{1 \text{ kJ}} \right) = -33.0432 \text{ (unrounded)} \\ K &= e^{-33.0432} = 4.4619 \times 10^{-15} = \mathbf{4.46 \times 10^{-15}} \end{aligned}$$

$$\text{c) } \Delta G_{\text{rxn}}^\circ = [(1 \text{ mol}) (\Delta G_f^\circ (\text{NaCN})) + (1 \text{ mol}) (\Delta G_f^\circ (\text{H}_2\text{O}))] - [(1 \text{ mol}) (\Delta G_f^\circ (\text{HCN})) + (1 \text{ mol}) (\Delta G_f^\circ (\text{NaOH}))]$$

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

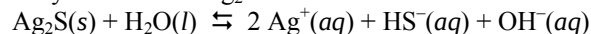
Converting the equation to net ionic form will simplify the problem:



$$\begin{aligned} \Delta G_{\text{rxn}}^\circ &= [(1 \text{ mol}) (\Delta G_f^\circ (\text{CN}^-)) + (1 \text{ mol}) (\Delta G_f^\circ (\text{H}_2\text{O}))] - [(1 \text{ mol}) (\Delta G_f^\circ (\text{HCN})) + (1 \text{ mol}) (\Delta G_f^\circ (\text{OH}^-))] \\ \Delta G_{\text{rxn}}^\circ &= [(1 \text{ mol}) (166 \text{ kJ/mol}) + (1 \text{ mol}) (-237.192 \text{ kJ/mol})] \\ &\quad - [(1 \text{ mol}) (112 \text{ kJ/mol}) + (1 \text{ mol}) (-157.30 \text{ kJ/mol})] \\ \Delta G_{\text{rxn}}^\circ &= -25.892 \text{ kJ (unrounded)} \end{aligned}$$

$$\begin{aligned} \ln K &= \frac{\Delta G^\circ}{-RT} = \left(\frac{-25.892 \text{ kJ/mol}}{-(8.314 \text{ J/mol} \cdot \text{K})(298 \text{ K})} \right) \left(\frac{10^3 \text{ J}}{1 \text{ kJ}} \right) = 10.45055 \text{ (unrounded)} \\ K &= e^{10.45055} = 3.4563 \times 10^4 = \mathbf{3.46 \times 10^4} \end{aligned}$$

20.58 The solubility reaction for Ag_2S is



$$\begin{aligned}\Delta G^\circ &= [2 \text{ mol } (\Delta G_f^\circ \text{Ag}^+(aq)) + 1 \text{ mol } (\Delta G_f^\circ \text{HS}^-(aq)) + 1 \text{ mol } (\Delta G_f^\circ \text{OH}^-(aq))] \\ &\quad - [1 \text{ mol } (\Delta G_f^\circ \text{Ag}_2\text{S}(s)) + 1 \text{ mol } (\Delta G_f^\circ \text{H}_2\text{O}(l))] \\ &= [(2 \text{ mol}) (77.111 \text{ kJ/mol}) + (1 \text{ mol}) (12.6 \text{ kJ/mol}) + (1 \text{ mol}) (-157.30 \text{ kJ/mol})] \\ &\quad - [(1 \text{ mol}) (-40.3 \text{ kJ/mol}) + (1 \text{ mol}) (-237.192 \text{ kJ/mol})] \\ &= 287.014 \text{ kJ (unrounded)} \\ \ln K &= \frac{\Delta G^\circ}{-RT} = \left(\frac{287.014 \text{ kJ/mol}}{-(8.314 \text{ J/mol} \cdot \text{K})(298 \text{ K})} \right) \left(\frac{10^3 \text{ J}}{1 \text{ kJ}} \right) = -115.8448675 \text{ (unrounded)} \\ K &= e^{-115.8448675} = 4.8889241 \times 10^{-51} = \mathbf{4.89 \times 10^{-51}}\end{aligned}$$

20.59 $\text{CaF}_2(s) \rightleftharpoons \text{Ca}^{2+}(aq) + 2 \text{F}^-(aq)$

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

20.60 Calculate $\Delta G_{\text{rxn}}^\circ$, recognizing that $\text{I}_2(s)$, not $\text{I}_2(g)$, is the standard state for iodine.

Solve for K_p using the equation $\Delta G^\circ = -RT \ln K$.

$$\begin{aligned}\Delta G_{\text{rxn}}^\circ &= [(2 \text{ mol}) (\Delta G_f^\circ (\text{ICl}))] - [(1 \text{ mol}) (\Delta G_f^\circ (\text{I}_2)) + (1 \text{ mol}) (\Delta G_f^\circ (\text{Cl}_2))] \\ \Delta G_{\text{rxn}}^\circ &= [(2 \text{ mol}) (-6.075 \text{ kJ/mol})] - [(1 \text{ mol}) (19.38 \text{ kJ/mol}) + (1 \text{ mol}) (0)] \\ v &= -31.53 \text{ kJ} \\ \ln K_p &= \Delta G^\circ / -RT = \left(\frac{-31.53 \text{ kJ/mol}}{-(8.314 \text{ J/mol} \cdot \text{K})(298 \text{ K})} \right) \left(\frac{10^3 \text{ J}}{1 \text{ kJ}} \right) = 12.726169 \text{ (unrounded)} \\ K_p &= e^{12.726169} = 3.3643794 \times 10^5 = \mathbf{3.36 \times 10^5}\end{aligned}$$

20.61 $\text{CaCO}_3(s) \rightleftharpoons \text{CaO}(s) + \text{CO}_2(g)$

$$K_p = P_{\text{CO}_2}$$

$$\begin{aligned}\Delta G_{\text{rxn}}^\circ &= [1 \text{ mol } \text{CaO}(s) (-603.5 \text{ kJ/mol}) + 1 \text{ mol } \text{CO}_2(g) (-394.4 \text{ kJ/mol})] - [1 \text{ mol } \text{CaCO}_3(s) (-1128.8 \text{ kJ/mol})] \\ &= 130.9 \text{ kJ} \\ \ln K_p &= \Delta G^\circ / -RT = \left(\frac{130.9 \text{ kJ/mol}}{-(8.314 \text{ J/mol} \cdot \text{K})(298 \text{ K})} \right) \left(\frac{10^3 \text{ J}}{1 \text{ kJ}} \right) = -52.83398 \text{ (unrounded)} \\ K_p &= e^{-52.83398} = 1.1336892 \times 10^{-23} = \mathbf{1.13 \times 10^{-23} \text{ atm}} = P_{\text{CO}_2}\end{aligned}$$

20.62 $\Delta G^\circ = -RT \ln K = -(8.314 \text{ J/mol} \cdot \text{K})(298 \text{ K}) \ln (1.7 \times 10^{-5}) = 2.72094 \times 10^4 \text{ J/mol} = \mathbf{2.7 \times 10^4 \text{ J/mol}}$

The large positive ΔG° 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 this:

$$\begin{aligned}\text{this: } \text{PbCl}_2(s) &\rightleftharpoons \text{Pb}^{2+}(aq) + \text{Cl}^-(aq) \\ Q &= [\text{Pb}^{2+}][\text{Cl}^-]^2 \\ &= (1 \text{ M})(1 \text{ M})^2 \\ &= 1\end{aligned}$$

Since $Q > K_{\text{sp}}$, it is impossible to prepare a standard state solution of PbCl_2 .

- 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 ΔG° 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:

$$Q = \frac{[\text{Zn}^{2+}][\text{F}^-]^2}{(1 \text{ M})(1 \text{ M})^2} = 1$$

Since $Q > K_{\text{sp}}$, it is impossible to prepare a standard state solution of ZnF_2 .

- 20.64 a) The equilibrium constant, K , is related to ΔG° through the equation $\Delta G^\circ = -RT \ln K$.
 $\Delta G^\circ = -RT \ln K = -(8.314 \text{ J/mol}\cdot\text{K}) (298 \text{ K}) \ln (9.1 \times 10^{-6}) = 2.875776 \times 10^4 = \mathbf{2.9 \times 10^4 \text{ J/mol}}$
 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 to find ΔG .

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

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

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

- 20.65 a) The equilibrium constant, K , is related to ΔG° through the equation $\Delta G^\circ = -RT \ln K$.
 $\Delta G^\circ = -RT \ln K = -(8.314 \text{ J/mol}\cdot\text{K}) ((273 + 25) \text{ K}) \ln (5.6 \times 10^8) = -4.9906841 \times 10^4 = \mathbf{-5.0 \times 10^4 \text{ J/mol}}$
 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 to find ΔG .

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

$$\Delta G = \Delta G^\circ + RT \ln Q = -4.9906841 \times 10^4 \text{ J/mol} + (8.314 \text{ J/mol}\cdot\text{K}) (298) \ln (6.4 \times 10^{14}) = 3.4559755 \times 10^4 = \mathbf{3.5 \times 10^4 \text{ J/mol}}$$

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

- 20.66 Formation of O_3 from O_2 : $3 \text{ O}_2(\text{g}) \rightleftharpoons 2 \text{ O}_3(\text{g})$ or per mole of ozone: $3/2 \text{ O}_2(\text{g}) \rightleftharpoons \text{O}_3(\text{g})$

a) To decide when production of ozone is favored, both the signs of ΔH_f° and ΔS_f° for ozone are needed. From Appendix B, the values of ΔH_f° and S° can be used:

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

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

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

$$\Delta S_f^\circ = [1 \text{ mol } (238.82 \text{ J/mol}\cdot\text{K})] - [3/2 \text{ mol } (205.0 \text{ J/mol}\cdot\text{K})] = -68.68 \text{ J/mol}\cdot\text{K} \text{ (unrounded).}$$

The positive sign for ΔH_f° and the negative sign for ΔS_f° indicates the formation of ozone is favored at **no temperature**. The reaction is nonspontaneous at all temperatures.

b) At 298 K, ΔG° can be most easily calculated from ΔG_f° values for the reaction $3/2 \text{ O}_2(\text{g}) \rightleftharpoons \text{O}_3(\text{g})$.

$$\text{From } \Delta G_f^\circ: \Delta G^\circ = [1 \text{ mol O}_3 (\Delta G_f^\circ \text{ O}_3)] - [3/2 \text{ mol } (\Delta G_f^\circ \text{ O}_2)]$$

$$\Delta G^\circ = [1 \text{ mol } (163 \text{ kJ/mol O}_3)] - [3/2 \text{ mol } (0)] = \mathbf{163 \text{ kJ}}$$
 for the formation of one mole of O_3 .

c) Calculate the value for Q and then use to find ΔG .

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

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

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

20.67 $\text{BaSO}_4(\text{s}) \rightleftharpoons \text{Ba}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$

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

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

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

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

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

20.68 a) diamond $\rightarrow$ graphite

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

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

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

b) Since ΔG° 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.

c) graphite $\rightarrow$ diamond

For this process, the signs of ΔH and ΔS are, like the reaction, reversed. A process with ΔH positive and ΔS 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

	ΔS_{rxn}	ΔH_{rxn}	ΔG_{rxn}	Comment
(a)	+	–	–	Spontaneous
(b)	(+)	0	–	Spontaneous
(c)	–	+	(+)	Not spontaneous
(d)	0	(–)	–	Spontaneous
(e)	(–)	0	+	Not spontaneous
(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 $\Delta G_{\text{rxn}} = \Delta H - T\Delta S = -T\Delta S$, ΔS must be positive for ΔG_{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 $\Delta G_{\text{rxn}} = \Delta H - T\Delta S = \Delta H$, ΔH must be negative for ΔG_{rxn} to be negative.

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

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

20.70 At the freezing point, the system is at equilibrium, so $\Delta G^\circ = 0$

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

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

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

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

20.71 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:

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

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

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

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

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

b) Use Appendix B to locate the thermodynamic values.

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

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

$$\Delta G = \Delta H - T\Delta S = 117.3 \text{ kJ} - (298 \text{ K}) (174.74 \text{ J/K}) (1 \text{ kJ}/10^3 \text{ J}) = 65.22748 = \mathbf{65.2 \text{ kJ}}$$

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

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

$$T = \Delta H^\circ/\Delta S^\circ = [(117.3 \text{ kJ}) (10^3 \text{ J/kJ})]/(174.74 \text{ J/K}) = 671.2830 = \mathbf{671 \text{ K}}$$

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

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

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

e) This is similar to part (d) except a new ΔG° must be determined at 1200 K.

$$\Delta G = \Delta H - T\Delta S = 117.3 \text{ kJ} - (1200 \text{ K}) (174.74 \text{ J/K}) (1 \text{ kJ}/10^3 \text{ J}) = -92.388 \text{ kJ (unrounded)}$$

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

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

20.73 a) $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$

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

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

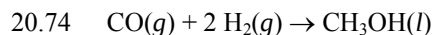
$$K_p = 50[(0.0821 \text{ Latm/molK})(733 \text{ K})]^0$$

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

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

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

The value of K_c is 50 in this situation as in a) so ΔG° does not change.



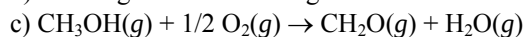
$$a) \Delta H_{\text{rxn}}^\circ = [1 \text{ mol CH}_3\text{OH}(l) (-238.6 \text{ kJ/mol})] - [1 \text{ mol CO}(g) (-110.5 \text{ kJ/mol}) + 2 \text{ mol H}_2(g) (0 \text{ kJ/mol})] \\ = -128.1 \text{ kJ}$$

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

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -128.1 \text{ kJ} - [(298 \text{ K}) (-331.7 \text{ J/K}) (1 \text{ kJ}/10^3 \text{ J})] = -29.2534 = -29.2 \text{ kJ}$$

The negative value of ΔG° indicates that the reaction is spontaneous (feasible).

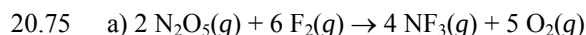
b) ΔH° negative and ΔS° negative means the reaction is favored at low temperature.



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

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

$$\Delta G_{373}^\circ = \Delta H^\circ - T\Delta S^\circ = -156.626 \text{ kJ} - [(273 + 100.)\text{K}] (67.22 \text{ J/K}) (1 \text{ kJ}/10^3 \text{ J}) = -181.699 = \mathbf{-182 \text{ kJ}}$$



b) Use the values from Appendix B to determine the value of ΔG° .

$$\Delta G_{\text{rxn}}^\circ = [(4 \text{ mol}) (\Delta G_f^\circ (\text{NF}_3)) + (5 \text{ mol}) (\Delta G_f^\circ (\text{O}_2))] - [(2 \text{ mol}) (\Delta G_f^\circ (\text{N}_2\text{O}_5)) + (6 \text{ mol}) (\Delta G_f^\circ (\text{F}_2))]$$

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

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

c) Calculate the value for Q and then use to find ΔG .

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

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

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

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

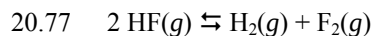
c) $\Delta G_{373}^\circ = \Delta H^\circ - T\Delta S^\circ$

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

d) $\Delta H_{\text{rxn}}^\circ = [2 \text{ mol NO}(g) (90.29 \text{ kJ/mol}) + 1 \text{ mol Br}_2(g) (30.91 \text{ kJ/mol})] - [2 \text{ mol NOBr}(g) (\Delta H_{\text{NOBr}}^\circ)] \\ = 4.8002265 \times 10^4 \text{ J} (1 \text{ kJ}/10^3 \text{ J}) \\ 2 \text{ mol NOBr}(g) (\Delta H_{\text{NOBr}}^\circ) = [2 (90.29 \text{ kJ}) + 1 (30.91 \text{ kJ})] - (4.8002265 \times 10^4 \text{ J} (1 \text{ kJ} / 10^3 \text{ J})) \\ (\Delta H_{\text{NOBr}}^\circ) = 81.7438675 = \mathbf{81.7 \text{ kJ/mol}}$

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

$$\begin{aligned} \text{f) } \Delta G_{\text{rxn}}^{\circ} &= [2 \text{ mol NO}(g) (86.60 \text{ kJ/mol}) + 1 \text{ mol Br}_2(g) (3.13 \text{ kJ/mol})] - [2 \text{ mol NOBr}(g) (\Delta G_{\text{NOBr}}^{\circ})] \\ &= 1.1801225 \times 10^4 \text{ J} (1 \text{ kJ}/10^3 \text{ J}) \\ 2 \text{ mol NOBr}(g) (\Delta G_{\text{NOBr}}^{\circ}) &= [2 (86.60 \text{ kJ}) + 1 (3.13 \text{ kJ})] - (1.1801225 \times 10^4 \text{ J} (1 \text{ kJ} / 10^3 \text{ J})) \\ (\Delta G_{\text{NOBr}}^{\circ}) &= 82.264 = \mathbf{82.3 \text{ kJ/mol}} \end{aligned}$$

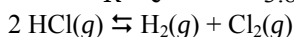


$$\Delta G_{\text{rxn}}^{\circ} = [1 \text{ mol H}_2(g) (0 \text{ kJ/mol}) + 1 \text{ mol F}_2(g) (0 \text{ kJ/mol})] - [2 \text{ mol HF}(g) (-275 \text{ kJ/mol})] = 550. \text{ kJ}$$

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

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

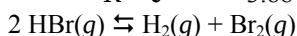
$$K = e^{-221.9915} = 3.8932879 \times 10^{-97} = \mathbf{4 \times 10^{-97}}$$



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

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

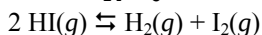
$$K = e^{-76.930} = 3.88799 \times 10^{-34} = \mathbf{4 \times 10^{-34}}$$



$$\Delta G_{\text{rxn}}^{\circ} = [0 + 1 \text{ mol Br}_2(g) (3.13 \text{ kJ/mol})] - [2 \text{ mol HBr}(g) (-53.5 \text{ kJ/mol})] = 110.1 \text{ kJ (unrounded)}$$

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

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



$$\Delta G_{\text{rxn}}^{\circ} = [0 + 1 \text{ mol I}_2(g) (19.38 \text{ kJ/mol})] - [2 \text{ mol HI}(g) (1.3 \text{ kJ/mol})] = 16.78 \text{ kJ (unrounded)}$$

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

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

$$K_{\text{d}}(\text{HI}) > K_{\text{d}}(\text{HBr}) > K_{\text{d}}(\text{HCl}) > K_{\text{d}}(\text{HF})$$

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.



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

$$\Delta H_{\text{rxn}}^{\circ} = [(3 \text{ mol}) (-393.5 \text{ kJ/mol}) + (4 \text{ mol}) (0)] - [(3 \text{ mol}) (0) + (2 \text{ mol}) (-825.5 \text{ kJ/mol})] = \mathbf{470.5 \text{ kJ}}$$

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

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

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

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

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

Because ΔG 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.

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

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

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

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

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

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

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

$$-0.88 \text{ kJ/mol} = -1.35 \text{ kJ/mol} - T \Delta S_{\text{rxn}}^{\circ}$$

$$0.88 \text{ kJ/mol} - 1.35 \text{ kJ/mol} = -0.47 \text{ kJ/mol} = T \Delta S_{\text{rxn}}^{\circ}$$

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

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

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

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

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

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

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

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

Calculate $\Delta G_{\text{rxn}}^{\circ}$ for the reaction and see if the value is positive or negative.

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

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

$$\Delta G_{\text{rxn}}^{\circ} = -36.636 = -37 \text{ kJ}$$

Yes, the reaction is spontaneous because the value of $\Delta G_{\text{rxn}}^{\circ}$ is negative.

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

The value of $\Delta G_{\text{rxn}}^{\circ}$ indicates the spontaneity of the reaction, and the individual $\Delta H_{\text{rxn}}^{\circ}$ and $\Delta S_{\text{rxn}}^{\circ}$ values are necessary to determine the temperature.

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

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

$$\Delta G_{\text{rxn}}^{\circ} = -24 \text{ kJ}$$

Yes, the reaction is spontaneous because the value of $\Delta G_{\text{rxn}}^{\circ}$ is negative.

$$\begin{aligned}\Delta H_{\text{rxn}}^{\circ} &= [(4 \text{ mol}) (\Delta H_f^{\circ}(\text{NO}_2)) + (1 \text{ mol}) (\Delta H_f^{\circ}(\text{O}_2))] - [(2 \text{ mol}) (\Delta H_f^{\circ}(\text{N}_2\text{O}_5))] \\ \Delta H_{\text{rxn}}^{\circ} &= [(4 \text{ mol}) (33.2 \text{ kJ/mol}) + (1 \text{ mol}) (0)] - [(2 \text{ mol}) (-43.1 \text{ kJ/mol})] \\ \Delta H_{\text{rxn}}^{\circ} &= 219.0 \text{ kJ} \\ \Delta S_{\text{rxn}}^{\circ} &= [(4 \text{ mol}) (S^{\circ}(\text{NO}_2)) + (1 \text{ mol}) (S^{\circ}(\text{O}_2))] - [(2 \text{ mol}) (S^{\circ}(\text{N}_2\text{O}_5))] \\ \Delta S_{\text{rxn}}^{\circ} &= [(4 \text{ mol}) (239.9 \text{ J/mol}\cdot\text{K}) + (1 \text{ mol}) (205 \text{ J/mol}\cdot\text{K})] - [(2 \text{ mol}) (178 \text{ J/mol}\cdot\text{K})] \\ \Delta S_{\text{rxn}}^{\circ} &= 808.6 \text{ J/K} \\ \Delta G_{\text{rxn}}^{\circ} = 0 &= \Delta H_{\text{rxn}}^{\circ} - T \Delta S_{\text{rxn}}^{\circ} \\ \Delta H_{\text{rxn}}^{\circ} &= T \Delta S_{\text{rxn}}^{\circ} \\ T &= \frac{\Delta H^{\circ}}{\Delta S^{\circ}} = \frac{219.0 \text{ kJ}}{808.6 \text{ J/K}} \left(\frac{10^3 \text{ J}}{1 \text{ kJ}} \right) = 270.838 = \mathbf{270.8 \text{ K}}\end{aligned}$$

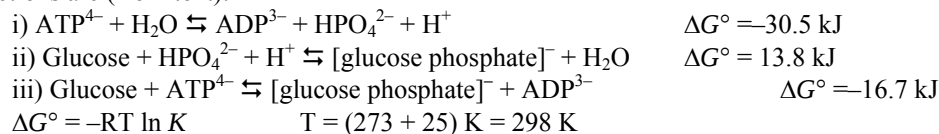
c) The balanced chemical equation is $2 \text{N}_2\text{O}_5(g) \rightarrow 4 \text{NO}_2(g) + \text{O}_2(g)$

The individual $\Delta H_{\text{rxn}}^{\circ}$ and $\Delta S_{\text{rxn}}^{\circ}$ values are necessary to determine the temperature.

$$\begin{aligned}\Delta H_{\text{rxn}}^{\circ} &= [(4 \text{ mol}) (\Delta H_f^{\circ}(\text{NO}_2)) + (1 \text{ mol}) (\Delta H_f^{\circ}(\text{O}_2))] - [(2 \text{ mol}) (\Delta H_f^{\circ}(\text{N}_2\text{O}_5))] \\ \Delta H_{\text{rxn}}^{\circ} &= [(4 \text{ mol}) (33.2 \text{ kJ/mol}) + (1 \text{ mol}) (0)] - [(2 \text{ mol}) (11 \text{ kJ/mol})] \\ \Delta H_{\text{rxn}}^{\circ} &= 110.8 = 111 \text{ kJ} \\ \Delta S_{\text{rxn}}^{\circ} &= [(4 \text{ mol}) (S^{\circ}(\text{NO}_2)) + (1 \text{ mol}) (S^{\circ}(\text{O}_2))] - [(2 \text{ mol}) (S^{\circ}(\text{N}_2\text{O}_5))] \\ \Delta S_{\text{rxn}}^{\circ} &= [(4 \text{ mol}) (239.9 \text{ J/mol}\cdot\text{K}) + (1 \text{ mol}) (205 \text{ J/mol}\cdot\text{K})] - [(2 \text{ mol}) (346 \text{ J/mol}\cdot\text{K})] \\ \Delta S_{\text{rxn}}^{\circ} &= 472.6 = 473 \text{ J/K} \\ \Delta G_{\text{rxn}}^{\circ} = 0 &= \Delta H_{\text{rxn}}^{\circ} - T \Delta S_{\text{rxn}}^{\circ} \\ \Delta H_{\text{rxn}}^{\circ} &= T \Delta S_{\text{rxn}}^{\circ} \\ T &= \frac{\Delta H^{\circ}}{\Delta S^{\circ}} = \frac{110.8 \text{ kJ}}{472.6 \text{ J/K}} \left(\frac{10^3 \text{ J}}{1 \text{ kJ}} \right) = 234.4477 = \mathbf{234 \text{ K}}\end{aligned}$$

The temperature is different because the values for N_2O_5 vary with physical state.

20.81 The reactions are (from text):



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

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

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

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

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

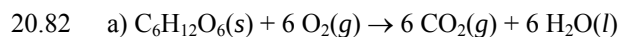
$$K = e^{11.8339} = 1.37847 \times 10^5 = \mathbf{1.38 \times 10^5}$$

$$\text{ii) } \ln K = \Delta G^\circ / -RT = \left(\frac{13.8 \text{ kJ/mol}}{-(8.314 \text{ J/mol} \cdot \text{K})(310. \text{ K})} \right) \left(\frac{10^3 \text{ J}}{1 \text{ kJ}} \right) = -5.3543576 \text{ (unrounded)}$$

$$K = e^{-5.3543576} = 4.7275 \times 10^{-3} = \mathbf{4.73 \times 10^{-3}}$$

$$\text{iii) } \ln K = \Delta G^\circ / -RT = \left(\frac{-16.7 \text{ kJ/mol}}{-(8.314 \text{ J/mol} \cdot \text{K})(310. \text{ K})} \right) \left(\frac{10^3 \text{ J}}{1 \text{ kJ}} \right) = 6.4795 \text{ (unrounded)}$$

$$K = e^{6.4795} = 6.51645 \times 10^2 = \mathbf{6.52 \times 10^2}$$



$$\begin{aligned} \Delta G^\circ &= [6 \text{ mol } (\Delta G_f^\circ \text{ CO}_2(\text{g})) + 6 \text{ mol } (\Delta G_f^\circ \text{ H}_2\text{O}(\text{l}))] - [1 \text{ mol } (\Delta G_f^\circ \text{ C}_6\text{H}_{12}\text{O}_6(\text{s})) + 6 \text{ mol } (\Delta G_f^\circ \text{ O}_2(\text{g}))] \\ &= [(6 \text{ mol}) (-394.4 \text{ kJ/mol}) + (6 \text{ mol}) (-237.192 \text{ kJ/mol})] \\ &\quad - [(1 \text{ mol}) (-910.56 \text{ kJ/mol}) + (6 \text{ mol}) (0 \text{ kJ/mol})] = -2878.992 = \mathbf{-2879.0 \text{ kJ}} \end{aligned}$$

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

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

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

20.83 a) Graph **D** depicts how G_{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_{sys} changes as ice melts at 1°C . 1°C is higher than the melting point of water, therefore the system is not at equilibrium. Melting is spontaneous at 1°C and 1 atm, and the G_{sys} will decrease until the system reaches equilibrium.

20.84 a) $K_p = 1.00$ when $\Delta G = 0$; combine this with $\Delta G = \Delta H - T\Delta S$. First, calculate ΔH and ΔS , using values in the Appendix.

$$\begin{aligned} \Delta H^\circ &= [(2 \text{ mol NH}_3) (\Delta H_f^\circ \text{ NH}_3)] - [(1 \text{ mol N}_2) (\Delta H_f^\circ \text{ N}_2) + (3 \text{ mol H}_2) (\Delta H_f^\circ \text{ H}_2)] \\ &= [(2 \text{ mol NH}_3) (-45.9 \text{ kJ/mol})] - [(1 \text{ mol N}_2) (0) + (3 \text{ mol H}_2) (0)] = -91.8 \text{ kJ} \end{aligned}$$

$$\begin{aligned} \Delta S^\circ &= [(2 \text{ mol NH}_3) (S^\circ \text{ NH}_3)] - [(1 \text{ mol N}_2) (S^\circ \text{ N}_2) + (3 \text{ mol H}_2) (S^\circ \text{ H}_2)] \\ &= [(2 \text{ mol NH}_3) (193 \text{ J/mol} \cdot \text{K})] - [(1 \text{ mol N}_2) (191.50 \text{ J/mol} \cdot \text{K}) + (3 \text{ mol H}_2) (130.6 \text{ J/mol} \cdot \text{K})] \\ &= -197.3 \text{ J/K (unrounded)} \end{aligned}$$

$\Delta G = 0$ (at equilibrium)

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

$$\Delta H = T\Delta S$$

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

b) Use the relationships: $\Delta G = \Delta H - T\Delta S$ and $\Delta G = -RT \ln K$ with $T = (273 + 400.) \text{ K} = 673 \text{ K}$

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

$$\Delta G = 4.09829 \times 10^4 \text{ J (unrounded)}$$

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

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

$$K = e^{-7.32449} = 6.591934 \times 10^{-4} = \mathbf{6.59 \times 10^{-4}}$$

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