CHAPTER 17

SPONTANEITY, ENTROPY, AND FREE ENERGY

Questions

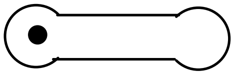
11. Living organisms need an external source of energy to carry out these processes. Green plants use the energy from sunlight to produce glucose from carbon dioxide and water by photosynthesis. In the human body, the energy released from the metabolism of glucose helps drive the synthesis of proteins. For all processes combined, ΔS_{univ} must be greater than zero (the second law).

12. Dispersion increases the entropy of the universe because the more widely something is dispersed, the greater the disorder. We must do work to overcome this disorder. In terms of the second law, it would be more advantageous to prevent contamination of the environment rather than to clean it up later. As a substance disperses, we have a much larger area that must be decontaminated.

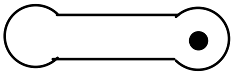
13. As a process occurs, ΔS_{univ} will increase; ΔS_{univ} cannot decrease. Time, like ΔS_{univ}, only goes in one direction.

14. This reaction is kinetically slow but thermodynamically favorable ($\Delta G < 0$). Thermodynamics only tells us if a reaction can occur. To answer the question will it occur, one also needs to consider the kinetics (speed of reaction). The ultraviolet light provides the activation energy for this slow reaction to occur.

15. Possible arrangements for one molecule:



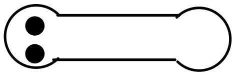
1 way



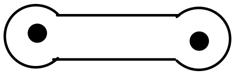
1 way

Both are equally probable.

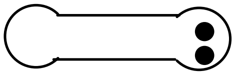
Possible arrangements for two molecules:



1 way

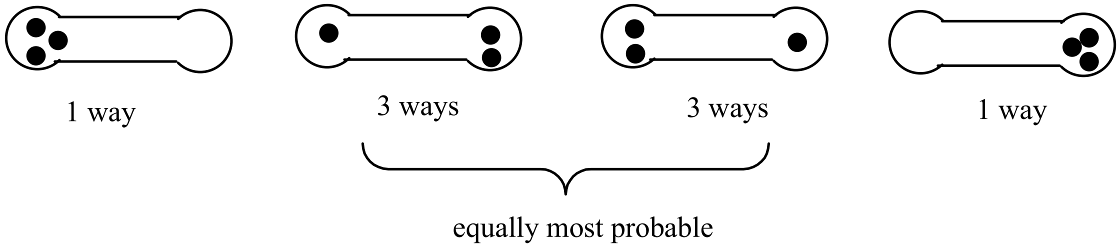


2 ways,
most probable



1 way

Possible arrangement for three molecules:



16. $\Delta S_{surr} = -\Delta H/T$; heat flow ($\Delta H$) into or out of the system dictates ΔS_{surr}. If heat flows into the surroundings, the random motions of the surroundings increase, and the entropy of the surroundings increases. The opposite is true when heat flows from the surroundings into the system (an endothermic reaction). Although the driving force described here really results from the change in entropy of the surroundings, it is often described in terms of energy. Nature tends to seek the lowest possible energy.

17. Note that these substances are not in the solid state but are in the aqueous state; water molecules are also present. There is an apparent increase in ordering when these ions are placed in water as compared to the separated state. The hydrating water molecules must be in a highly ordered arrangement when surrounding these anions.

18. $\Delta G° = -RT \ln K = \Delta H° - T\Delta S°$; $HX(aq) \rightleftharpoons H^+(aq) + X^-(aq)$ K_a reaction; the value of K_a for HF is less than one, while the other hydrogen halide acids have $K_a > 1$. In terms of $\Delta G°$, HF must have a positive ΔG^{o}_{rxn} value, while the other HX acids have $\Delta G°_{rxn} < 0$. The reason for the sign change in the K_a value, between HF versus HCl, HBr, and HI is entropy. ΔS for the dissociation of HF is very large and negative. There is a high degree of ordering that occurs as the water molecules associate (hydrogen bond) with the small F^- ions. The entropy of hydration strongly opposes HF dissociating in water, so much so that it overwhelms the favorable hydration energy making HF a weak acid.

19. One can determine $\Delta S°$ and $\Delta H°$ for the reaction using the standard entropies and standard enthalpies of formation in Appendix 4; then use the equation $\Delta G° = \Delta H° - T\Delta S°$. One can also use the standard free energies of formation in Appendix 4. And finally, one can use Hess's law to calculate $\Delta G°$. Here, reactions having known $\Delta G°$ values are manipulated to determine $\Delta G°$ for a different reaction.

    For temperatures other than 25°C, $\Delta G°$ is estimated using the $\Delta G° = \Delta H° - T\Delta S°$ equation. The assumptions made are that the $\Delta H°$ and $\Delta S°$ values determined from Appendix 4 data are temperature-independent. We use the same $\Delta H°$ and $\Delta S°$ values as determined when T = 25°C; then we plug in the new temperature in Kelvin into the equation to estimate $\Delta G°$ at the new temperature.

20. The sign of ΔG tells us if a reaction is spontaneous or not at whatever concentrations are present (at constant T and P). The magnitude of ΔG equals w_{max}. When $\Delta G < 0$, the magnitude tells us how much work, in theory, could be harnessed from the reaction. When $\Delta G > 0$, the magnitude tells us the minimum amount of work that must be supplied to make

the reaction occur. $\Delta G°$ gives us the same information only when the concentrations for all reactants and products are at standard conditions (1 atm for gases, 1 *M* for solute). These conditions rarely occur.

$\Delta G° = -RT \ln K$; from this equation, one can calculate K for a reaction if $\Delta G°$ is known at that temperature. Therefore, $\Delta G°$ gives the equilibrium position for a reaction. To determine K at a temperature other than 25°C, one needs to know $\Delta G°$ at that temperature. We assume $\Delta H°$ and $\Delta S°$ are temperature-independent and use the equation $\Delta G° = \Delta H° - T\Delta S°$ to estimate $\Delta G°$ at the different temperature. For K = 1, we want $\Delta G° = 0$, which occurs when $\Delta H° = T\Delta S°$. Again, assume $\Delta H°$ and $\Delta S°$ are temperature-independent; then solve for T ($= \Delta H°/\Delta S°$). At this temperature, K = 1 because $\Delta G° = 0$. This only works for reactions where the signs of $\Delta H°$ and $\Delta S°$ are the same (either both positive or both negative). When the signs are opposite, K will always be greater than 1 (when $\Delta H°$ is negative and $\Delta S°$ is positive) or K will always be less than 1 (when $\Delta H°$ is positive and $\Delta S°$ is negative). When the signs of $\Delta H°$ and $\Delta S°$ are opposite, K can never equal 1.

21. The light source for the first reaction is necessary for kinetic reasons. The first reaction is just too slow to occur unless a light source is available. The kinetics of a reaction are independent of the thermodynamics of a reaction. Even though the first reaction is more favorable thermodynamically (assuming standard conditions), it is unfavorable for kinetic reasons. The second reaction has a negative $\Delta G°$ value and is a fast reaction, so the second reaction occurs very quickly. When considering if a reaction will occur, thermodynamics and kinetics must both be considered.

22. Using Le Chatelier's principle, a decrease in pressure (volume increases) will favor the side with the greater number of particles. Thus 2 I(g) will be favored at low pressure.

    Looking at ΔG: $\Delta G = \Delta G° + RT \ln(P_I^2 / P_{I_2})$; $\ln(P_I^2 / P_{I_2}) > 0$ when $P_I = P_{I_2} = 10$ atm and ΔG is positive (not spontaneous). But at $P_I = P_{I_2} = 0.10$ atm, the logarithm term is negative. If $|RT \ln Q| > \Delta G°$, then ΔG becomes negative, and the reaction is spontaneous.

Exercises

Spontaneity, Entropy, and the Second Law of Thermodynamics: Free Energy

23. a, b, and c; from our own experiences, salt water, colored water, and rust form without any outside intervention. It takes an outside energy source to clean a bedroom, so this process is not spontaneous.

24. c and d; it takes an outside energy source to build a house and to launch and keep a satellite in orbit, so these processes are not spontaneous.

25. We draw all the possible arrangements of the two particles in the three levels.

2 kJ	___	___	x	___	x	xx
1 kJ	___	x	___	xx	x	__
0 kJ	xx	x	x	___	___	__
Total E =	0 kJ	1 kJ	2 kJ	2 kJ	3 kJ	4 kJ

The most likely total energy is 2 kJ.

26.

2 kJ	___	___	AB	___	___	B	A	B	A
1 kJ	___	AB	___	B	A	___	___	A	B
0 kJ	AB	___	___	A	B	A	B	___	___
E_T =	0 kJ	2 kJ	4 kJ	1 kJ	1 kJ	2 kJ	2 kJ	3 kJ	3 kJ

The most likely total energy is 2 kJ.

27. a. H_2 at 100°C and 0.5 atm; higher temperature and lower pressure means greater volume and hence larger positional probability.

b. N_2 at STP has the greater volume.

c. $H_2O(l)$ has a larger positional probability than $H_2O(s)$.

28. Of the three phases (solid, liquid, and gas), solids are most ordered (have the smallest positional probability) and gases are most disordered (have the largest positional probability). Thus a , b, and f (melting, sublimation, and boiling) involve an increase in the entropy of the system since going from a solid to a liquid or from a solid to a gas or from a liquid to a gas increases disorder (increases positional probability). For freezing (process c), a substance goes from the more disordered liquid state to the more ordered solid state; hence, entropy decreases. Process d (mixing) involves an increase in disorder (an increase in positional probability), while separation (phase e) increases order (decreases positional probability). So, of all the processes, a, b, d, and f result in an increase in the entropy of the system.

29. a. To boil a liquid requires heat. Hence this is an endothermic process. All endothermic processes decrease the entropy of the surroundings (ΔS_{surr} is negative).

b. This is an exothermic process. Heat is released when gas molecules slow down enough to form the solid. In exothermic processes, the entropy of the surroundings increases (ΔS_{surr} is positive).

30. a. $\Delta S_{surr} = \dfrac{-\Delta H}{T} = \dfrac{-(-2221\text{ kJ})}{298\text{ K}} = 7.45\text{ kJ/K} = 7.45 \times 10^3\text{ J/K}$

b. $\Delta S_{surr} = \dfrac{-\Delta H}{T} = \dfrac{-112\text{ kJ}}{298\text{ K}} = -0.376\text{ kJ/K} = -376\text{ J/K}$

31. $\Delta G = \Delta H - T\Delta S$; when ΔG is negative, then the process will be spontaneous.

a. $\Delta G = \Delta H - T\Delta S = 25 \times 10^3$ J – (300. K)(5.0 J/K) = 24,000 J; not spontaneous

b. ΔG = 25,000 J – (300. K)(100. J/K) = −5000 J; spontaneous

c. Without calculating ΔG, we know this reaction will be spontaneous at all temperatures. ΔH is negative and ΔS is positive ($-T\Delta S < 0$). ΔG will always be less than zero with these sign combinations for ΔH and ΔS.

d. $\Delta G = -1.0 \times 10^4$ J – (200. K)(–40. J/K) = −2000 J; spontaneous

32. $\Delta G = \Delta H - T\Delta S$; a process is spontaneous when $\Delta G < 0$. For the following, assume ΔH and ΔS are temperature-independent.

a. When ΔH and ΔS are both negative, ΔG will be negative below a certain temperature where the favorable ΔH term dominates. When $\Delta G = 0$, then $\Delta H = T\Delta S$. Solving for this temperature:

$$T = \frac{\Delta H}{\Delta S} = \frac{-18{,}000\ \text{J}}{-60.\ \text{J/K}} = 3.0 \times 10^2\ \text{K}$$

At $T < 3.0 \times 10^2$ K, this process will be spontaneous ($\Delta G < 0$).

b. When ΔH and ΔS are both positive, ΔG will be negative above a certain temperature where the favorable ΔS term dominates.

$$T = \frac{\Delta H}{\Delta S} = \frac{18{,}000\ \text{J}}{60.\ \text{J/K}} = 3.0 \times 10^2\ \text{K}$$

At $T > 3.0 \times 10^2$ K, this process will be spontaneous ($\Delta G < 0$).

c. When ΔH is positive and ΔS is negative, this process can never be spontaneous at any temperature because ΔG can never be negative.

d. When ΔH is negative and ΔS is positive, this process is spontaneous at all temperatures because ΔG will always be negative.

33. At the boiling point, $\Delta G = 0$, so $\Delta H = T\Delta S$.

$$\Delta S = \frac{\Delta H}{T} = \frac{27.5\ \text{kJ/mol}}{(273 + 35)\ \text{K}} = 8.93 \times 10^{-2}\ \text{kJ/K•mol} = 89.3\ \text{J/K•mol}$$

34. At the boiling point, $\Delta G = 0$, so $\Delta H = T\Delta S$. $T = \dfrac{\Delta H}{\Delta S} = \dfrac{58.51 \times 10^3\ \text{J/mol}}{92.92\ \text{J/K•mol}} = 629.7\ \text{K}$

35. a. $NH_3(s) \rightarrow NH_3(l)$; $\Delta G = \Delta H - T\Delta S$ = 5650 J/mol – 200. K (28.9 J/K•mol)

ΔG = 5650 J/mol – 5780 J/mol = T = –130 J/mol

Yes, NH_3 will melt because $\Delta G < 0$ at this temperature.

b. At the melting point, $\Delta G = 0$, so $T = \dfrac{\Delta H}{\Delta S} = \dfrac{5650\ \text{J/mol}}{28.9\ \text{J/K}\bullet\text{mol}} = 196$ K.

36. At the boiling point, $\Delta S_{univ} = 0$ because the system is at equilibrium.

$\Delta S_{univ} = 0 = \Delta S_{sys} + \Delta S_{surr},\ \ \Delta S_{sys} = -\Delta S_{surr}$

Because we are at the boiling point, $\Delta G = 0$. So:

$$\Delta H = T\Delta S,\ \ \Delta S = \frac{\Delta H}{T} = \frac{31.4 \times 10^3\ \text{J/mol}}{(273.2 + 61.7)\ \text{K}} = 93.8\ \text{J/K}\bullet\text{mol}$$

$\Delta S_{sys} = -\Delta S_{surr}$ (at the boiling point). So:

$\Delta S_{surr} = -\Delta S_{sys} = -93.8\ \text{J/K}\bullet\text{mol}$

Chemical Reactions: Entropy Changes and Free Energy

37. a. Decrease in positional probability; $\Delta S°(-)$

b. Increase in positional probability; $\Delta S°(+)$

c. Decrease in positional probability ($\Delta n < 0$); $\Delta S°(-)$

d. Increase in positional probability ($\Delta n > 0$); $\Delta S°(+)$

For c and d, concentrate on the gaseous products and reactants. When there are more gaseous product molecules than gaseous reactant molecules ($\Delta n > 0$), then $\Delta S°$ will be positive (positional probability increases). When Δn is negative, then $\Delta S°$ is negative (positional probability decreases).

38. a. Decrease in positional probability ($\Delta n < 0$); $\Delta S°(-)$

b. Decrease in positional probability ($\Delta n < 0$); $\Delta S°(-)$

c. Increase in positional probability; $\Delta S°(+)$

d. Increase in positional probability; $\Delta S°(+)$

39. a. $C_{graphite}(s)$; diamond has a more ordered structure (has a smaller positional probability) than graphite.

b. $C_2H_5OH(g)$; the gaseous state is more disordered (has a larger positional probability) than the liquid state.

c. $CO_2(g)$; the gaseous state is more disordered (has a larger positional probability) than the solid state.

40. a. He (10 K); S = 0 at 0 K

b. N_2O; more complicated molecule, so has the larger positional probability.

c. $NH_3(l)$; the liquid state is more disordered (has a larger positional probability) than the solid state.

41. a. $2\ H_2S(g) + SO_2(g) \rightarrow 3\ S_{rhombic}(s) + 2\ H_2O(g)$; because there are more molecules of reactant gases than product molecules of gas ($\Delta n = 2 - 3 < 0$), ΔS° will be negative.

$$\Delta S° = \sum n_p S^o_{products} - \sum n_r S^o_{reactants}$$

$$\Delta S° = [3 \text{ mol } S_{rhombic}(s)\ (32 \text{ J/K•mol}) + 2 \text{ mol } H_2O(g)\ (189 \text{ J/K•mol})]$$

$$- [2 \text{ mol } H_2S(g)\ (206 \text{ J/K•mol}) + 1 \text{ mol } SO_2(g)\ (248 \text{ J/K•mol})]$$

$$\Delta S° = 474 \text{ J/K} - 660. \text{ J/K} = -186 \text{ J/K}$$

b. $2\ SO_3(g) \rightarrow 2\ SO_2(g) + O_2(g)$; because Δn of gases is positive ($\Delta n = 3 - 2$), ΔS° will be positive.

$$\Delta S = 2 \text{ mol}(248 \text{ J/K•mol}) + 1 \text{ mol}(205 \text{ J/K•mol}) - [2 \text{ mol}(257 \text{ J/K•mol})] = 187 \text{ J/K}$$

c. $Fe_2O_3(s) + 3\ H_2(g) \rightarrow 2\ Fe(s) + 3\ H_2O(g)$; because Δn of gases = 0 ($\Delta n = 3 - 3$), we can't easily predict if ΔS° will be positive or negative.

$$\Delta S = 2 \text{ mol}(27 \text{ J/K•mol}) + 3 \text{ mol}(189 \text{ J/K•mol}) -$$

$$[1 \text{ mol}(90. \text{ J/K•mol}) + 3 \text{ mol } (141 \text{ J/K•mol})] = 138 \text{ J/K}$$

42. a. $H_2(g) + 1/2\ O_2(g) \rightarrow H_2O(l)$; since Δn of gases is negative, ΔS° will be negative.

$$\Delta S° = 1 \text{ mol } H_2O(l)\ (70. \text{ J/K•mol}) -$$

$$[1 \text{ mol } H_2(g)\ (131 \text{ J/K•mol}) + 1/2 \text{ mol } O_2(g)\ (205 \text{ J/K•mol})]$$

$$\Delta S° = 70. \text{ J/K} - 234 \text{ J/K} = -164 \text{ J/K}$$

b. $2\ CH_3OH(g) + 3\ O_2(g) \rightarrow 2\ CO_2(g) + 4\ H_2O(g)$; because Δn of gases is positive, ΔS° will be positive.

$$[2 \text{ mol } (214 \text{ J/K•mol}) + 4 \text{ mol } (189 \text{ J/K•mol})] -$$

$$[2 \text{ mol } (240. \text{ J/K•mol}) + 3 \text{ mol } (205 \text{ J/K•mol})] = 89 \text{ J/K}$$

c. $HCl(g) \rightarrow H^+(aq) + Cl^-(aq)$; the gaseous state dominates predictions of ΔS°. Here, the gaseous state is more disordered than the ions in solution, so ΔS° will be negative.

$$\Delta S° = 1 \text{ mol } H^+(0) + 1 \text{ mol } Cl^-(57 \text{ J/K•mol}) - 1 \text{ mol } HCl(187 \text{ J/K•mol}) = -130. \text{ J/K}$$

43. $C_2H_2(g) + 4\ F_2(g) \rightarrow 2\ CF_4(g) + H_2(g)$; $\Delta S° = 2S^o_{CF_4} + S^o_{H_2} - [S^o_{C_2H_2} + 4S^o_{F_2}]$

$-358\text{ J/K} = (2\text{ mol})S^o_{CF_4} + 131\text{ J/K} - [201\text{ J/K} + 4(203\text{ J/K})]$, $S^o_{CF_4} = 262\text{ J/K•mol}$

44. $CS_2(g) + 3\ O_2(g) \rightarrow CO_2(g) + 2\ SO_2(g)$; $\Delta S° = S^o_{CO_2} + 2S^o_{SO_2} - [3S^o_{O_2} + S^o_{CS_2}]$

$-143\text{ J/K} = 214\text{ J/K} + 2(248\text{ J/K}) - 3(205\text{ J/K}) - (1\text{ mol})S^o_{CS_2}$, $S^o_{CS_2} = 238\text{ J/K•mol}$

45. a. $S_{rhombic} \rightarrow S_{monoclinic}$; this phase transition is spontaneous ($\Delta G < 0$) at temperatures above 95°C. $\Delta G = \Delta H - T\Delta S$; for ΔG to be negative only above a certain temperature, then ΔH is positive and ΔS is positive (see Table 17.5 of text).

b. Because ΔS is positive, $S_{rhombic}$ is the more ordered crystalline structure (has the smaller positional probability).

46. $P_4(s,\alpha) \rightarrow P_4(s,\beta)$

a. At T < –76.9°C, this reaction is spontaneous, and the sign of ΔG is (–). At –76.9°C, ΔG = 0, and above –76.9 °C, the sign of ΔG is (+). This is consistent with ΔH (–) and ΔS (–).

b. Because the sign of ΔS is negative, the β form has the more ordered structure (has the smaller positional probability).

47. a. When a bond is formed, energy is released, so ΔH is negative. There are more reactant molecules of gas than product molecules of gas ($\Delta n < 0$), so ΔS will be negative.

b. $\Delta G = \Delta H - T\Delta S$; for this reaction to be spontaneous ($\Delta G < 0$), the favorable enthalpy term must dominate. The reaction will be spontaneous at low temperatures (at a temperature below some number), where the ΔH term dominates.

48. Because there are more product gas molecules than reactant gas molecules ($\Delta n > 0$), ΔS will be positive. From the signs of ΔH and ΔS, this reaction is spontaneous at all temperatures. It will cost money to heat the reaction mixture. Because there is no thermodynamic reason to do this, the purpose of the elevated temperature must be to increase the rate of the reaction, that is, kinetic reasons.

49. a. $CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(g)$

	$CH_4(g)$	$2\ O_2(g)$	$CO_2(g)$	$2\ H_2O(g)$	
ΔH^o_f	−75 kJ/mol	0	−393.5	−242	
ΔG^o_f	−51 kJ/mol	0	−394	−229	Data from Appendix 4
S°	186 J/K•mol	205	214	189	

$\Delta H° = \sum n_p \Delta H^o_{f,\text{ products}} - \sum n_r \Delta H^o_{f,\text{ reactants}}$; $\Delta S° = \sum n_p S^o_{\text{products}} - \sum n_r S^o_{\text{reactants}}$

$\Delta H° = 2\text{ mol}(-242\text{ kJ/mol}) + 1\text{ mol}(-393.5\text{ kJ/mol}) - [1\text{ mol}(-75\text{ kJ/mol})] = -803\text{ kJ}$

$$\Delta S^\circ = 2\text{ mol}(189\text{ J/K·mol}) + 1\text{ mol}(214\text{ J/K•mol}) - [1\text{ mol}(186\text{ J/K•mol}) + 2\text{ mol}(205\text{ J/K•mol})] = -4\text{ J/K}$$

There are two ways to get ΔG°. We can use $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ (be careful of units):

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -803 \times 10^3\text{ J} - (298\text{ K})(-4\text{ J/K}) = -8.018 \times 10^5\text{ J} = -802\text{ kJ}$$

or we can use ΔG_f^o values, where $\Delta G^\circ = \sum n_p \Delta G^o_{f,\text{ products}} - \sum n_r \Delta G^o_{f,\text{ reactants}}$:

$$\Delta G^\circ = 2\text{ mol}(-229\text{ kJ/mol}) + 1\text{ mol}(-394\text{ kJ/mol}) - [1\text{ mol}(-51\text{ kJ/mol})]$$

$\Delta G^\circ = -801$ kJ (Answers are the same within round off error.)

b. $6\ CO_2(g) + 6\ H_2O(l) \rightarrow C_6H_{12}O_6(s) + 6\ O_2(g)$

	$6\ CO_2(g)$	$6\ H_2O(l)$	$C_6H_{12}O_6(s)$	$6\ O_2(g)$
ΔH_f^o	−393.5 kJ/mol	−286	−1275	0
S°	214 J/K•mol	70.	212	205

$$\Delta H^\circ = -1275 - [6(-286) + 6(-393.5)] = 2802\text{ kJ}$$

$$\Delta S^\circ = 6(205) + 212 - [6(214) + 6(70.)] = -262\text{ J/K}$$

$$\Delta G^\circ = 2802\text{ kJ} - (298\text{ K})(-0.262\text{ kJ/K}) = 2880.\text{ kJ}$$

c. $P_4O_{10}(s) + 6\ H_2O(l) \rightarrow 4\ H_3PO_4(s)$

	$P_4O_{10}(s)$	$6\ H_2O(l)$	$4\ H_3PO_4(s)$
ΔH_f^o (kJ/mol)	−2984	−286	−1279
S° (J/K•mol)	229	70.	110.

$$\Delta H^\circ = 4\text{ mol}(-1279\text{ kJ/mol}) - [1\text{ mol}(-2984\text{ kJ/mol}) + 6\text{ mol}(-286\text{ kJ/mol})] = -416\text{ kJ}$$

$$\Delta S^\circ = 4(110.) - [229 + 6(70.)] = -209\text{ J/K}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -416\text{ kJ} - (298\text{ K})(-0.209\text{ kJ/K}) = -354\text{ kJ}$$

d. $HCl(g) + NH_3(g) \rightarrow NH_4Cl(s)$

	$HCl(g)$	$NH_3(g)$	$NH_4Cl(s)$
ΔH_f^o (kJ/mol)	−92	−46	−314
S° (J/K•mol)	187	193	96

$\Delta H^\circ = -314 - [-92 - 46] = -176$ kJ; $\Delta S^\circ = 96 - [187 + 193] = -284$ J/K

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -176\text{ kJ} - (298\text{ K})(-0.284\text{ kJ/K}) = -91\text{ kJ}$$

50. a. $\Delta H° = 2(-46\text{ kJ}) = -92\text{ kJ}$; $\Delta S° = 2(193\text{ J/K}) - [3(131\text{ J/K}) + 192\text{ J/K}] = -199\text{ J/K}$

$\Delta G° = \Delta H° - T\Delta S° = -92\text{ kJ} - 298\text{ K}(-0.199\text{ kJ/K}) = -33\text{ kJ}$

b. $\Delta G°$ is negative, so this reaction is spontaneous at standard conditions.

c. $\Delta G° = 0$ when $T = \dfrac{\Delta H^{o}}{\Delta S^{o}} = \dfrac{-92\text{ kJ}}{-0.199\text{ kJ/K}} = 460\text{ K}$

At $T < 460$ K and standard pressures (1 atm), the favorable $\Delta H°$ term dominates, and the reaction is spontaneous ($\Delta G° < 0$).

51. $\Delta G° = -58.03\text{ kJ} - (298\text{ K})(-0.1766\text{ kJ/K}) = -5.40\text{ kJ}$

$\Delta G° = 0 = \Delta H° - T\Delta S°,\ T = \dfrac{\Delta H^{o}}{\Delta S^{o}} = \dfrac{-58.03\text{ kJ}}{-0.1766\text{ kJ/K}} = 328.6\text{ K}$

$\Delta G°$ is negative below 328.6 K, where the favorable $\Delta H°$ term dominates.

52. $H_2O(l) \rightarrow H_2O(g)$; $\Delta G° = 0$ at the boiling point of water at 1 atm and 100.°C.

$\Delta H° = T\Delta S°,\ \Delta S° = \dfrac{\Delta H^{o}}{T} = \dfrac{40.6 \times 10^{3}\text{ J/mol}}{373\text{ K}} = 109\text{ J/K•mol}$

At 90.°C: $\Delta G° = \Delta H° - T\Delta S° = 40.6\text{ kJ/mol} - (363\text{ K})(0.109\text{ kJ/K•mol}) = 1.0\text{ kJ/mol}$

As expected, $\Delta G° > 0$ at temperatures below the boiling point of water at 1 atm (process is nonspontaneous).

At 110.°C: $\Delta G° = \Delta H° - T\Delta S° = 40.6\text{ kJ/mol} - (383\text{ K})(0.109\text{ J/K•mol}) = -1.1\text{ kJ/mol}$

When $\Delta G° < 0$, the boiling of water is spontaneous at 1 atm, and T > 100.°C (as expected).

53.

$$\begin{array}{rl}
CH_4(g) \rightarrow 2\,H_2(g) + C(s) & \Delta G° = -(-51\text{ kJ}) \\
2\,H_2(g) + O_2(g) \rightarrow 2\,H_2O(l) & \Delta G° = -474\text{ kJ}) \\
C(s) + O_2(g) \rightarrow CO_2(g) & \Delta G° = -394\text{ kJ} \\
\hline
CH_4(g) + 2\,O_2(g) \rightarrow 2\,H_2O(l) + CO_2(g) & \Delta G° = -817\text{ kJ}
\end{array}$$

54.

$$\begin{array}{rl}
6\,C(s) + 6\,O_2(g) \rightarrow 6\,CO_2(g) & \Delta G° = 6(-394\text{ kJ}) \\
3\,H_2(g) + 3/2\,O_2(g) \rightarrow 3\,H_2O(l) & \Delta G° = 3(-237\text{ kJ}) \\
6\,CO_2(g) + 3\,H_2O(l) \rightarrow C_6H_6(l) + 15/2\,O_2(g) & \Delta G° = -1/2\,(-6399\text{ kJ}) \\
\hline
6\,C(s) + 3\,H_2(g) \rightarrow C_6H_6(l) & \Delta G° = 125\text{ kJ}
\end{array}$$

55. $\Delta G° = \sum n_p \Delta G^{o}_{f,\text{ products}} - \sum n_r \Delta G^{o}_{f,\text{ reactants}}$, $-374\text{ kJ} = -1105\text{ kJ} - \Delta G^{o}_{f,\,SF_4}$

$\Delta G^{o}_{f,\,SF_4} = -731\text{ kJ/mol}$

56. $-5490.\ \text{kJ} = 8(-394\ \text{kJ}) + 10(-237\ \text{kJ}) - 2\Delta G^{\circ}_{f,\,C_4H_{10}},\ \ \Delta G^{\circ}_{f,\,C_4H_{10}} = -16\ \text{kJ/mol}$

57. a. $\Delta G^{\circ} = 2\ \text{mol}(0) + 3\ \text{mol}(-229\ \text{kJ/mol}) - [1\ \text{mol}(-740.\ \text{kJ/mol}) + 3\ \text{mol}(0)] = 53\ \text{kJ}$

b. Because ΔG° is positive, this reaction is not spontaneous at standard conditions and 298 K.

c. $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ},\ \ \Delta S^{\circ} = \dfrac{\Delta H^{\circ} - \Delta G^{\circ}}{T} = \dfrac{100.\ \text{kJ} - 53\ \text{kJ}}{298\ \text{K}} = 0.16\ \text{kJ/K}$

We need to solve for the temperature when ΔG° = 0:

$$\Delta G^{\circ} = 0 = \Delta H^{\circ} - T\Delta S^{\circ},\ \Delta H^{\circ} = T\Delta S^{\circ},\ \ T = \frac{\Delta H^{\circ}}{\Delta S^{\circ}} = \frac{100.\ \text{kJ}}{0.16\ \text{kJ/K}} = 630\ \text{K}$$

This reaction will be spontaneous (ΔG < 0) at T > 630 K, where the favorable entropy term will dominate.

58. a. $\Delta G^{\circ} = 2(-270.\ \text{kJ}) - 2(-502\ \text{kJ}) = 464\ \text{kJ}$

b. Because ΔG° is positive, this reaction is not spontaneous at standard conditions at 298 K.

c. $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ},\ \ \Delta H^{\circ} = \Delta G^{\circ} + T\Delta S^{\circ} = 464\ \text{kJ} + 298\ \text{K}(0.179\ \text{kJ/K}) = 517\ \text{kJ}$

We need to solve for the temperature when ΔG° = 0:

$$\Delta G^{\circ} = 0 = \Delta H^{\circ} - T\Delta S^{\circ},\ \ T = \frac{\Delta H^{\circ}}{\Delta S^{\circ}} = \frac{517\ \text{kJ}}{0.179\ \text{kJ/K}} = 2890\ \text{K}$$

This reaction will be spontaneous at standard conditions (ΔG° < 0) when T > 2890 K. Here the favorable entropy term will dominate.

Free Energy: Pressure Dependence and Equilibrium

59. $\Delta G = \Delta G^{\circ} + RT\ln Q$; for this reaction: $\Delta G = \Delta G^{\circ} + RT\ln\dfrac{P_{NO_2} \times P_{O_2}}{P_{NO} \times P_{O_3}}$

$\Delta G^{\circ} = 1\ \text{mol}(52\ \text{kJ/mol}) + 1\ \text{mol}(0) - [1\ \text{mol}(87\ \text{kJ/mol}) + 1\ \text{mol}(163\ \text{kJ/mol})] = -198\ \text{kJ}$

$$\Delta G = -198\ \text{kJ} + \frac{8.3145\ \text{J/K} \bullet \text{mol}}{1000\ \text{J/kJ}}(298\ \text{K})\ln\frac{(1.00 \times 10^{-7})(1.00 \times 10^{-3})}{(1.00 \times 10^{-6})(1.00 \times 10^{-6})}$$

$\Delta G = -198\ \text{kJ} + 9.69\ \text{kJ} = -188\ \text{kJ}$

60. $\Delta G^{\circ} = 3(0) + 2(-229) - [2(-34) + 1(-300.)] = -90.\ \text{kJ}$

$$\Delta G = \Delta G° + RT\ln\frac{P^2_{H_2O}}{P^2_{H_2S} \times P_{SO_2}} = -90.\text{ kJ} + \frac{(8.3145)(298)}{1000}\text{ kJ}\left[\ln\frac{(0.030)^2}{(1.0\times10^{-4})(0.010)}\right]$$

$\Delta G = -90.\text{ kJ} + 39.7\text{ kJ} = -50.\text{ kJ}$

61. $\Delta G = \Delta G° + RT\ln Q = \Delta G° + RT\ln\frac{P_{N_2O_4}}{P^2_{NO_2}}$

$\Delta G° = 1\text{ mol}(98\text{ kJ/mol}) - 2\text{ mol}(52\text{ kJ/mol}) = -6\text{ kJ}$

a. These are standard conditions, so ΔG = ΔG° because Q = 1 and ln Q = 0. Because ΔG° is negative, the forward reaction is spontaneous. The reaction shifts right to reach equilibrium.

b. $\Delta G = -6\times10^3\text{ J} + 8.3145\text{ J/K•mol }(298\text{ K})\ln\frac{0.50}{(0.21)^2}$

$\Delta G = -6\times10^3\text{ J} + 6.0\times10^3\text{ J} = 0$

Because ΔG = 0, this reaction is at equilibrium (no shift).

c. $\Delta G = -6\times10^3\text{ J} + 8.3145\text{ J/K•mol }(298\text{ K})\ln\frac{1.6}{(0.29)^2}$

$\Delta G = -6\times10^3\text{ J} + 7.3\times10^3\text{ J} = 1.3\times10^3\text{ J} = 1\times10^3\text{ J}$

Because ΔG is positive, the reverse reaction is spontaneous, and the reaction shifts to the left to reach equilibrium.

62. a. $\Delta G = \Delta G° + RT\ln\frac{P^2_{NH_3}}{P_{N_2}\times P^2_{H_2}}$; $\Delta G° = 2\Delta G^o_{f,NH_3} = 2(-17) = -34\text{ kJ}$

$$\Delta G = -34\text{ kJ} + \frac{(8.3145\text{ J/K}\bullet\text{mol})(298\text{ K})}{1000\text{ J/kJ}}\ln\frac{(50.)^2}{(200.)(200.)^3}$$

$\Delta G = -34\text{ kJ} - 33\text{ kJ} = -67\text{ kJ}$

b. $\Delta G = -34\text{ kJ}\ \frac{(8.3145\text{ J/K}\bullet\text{mol})(298\text{ K})}{1000\text{ J/kJ}}\ln\frac{(200.)^2}{(200.)(600.)^3}$

$\Delta G = -34\text{ kJ} - 34.4\text{ kJ} = -68\text{ kJ}$

63. $NO(g) + O_3(g) \rightleftharpoons NO_2(g) + O_2(g)$; $\Delta G° = \Sigma n_p\Delta G^o_{f,\text{ products}} - \Sigma n_r\Delta G^o_{f,\text{ reactants}}$

$\Delta G° = 1\text{ mol}(52\text{ kJ/mol}) - [1\text{ mol}(87\text{ kJ/mol}) + 1\text{ mol}(163\text{ kJ/mol})] = -198\text{ kJ}$

$$\Delta G° = -RT\ln K,\ K = \exp\frac{-\Delta G^{o}}{RT} = \exp\left[\frac{-(-1.98\times10^{5}\text{ J})}{8.3145\text{ J/K}\bullet\text{mol}(298\text{ K})}\right] = e^{79.912} = 5.07\times10^{34}$$

Note: When determining exponents, we will round off after the calculation is complete. This helps eliminate excessive round off error.

64. $\Delta G° = 2\text{ mol}(-229\text{ kJ/mol}) - [2\text{ mol}(-34\text{ kJ/mol}) + 1\text{ mol}(-300.\text{ kJ/mol})] = -90.\text{ kJ}$

$$K = \exp\frac{-\Delta G^{o}}{RT} = \exp\left[\frac{-(-9.0\times10^{4}\text{ J})}{8.3145\text{ J/K}\bullet\text{mol}(298\text{ K})}\right] = e^{36.32} = 5.9\times10^{15}$$

Because there is a decrease in the number of moles of gaseous particles, ΔS° is negative. Because ΔG° is negative, ΔH° must be negative. The reaction will be spontaneous at low temperatures (the favorable ΔH° term dominates at low temperatures).

65. At 25.0°C: $\Delta G° = \Delta H° - T\Delta S° = -58.03\times10^{3}\text{ J/mol} - (298.2\text{ K})(-176.6\text{ J/K}\bullet\text{mol})$

$$= -5.37\times10^{3}\text{ J/mol}$$

$$\Delta G° = -RT\ln K,\ \ln K = \frac{-\Delta G^{o}}{RT} = \exp\left[\frac{-(-5.37\times10^{3}\text{ J/mol})}{(8.3145\text{ J/K}\bullet\text{mol})(298.2\text{ K})}\right] = 2.166$$

$K = e^{2.166} = 8.72$

At 100.0°C: $\Delta G° = -58.03\times10^{3}\text{ J/mol} - (373.2\text{ K})(-176.6\text{ J/K}\bullet\text{mol}) = 7.88\times10^{3}\text{ J/mol}$

$$\ln K = \frac{-(7.88\times10^{3}\text{ J/mol})}{(8.3145\text{ J/K}\bullet\text{mol})(373.2\text{ K})} = -2.540,\ K = e^{-2.540} = 0.0789$$

Note: When determining exponents, we will round off after the calculation is complete. This helps eliminate excessive round off error.

66. a. $\Delta G° = 3(191.2) - 78.2 = 495.4\text{ kJ};\ \Delta H° = 3(241.3) - 132.8 = 591.1\text{ kJ}$

$$\Delta S° = \frac{\Delta H^{o} - \Delta G^{o}}{T} = \frac{591.1\text{ kJ} - 495.4\text{ kJ}}{298\text{ K}} = 0.321\text{ kJ/K} = 321\text{ J/K}$$

b. $$\Delta G° = -RT\ln K,\ \ln K = \frac{-\Delta G^{o}}{RT} = \frac{-495{,}400\text{ J}}{8.3145\text{ J/K}\bullet\text{mol}(298\text{ K})} = -199.942$$

$K = e^{-199.942} = 1.47\times10^{-87}$

c. Assuming ΔH° and ΔS° are temperature-independent:

$$\Delta G^{o}_{3000} = 591.1\text{ kJ} - 3000.\text{ K}(0.321\text{ kJ/K}) = -372\text{ kJ}$$

$$\ln K = \frac{-(-372{,}000\text{ J})}{8.3145\text{ J/K}\bullet\text{mol}(3000.\text{ K})} = 14.914,\ K = e^{14.914} = 3.00\times10^{6}$$

67. When reactions are added together, the equilibrium constants are multiplied together to determine the K value for the final reaction.

$$\begin{array}{rcll} H_2(g) + O_2(g) & \rightleftharpoons & H_2O_2(g) & K = 2.3 \times 10^{6} \\ H_2O(g) & \rightleftharpoons & H_2(g) + 1/2O_2(g) & K = (1.8 \times 10^{37})^{-1/2} \\ \hline H_2O(g) + 1/2O_2(g) & \rightleftharpoons & H_2O_2(g) & K = 2.3 \times 10^{6}(1.8 \times 10^{-37})^{-1/2} = 5.4 \times 10^{-13} \end{array}$$

$\Delta G° = -RT \ln K = -8.3145$ J/K•mol (600. K) $\ln(5.4 \times 10^{-13}) = 1.4 \times 10^{5}$ J/mol = 140 kJ/mol

68. a.

	ΔH_f^o (kJ/mol)	S° (J/K•mol)
$NH_3(g)$	−46	193
$O_2(g)$	0	205
$NO(g)$	90.	211
$H_2O(g)$	−242	189
$NO_2(g)$	34	240.
$HNO_3(l)$	−174	156
$H_2O(l)$	−286	70.

$4\ NH_3(g) + 5\ O_2(g) \rightarrow 4\ NO(g) + 6\ H_2O(g)$

$\Delta H° = 6(-242) + 4(90.) - [4(-46)] = -908$ kJ

$\Delta S° = 4(211) + 6(189) - [4(193) + 5(205)] = 181$ J/K

$\Delta G° = -908$ kJ $- 298$ K (0.181 kJ/K) $= -962$ kJ

$$\Delta G° = -RT \ln K,\ \ \ln K = \frac{-\Delta G^o}{RT} = \left[\frac{-(-962 \times 10^3\ J)}{8.3145\ J/K \bullet mol \times 298\ K}\right] = 388$$

$\ln K = 2.303 \log K$, $\log K = 168$, $K = 10^{168}$ (an extremely large number)

$2\ NO(g) + O_2(g) \rightarrow 2\ NO_2(g)$

$\Delta H° = 2(34) - [2(90.)] = -112$ kJ; $\Delta S° = 2(240.) - [2(211) + (205)] = -147$ J/K

$\Delta G° = -112$ kJ $- (298$ K$)(-0.147$ kJ/K$) = -68$ kJ

$$K = \exp\frac{-\Delta G^o}{RT} = \exp\left[\frac{-(-68{,}000\ J)}{8.3145\ J/K \bullet mol\ (298\ K)}\right] = e^{27.44} = 8.3 \times 10^{11}$$

Note: When determining exponents, we will round off after the calculation is complete.

$3\ NO_2(g) + H_2O(l) \rightarrow 2\ HNO_3(l) + NO(g)$

$\Delta H° = 2(-174) + (90.) - [3(34) + (-286)] = -74$ kJ

$\Delta S° = 2(156) + (211) - [3(240.) + (70.)] = -267$ J/K

$\Delta G° = -74\ \text{kJ} - (298\ \text{K})(-0.267\ \text{kJ/K}) = 6\ \text{kJ}$

$$K = \exp\frac{-\Delta G^{\circ}}{RT} = \exp\left[\frac{-6000\ \text{J}}{8.3145\ \text{J/K}\bullet\text{mol}\,(298\ \text{K})}\right] = e^{-2.4} = 9\times 10^{-2}$$

b. $\Delta G° = -RT\ln K$; $T = 825°C = (825 + 273)\ \text{K} = 1098\ \text{K}$; we must determine $\Delta G°$ at 1098 K.

$$\Delta G^{\circ}_{1098} = \Delta H° - T\Delta S° = -908\ \text{kJ} - (1098\ \text{K})(0.181\ \text{kJ/K}) = -1107\ \text{kJ}$$

$$K = \exp\frac{-\Delta G^{\circ}}{RT} = \exp\left[\frac{-(-1.107\times 10^{6}\ \text{J})}{8.3145\ \text{J/K}\bullet\text{mol}\ (1098\ \text{K})}\right] = e^{121.258} = 4.589\times 10^{52}$$

c. There is no thermodynamic reason for the elevated temperature because $\Delta H°$ is negative and $\Delta S°$ is positive. Thus the purpose for the high temperature must be to increase the rate of the reaction.

69. $$K = \frac{P^2_{NF_3}}{P_{N_2}\times P^3_{F_2}} = \frac{(0.48)^2}{0.021(0.063)^3} = 4.4\times 10^4$$

$$\Delta G^{\circ}_{800} = -RT\ln K = -8.3145\ \text{J/K}\bullet\text{mol}\ (800.\ \text{K})\ \ln(4.4\times 10^4) = -7.1\times 10^4\ \text{J/mol} = -71\ \text{kJ/mol}$$

70. $2\,SO_2(g) + O_2(g) \rightarrow 2\,SO_3(g)$; $\Delta G° = 2(-371\ \text{kJ}) - [2(-300.\ \text{kJ})] = -142\ \text{kJ}$

$$\Delta G° = -RT\ln K,\ \ln K = \frac{-\Delta G^{\circ}}{RT} = \frac{-(-142.000\ \text{J})}{8.3145\ \text{J/K}\bullet\text{mol}\ (298\ \text{K})} = 57.311$$

$K = e^{57.311} = 7.76\times 10^{24}$

$$K = 7.76\times 10^{24} = \frac{P^2_{SO_3}}{P^2_{SO_2}\times P_{O_2}} = \frac{(2.0)^2}{P^2_{SO_2}\times(0.50)},\ P_{SO_2} = 1.0\times 10^{-12}\ \text{atm}$$

From the negative value of $\Delta G°$, this reaction is spontaneous at standard conditions. There are more molecules of reactant gases than product gases, so $\Delta S°$ will be negative (unfavorable). Therefore, this reaction must be exothermic ($\Delta H° < 0$). When $\Delta H°$ and $\Delta S°$ are both negative, the reaction will be spontaneous at relatively low temperatures where the favorable $\Delta H°$ term dominates.

71. The equation $\ln K = \frac{-\Delta H^{\circ}}{R}\left(\frac{1}{T}\right) + \frac{\Delta S^{\circ}}{R}$ is in the form of a straight line equation ($y = mx + b$). A graph of ln K versus 1/T will yield a straight line with slope = $m = -\Delta H°/R$ and a y intercept = $b = \Delta S°/R$.

From the plot:

$$\text{slope} = \frac{\Delta y}{\Delta x} = \frac{0 - 40.}{3.0 \times 10^{-3}\ \text{K}^{-1} - 0} = -1.3 \times 10^{4}\ \text{K}$$

-1.3×10^4 K $= -\Delta H°/R$, $\Delta H° = 1.3 \times 10^4$ K × 8.3145 J/K•mol $= 1.1 \times 10^5$ J/mol

y intercept = 40. = $\Delta S°/R$, $\Delta S°$ = 40. × 8.3145 J/K•mol = 330 J/K•mol

As seen here, when ΔH° is positive, the slope of the ln K versus 1/T plot is negative. When ΔH° is negative as in an exothermic process, then the slope of the ln K versus 1/T plot will be positive (slope = −ΔH°/R).

72. The ln K versus 1/T plot gives a straight line with slope = −ΔH°/R and y intercept = ΔS°/R.

1.352×10^4 K $= -\Delta H°/R$, $\Delta H° = -(8.3145$ J/K•mol$)(1.352 \times 10^4$ K$)$

$\Delta H° = -1.124 \times 10^5$ J/mol $= -112.4$ kJ/mol

$-14.51 = \Delta S°/R$, $\Delta S° = (-14.51)(8.3145$ J/K•mol$) = -120.6$ J/K•mol

Note that the signs for ΔH° and ΔS° make sense. When a bond forms, $\Delta H° < 0$ and $\Delta S° < 0$.

Connecting to Biochemistry

73. It appears that the sum of the two processes has no net change. This is not so. By the second law of thermodynamics, ΔS_{univ} must have increased even though it looks as if we have gone through a cyclic process.

74. The introduction of mistakes is an effect of entropy. The purpose of redundant information is to provide a control to check the "correctness" of the transmitted information.

75. $CH_4(g) + CO_2(g) \rightarrow CH_3CO_2H(l)$

$\Delta H° = -484 - [-75 + (-393.5)] = -16$ kJ; $\Delta S° = 160. - (186 + 214) = -240.$ J/K

$\Delta G° = \Delta H° - T\Delta S° = -16$ kJ $- (298$ K$)(-0.240$ kJ/K$) = 56$ kJ

At standard concentrations, where ΔG = ΔG°, this reaction is spontaneous only at temperatures below T = ΔH°/ΔS° = 67 K (where the favorable ΔH° term will dominate, giving a negative ΔG° value). This is not practical. Substances will be in condensed phases and rates will be very slow at this extremely low temperature.

$CH_3OH(g) + CO(g) \rightarrow CH_3CO_2H(l)$

$\Delta H° = -484 - [-110.5 + (-201)] = -173$ kJ; $\Delta S° = 160. - (198 + 240.) = -278$ J/K

$\Delta G° = -173$ kJ $- (298$ K$)(-0.278$ kJ/K$) = -90.$ kJ

This reaction also has a favorable enthalpy and an unfavorable entropy term. This reaction is spontaneous at temperatures below T = $\Delta H°/\Delta S°$ = 622 K (assuming standard concentrations). The reaction of CH_3OH and CO will be preferred at standard conditions. It is spontaneous at high enough temperatures that the rates of reaction should be reasonable.

76. $C_2H_5OH(l) \rightarrow C_2H_5OH(g)$; at the boiling point, $\Delta G = 0$ and $\Delta S_{univ} = 0$. For the vaporization process, ΔS is a positive value, whereas ΔH is a negative value. To calculate ΔS_{sys}, we will determine ΔS_{surr} from ΔH and the temperature; then $\Delta S_{sys} = -\Delta S_{surr}$ for a system at equilibrium.

$$\Delta S_{surr} = \frac{-\Delta H}{T} = \frac{38.7 \times 10^3 \text{ J/mol}}{351 \text{ K}} = -110. \text{ J/K•mol}$$

$$\Delta S_{sys} = -\Delta S_{surr} = -(-110.) = 110. \text{ J/K•mol}$$

77.
$$\begin{array}{ll} HgbO_2 \rightarrow Hgb + O_2 & \Delta G° = -(-70 \text{ kJ}) \\ Hgb + CO \rightarrow HgbCO & \Delta G° = -80 \text{ kJ} \\ \hline HgbO_2 + CO \rightarrow HgbCO + O_2 & \Delta G° = -10 \text{ kJ} \end{array}$$

$$\Delta G° = -RT \ln K, \quad K = \exp\left(\frac{-\Delta G^o}{RT}\right) = \exp\left[\frac{-(-10 \times 10^3 \text{ J})}{(8.3145 \text{ J/K} \bullet \text{mol})(298 \text{ K})}\right] = 60$$

78. $K^+(\text{blood}) \rightleftharpoons K^+(\text{muscle}) \quad \Delta G° = 0; \ \Delta G = RT \ln\left(\frac{[K^+]_m}{[K^+]_b}\right); \ \Delta G = w_{max}$

$$\Delta G = \frac{8.3145 \text{ J}}{\text{K mol}}(310. \text{ K}) \ln\left(\frac{0.15}{0.0050}\right), \ \Delta G = 8.8 \times 10^3 \text{ J/mol} = 8.8 \text{ kJ/mol}$$

At least 8.8 kJ of work must be applied to transport 1 mol K^+.

Other ions will have to be transported in order to maintain electroneutrality. Either anions must be transported into the cells, or cations (Na^+) in the cell must be transported to the blood. The latter is what happens: $[Na^+]$ in blood is greater than $[Na^+]$ in cells as a result of this pumping.

$$\frac{8.8 \text{ kJ}}{\text{mol } K^+} \times \frac{1 \text{ mol ATP}}{30.5 \text{ kJ}} = 0.29 \text{ mol ATP}$$

79. a. $\Delta G° = -RT \ln K, \ K = \exp\left[\frac{-(-30{,}500 \text{ J})}{8.3145 \text{ J/K} \bullet \text{mol} \times 298 \text{ K}}\right] = 2.22 \times 10^5$

b. $C_6H_{12}O_6(s) + 6\, O_2(g) \rightarrow 6\, CO_2(g) + 6\, H_2O(l)$

$$\Delta G° = 6 \text{ mol}(-394 \text{ kJ/mol}) + 6 \text{ mol}(-237 \text{ kJ/mol}) - 1 \text{ mol}(-911 \text{ kJ/mol}) = -2875 \text{ kJ}$$

$$\frac{2875\ \text{kJ}}{\text{mol glucose}} \times \frac{1\ \text{mol ATP}}{30.5\ \text{kJ}} = 94.3\ \text{mol ATP};\ \ 94.3\ \text{molecules ATP/molecule glucose}$$

This is an overstatement. The assumption that all the free energy goes into this reaction is false. Actually, only 38 moles of ATP are produced by metabolism of 1 mole of glucose.

c. From Exercise 17.78, $\Delta G = 8.8$ kJ in order to transport 1.0 mol K^+ from the blood to the muscle cells.

$$8.8\ \text{kJ} \times \frac{1\ \text{mol ATP}}{30.5\ \text{kJ}} = 0.29\ \text{mol ATP}$$

80. a. $\ln K = \dfrac{-\Delta G^o}{RT} = \dfrac{-14{,}000\ \text{J}}{(8.3145\ \text{J/K}\bullet\text{mol})(298\ \text{K})} = -5.65,\quad K = e^{-5.65} = 3.5 \times 10^{-3}$

b.

$$\begin{array}{lr}
\text{Glutamic acid} + NH_3 \rightarrow \text{Glutamine} + H_2O & \Delta G^\circ = 14\ \text{kJ} \\
ATP + H_2O \rightarrow ADP + H_2PO_4^- & \Delta G^\circ = -30.5\ \text{kJ} \\
\hline
\text{Glutamic acid} + ATP + NH_3 \rightarrow \text{Glutamine} + ADP + H_2PO_4^- & \Delta G^\circ = 14 - 30.5 = -17\ \text{kJ}
\end{array}$$

$$\ln K = \frac{-\Delta G^o}{RT} = \frac{-(-17{,}000\ \text{J})}{8.3145\ \text{J/K}\bullet\text{mol}(298\ \text{K})} = 6.86,\ \ K = e^{6.86} = 9.5 \times 10^2$$

81. Enthalpy is not favorable, so ΔS must provide the driving force for the change. Thus ΔS is positive. There is an increase in positional probability, so the original enzyme has the more ordered structure (has the smaller positional probability).

82. $\Delta G = \Delta H - T\Delta S$; for the reaction, we break a P–O and O–H bond and form a P–O and O–H bond, so $\Delta H \approx 0$. ΔS for this process is negative because positional probability decreases (the dinucleotide has a more ordered structure). Thus $\Delta G > 0$, and the reaction is not spontaneous.

Nucleic acids must form for life to exist. From the simple analysis, it looks as if life can't exist, an obviously incorrect assumption. A cell is not an isolated system. There is an external source of energy to drive the reactions. A photosynthetic plant uses sunlight, and animals use the carbohydrates produced by plants as sources of energy. When all processes are combined, ΔS_{univ} must be greater than zero for the formation of nucleic acids, as is dictated by the second law of thermodynamics.

Additional Exercises

83. From Appendix 4, $S^\circ = 198$ J/K•mol for CO(g) and $S^\circ = 27$ J/K•mol for Fe(s).

Let $S_l^o = S^\circ$ for $Fe(CO)_5(l)$ and $S_g^o = S^\circ$ for $Fe(CO)_5(g)$.

$\Delta S^\circ = -677\ \text{J/K} = 1\ \text{mol}(S_l^o) - [1\ \text{mol}\ (27\ \text{J/K}\bullet\text{mol}) + 5\ \text{mol}(198\ \text{J/ K}\bullet\text{mol}]$

$S_l^o = 340.\ \text{J/K}\bullet\text{mol}$

$\Delta S^\circ = 107 \text{ J/K} = 1 \text{ mol } (S^\circ_g) - 1 \text{ mol } (340. \text{ J/K•mol})$

$S^\circ_g = S^\circ$ for $Fe(CO)_5(g) = 447$ J/K•mol

84. When an ionic solid dissolves, one would expect the disorder of the system to increase, so ΔS_{sys} is positive. Because temperature increased as the solid dissolved, this is an exothermic process, and ΔS_{surr} is positive ($\Delta S_{surr} = -\Delta H/T$). Because the solid did dissolve, the dissolving process is spontaneous, so ΔS_{univ} is positive.

85. ΔS will be negative because 2 mol of gaseous reactants form 1 mol of gaseous product. For ΔG to be negative, ΔH must be negative (exothermic). For exothermic reactions, K decreases as T increases. Therefore, the ratio of the partial pressure of PCl_5 to the partial pressure of PCl_3 will decrease when T is raised.

86. At boiling point, $\Delta G = 0$ so $\Delta S = \dfrac{\Delta H_{vap}}{T}$; for methane: $\Delta S = \dfrac{8.20 \times 10^3 \text{ J/mol}}{112 \text{ K}}$
$= 73.2$ J/mol•K

For hexane: $\Delta S = \dfrac{28.9 \times 10^3 \text{ J/mol}}{342 \text{ K}} = 84.5$ J/mol•K.

$$V_{met} = \frac{nRT}{P} = \frac{1.00 \text{ mol } (0.08206)(112 \text{ K})}{1.00 \text{ atm}} = 9.19 \text{ L}; \;\; V_{hex} = \frac{nRT}{P} = R(342 \text{ K}) = 28.1 \text{ L}$$

Hexane has the larger molar volume at the boiling point, so hexane should have the larger entropy. As the volume of a gas increases, positional disorder increases.

87. solid I → solid II; equilibrium occurs when $\Delta G = 0$.

$$\Delta G = \Delta H - T\Delta S, \;\; \Delta H = T\Delta S, \;\; T = \Delta H/\Delta S = \frac{-743.1 \text{ J/mol}}{-17.0 \text{ J/K} \bullet \text{mol}} = 43.7 \text{ K} = -229.5°\text{C}$$

88. a. $\Delta G^\circ = -RT \ln K = -(8.3145 \text{ J/K•mol})(298 \text{ K}) \ln 0.090 = 6.0 \times 10^3 \text{ J/mol} = 6.0 \text{ kJ/mol}$

b. H–O–H + Cl–O–Cl → 2 H–O–Cl

On each side of the reaction there are 2 H–O bonds and 2 O–Cl bonds. Both sides have the same number and type of bonds. Thus $\Delta H \approx \Delta H^\circ \approx 0$.

c. $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ, \;\; \Delta S^\circ = \dfrac{\Delta H^\circ - \Delta G^\circ}{T} = \dfrac{0 - 6.0 \times 10^3 \text{ J}}{298 \text{ K}} = -20. \text{ J/K}$

d. For $H_2O(g)$, $\Delta H^\circ_f = -242$ kJ/mol and $S^\circ = 189$ J/K•mol.

$\Delta H^\circ = 0 = 2\Delta H^\circ_{f,\,HOCl} - [1 \text{ mol}(-242 \text{ kJ/mol}) + 1 \text{ mol}(80.3 \text{ J/K/mol})], \;\; \Delta H^\circ_{f,\,HOCl}$
$= -81$ kJ/mol

$$-20.\ \text{J/K} = 2S^{o}_{\text{HOCl}} - [1\ \text{mol}(189\ \text{J/K}\bullet\text{mol}) + 1\ \text{mol}(266.1\ \text{J/K}\cdot\text{mol})],\ S^{o}_{\text{HOCl}} = 218\ \text{J/K}\bullet\text{mol}$$

e. Assuming ΔH° and ΔS° are T-independent: $\Delta G^{o}_{500} = 0 - (500.\ \text{K})(-20.\ \text{J/K}) = 1.0 \times 10^4\ \text{J}$

$$\Delta G° = -RT \ln K,\ K = \exp\left(\frac{-\Delta G^{o}}{RT}\right) = \exp\left[\frac{-1.0 \times 10^4}{(8.3145)(500.)}\right] = e^{-2.41} = 0.090$$

f. $\Delta G = \Delta G° + RT \ln \dfrac{P^2_{\text{HOCl}}}{P_{\text{H}_2\text{O}} \times P_{\text{Cl}_2\text{O}}}$; from part a, ΔG° = 6.0 kJ/mol.

We should express all partial pressures in atm. However, we perform the pressure conversion the same number of times in the numerator and denominator, so the factors of 760 torr/atm will all cancel. Thus we can use the pressures in units of torr.

$$\Delta G = \frac{6.0\ \text{kJ/mol} + (8.3145\ \text{J/K}\bullet\text{mol})(298\ \text{K})}{1000\ \text{J/kJ}} \ln\left[\frac{(0.10)^2}{(18)(2.0)}\right] = 6.0 - 20. = -14\ \text{kJ/mol}$$

89. $\text{Ba(NO}_3)_2(s) \rightleftharpoons \text{Ba}^{2+}(aq) + 2\ \text{NO}_3^-(aq)$ $K = K_{sp}$; ΔG° = −561 + 2(−109) − (−797) = 18 kJ

$$\Delta G° = -RT \ln K_{sp},\ \ln K_{sp} = \frac{-\Delta G^{o}}{RT} = \frac{-18{,}000\ \text{J}}{8.3145\ \text{J/K}\bullet\text{mol}(298\ \text{K})} = -7.26,\ K_{sp} = e^{-7.26} = 7.0 \times 10^{-4}$$

90. $\text{HF}(aq) \rightleftharpoons \text{H}^+(aq) + \text{F}^-(aq)$; $\Delta G = \Delta G° + RT \ln \dfrac{[\text{H}^+][\text{F}^-]}{[\text{HF}]}$

$\Delta G° = -RT \ln K = -(8.3145\ \text{J/K}\bullet\text{mol})(298\ \text{K}) \ln(7.2 \times 10^{-4}) = 1.8 \times 10^4\ \text{J/mol}$

a. The concentrations are all at standard conditions, so ΔG = ΔG = 1.8×10^4 J/mol (Q = 1.0 and ln Q = 0). Because ΔG° is positive, the reaction shifts left to reach equilibrium.

b. $\Delta G = 1.8 \times 10^4\ \text{J/mol} + (8.3145\ \text{J/K}\bullet\text{mol})(298\ \text{K}) \ln \dfrac{(2.7 \times 10^{-2})^2}{0.98}$

$\Delta G = 1.8 \times 10^4\ \text{J/mol} - 1.8 \times 10^4\ \text{J/mol} = 0$

ΔG = 0, so the reaction is at equilibrium (no shift).

c. $\Delta G = 1.8 \times 10^4\ \text{J/mol} + 8.3145(298\ \text{K}) \ln \dfrac{(1.0 \times 10^{-5})^2}{1.0 \times 10^{-5}} = -1.1 \times 10^4\ \text{J/mol}$; shifts right

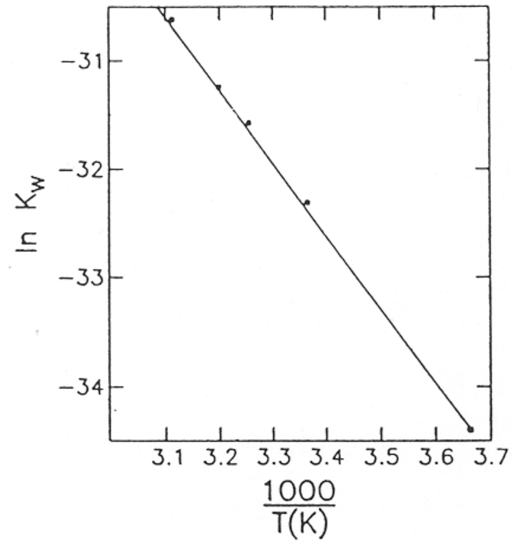
d. $\Delta G = 1.8 \times 10^4 + 8.3145(298) \ln \dfrac{7.2 \times 10^{-4}(0.27)}{0.27} = 1.8 \times 10^4 - 1.8 \times 10^4 = 0$; at equilibrium

e. $\Delta G = 1.8 \times 10^4 + 8.3145(298) \ln\dfrac{1.0 \times 10^{-3}(0.67)}{0.52} = 2 \times 10^3$ J/mol; shifts left

91. ΔS is more favorable (less negative) for reaction 2 than for reaction 1, resulting in $K_2 > K_1$. In reaction 1, seven particles in solution are forming one particle in solution. In reaction 2, four particles are forming one, which results in a smaller decrease in positional probability than for reaction 1.

92. A graph of ln K versus 1/T will yield a straight line with slope equal to –ΔH°/R and *y* intercept equal to ΔS°/R.

Temp (°C)	T (K)	1000/T (K^{-1})	K_w	ln K_w
0	273	3.66	1.14×10^{-15}	−34.408
25	298	3.36	1.00×10^{-14}	−32.236
35	308	3.25	2.09×10^{-14}	−31.499
40.	313	3.19	2.92×10^{-14}	−31.165
50.	323	3.10	5.47×10^{-14}	−30.537



The straight-line equation (from a calculator) is $\ln K = -6.91 \times 10^3\left(\dfrac{1}{T}\right) - 9.09$.

Slope $= -6.91 \times 10^3\ K = \dfrac{-\Delta H^\circ}{R}$, $\Delta H^\circ = -\,(-6.91 \times 10^3\ K \times 8.3145\ J/K{\bullet}mol)$

$= 5.75 \times 10^4$ J/mol

y intercept $= -9.09 = \dfrac{\Delta S^\circ}{R}$, $\Delta S^\circ = -9.09 \times 8.3145\ J/K{\bullet}mol = -75.6\ J/K{\bullet}mol$

93. $\Delta G^\circ = -RT \ln K$; when K = 1.00, ΔG° = 0 since ln 1.00 = 0. $\Delta G^\circ = 0 = \Delta H^\circ - T\Delta S^\circ$

$\Delta H° = 3(-242 \text{ kJ}) - [-826 \text{ kJ}] = 100.\text{ kJ}$; $\Delta S° = [2(27 \text{ J/K}) + 3(189 \text{ J/K})] - [90.\text{ J/K} + 3(131 \text{ J/K})] = 138 \text{ J/K}$

$$\Delta H° = T\Delta S°,\ T = \frac{\Delta H^{o}}{\Delta S^{o}} = \frac{100.\text{ kJ}}{0.138 \text{ kJ/K}} = 725 \text{ K}$$

94. $C_2H_4(g) + H_2O(g) \rightarrow CH_3CH_2OH(l)$

$\Delta H° = -278 - (52 - 242) = -88 \text{ kJ}$; $\Delta S° = 161 - (219 + 189) = -247 \text{ J/K}$

When $\Delta G° = 0$, $\Delta H° = T\Delta S°$, so $T = \dfrac{\Delta H^{o}}{\Delta S^{o}} = \dfrac{-88 \times 10^3 \text{ J}}{-247 \text{ J/K}} = 360 \text{ K}$.

At standard concentrations, ΔG = ΔG°, so the reaction will be spontaneous when ΔG° < 0. Since the signs of ΔH° and ΔS° are both negative, this reaction will be spontaneous at temperatures below 360 K (where the favorable ΔH° term will dominate).

$C_2H_6(g) + H_2O(g) \rightarrow CH_3CH_2OH(l) + H_2(g)$

$\Delta H° = -278 - (-84.7 - 242) = 49 \text{ kJ}$; $\Delta S° = 131 + 161 - (229.5 + 189) = -127 \text{ J/K}$

This reaction can never be spontaneous at standard conditions because of the signs of ΔH° and ΔS°.

Thus the reaction $C_2H_4(g) + H_2O(g) \rightarrow C_2H_5OH(l)$ would be preferred at standard conditions.

Challenge Problems

95. a. Vessel 1: At 0°C, this system is at equilibrium, so $\Delta S_{univ} = 0$ and $\Delta S = \Delta S_{surr}$. Because the vessel is perfectly insulated, q = 0, so $\Delta S_{surr} = 0 = \Delta S_{sys}$.

b. Vessel 2: The presence of salt in water lowers the freezing point of water to a temperature below 0°C. In vessel 2, the conversion of ice into water will be spontaneous at 0°C, so $\Delta S_{univ} > 0$. Because the vessel is perfectly insulated, $\Delta S_{surr} = 0$. Therefore, ΔS_{sys} must be positive (ΔS > 0) in order for ΔS_{univ} to be positive.

96. The liquid water will evaporate at first and eventually an equilibrium will be reached (physical equilibrium).

- Because evaporation is an endothermic process, ΔH is positive.
- Because $H_2O(g)$ is more disordered (greater positional probability), ΔS is positive.
- The water will become cooler (the higher energy water molecules leave), thus ΔT_{water} will be negative.
- The vessel is insulated (q = 0), so $\Delta S_{surr} = 0$.
- Because the process occurs, it is spontaneous, so ΔS_{univ} is positive.

97. $3\ O_2(g) \rightleftharpoons 2\ O_3(g)$; ΔH° = 2(143 kJ) = 286 kJ; ΔG° = 2(163 kJ) = 326 kJ

$$\ln K = \frac{-\Delta G^\circ}{RT} = \frac{-326 \times 10^3\ \text{J}}{(8.3145\ \text{J/K} \bullet \text{mol})(298\ \text{K})} = -131.573,\ \ K = e^{-131.573} = 7.22 \times 10^{-58}$$

We need the value of K at 230. K. From Section 17.8 of the text:

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

For two sets of K and T:

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

Subtracting the first expression from the second:

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

Let $K_2 = 7.22 \times 10^{-58}$, T_2 = 298 K; $K_1 = K_{230}$, T_1 = 230. K; ΔH° = 286×10^3 J

$$\ln\frac{7.22 \times 10^{-58}}{K_{230}} = \frac{286 \times 10^3}{8.3145}\left(\frac{1}{230.} - \frac{1}{298}\right) = 34.13$$

$$\frac{7.22 \times 10^{-58}}{K_{230}} = e^{34.13} = 6.6 \times 10^{14},\ \ K_{230} = 1.1 \times 10^{-72}$$

$$K_{230} = 1.1 \times 10^{-72} = \frac{P_{O_3}^2}{P_{O_3}^3} = \frac{P_{O_3}^2}{(1.0 \times 10^{-3}\ \text{atm})^3},\ \ P_{O_3} = 3.3 \times 10^{-41}\ \text{atm}$$

The volume occupied by one molecule of ozone is:

$$V = \frac{nRT}{P} = \frac{(1/6.022 \times 10^{23}\ \text{mol})(0.08206\ \text{L atm/K} \bullet \text{mol})(230.\ \text{K})}{(3.3 \times 10^{-41}\ \text{atm})} = 9.5 \times 10^{17}\ \text{L}$$

Equilibrium is probably not maintained under these conditions. When only two ozone molecules are in a volume of 9.5×10^{17} L, the reaction is not at equilibrium. Under these conditions, Q > K, and the reaction shifts left. But with only 2 ozone molecules in this huge volume, it is extremely unlikely that they will collide with each other. At these conditions, the concentration of ozone is not large enough to maintain equilibrium.

98. Arrangement I and V: S = k ln W; W = 1; S = k ln 1 = 0

Arrangement II and IV: W = 4; S = k ln 4 = 1.38×10^{-23} J/K ln 4, S = 1.91×10^{-23} J/K

Arrangement III: W = 6; S = k ln 6 = 2.47×10^{-23} J/K

99. a. From the plot, the activation energy of the reverse reaction is $E_a + (-\Delta G°) = E_a - \Delta G°$ ($\Delta G°$ is a negative number as drawn in the diagram).

$$k_f = A\exp\left(\frac{-E_a}{RT}\right) \text{ and } k_r = A\exp\left[\frac{-(E_a - \Delta G^o)}{RT}\right], \quad \frac{k_f}{k_r} = \frac{A\exp\left(\frac{-E_a}{RT}\right)}{A\exp\left[\frac{-(E_a - \Delta G^o)}{RT}\right]}$$

If the A factors are equal: $\dfrac{k_f}{k_r} = \exp\left[\dfrac{-E_a}{RT} + \dfrac{(E_a - \Delta G^o)}{RT}\right] = \exp\left(\dfrac{-\Delta G^o}{RT}\right)$

From $\Delta G° = -RT \ln K$, $K = \exp\left(\dfrac{-\Delta G^o}{RT}\right)$; because K and $\dfrac{k_f}{k_r}$ are both equal to the same expression, $K = k_f/k_r$.

b. A catalyst will lower the activation energy for both the forward and reverse reactions (but not change $\Delta G°$). Therefore, a catalyst must increase the rate of both the forward and reverse reactions.

100. At equilibrium:

$$P_{H_2} = \frac{nRT}{V} = \frac{\left(\dfrac{1.10 \times 10^{13}\ \text{molecules}}{6.022 \times 10^{23}\ \text{molecules/mol}}\right)\left(\dfrac{0.08206\ \text{L atm}}{\text{K mol}}\right)(298\ \text{K})}{1.00\ \text{L}}$$

$$P_{H_2} = 4.47 \times 10^{-10}\ \text{atm}$$

The pressure of H_2 decreased from 1.00 atm to 4.47×10^{-10} atm. Essentially all of the H_2 and Br_2 has reacted. Therefore, P_{HBr} = 2.00 atm because there is a 2:1 mole ratio between HBr and H_2 in the balanced equation. Because we began with equal moles of H_2 and Br_2, we will have equal moles of H_2 and Br_2 at equilibrium. Therefore, $P_{H_2} = P_{Br_2} = 4.47 \times 10^{-10}$ atm.

$$K = \frac{P_{HBr}^2}{P_{H_2} \times P_{Br_2}} = \frac{(2.00)^2}{(4.47 \times 10^{-10})^2} = 2.00 \times 10^{19}; \quad \text{assumptions good.}$$

$$\Delta G° = -RT \ln K = -\ (8.3145\ \text{J/K}\bullet\text{mol})(298\ \text{K})\ \ln\ (2.00 \times 10^{19}) = -1.10 \times 10^5\ \text{J/mol}$$

$$\Delta S° = \frac{\Delta H^o - \Delta G^o}{T} = \frac{-103{,}800\ \text{J/mol} - (-1.0 \times 10^5\ \text{J/mol})}{298\ \text{K}} = 20\ \text{J/K}\bullet\text{mol}$$

101. a. $\Delta G° = G_B^o - G_A^o = 11{,}718 - 8996 = 2722$ J

$$K = \exp\left(\frac{-\Delta G^o}{RT}\right) = \exp\left[\frac{-2722\ \text{J}}{(8.3145\ \text{J/K}\bullet\text{mol})\ (298\ \text{K})}\right] = 0.333$$

b. When Q = 1.00 > K, the reaction shifts left. Let x = atm of B(g), which reacts to reach equilibrium.

	A(g) ⇌	B(g)
Initial	1.00 atm	1.00 atm
Equil.	$1.00 + x$	$1.00 - x$

$$K = \frac{P_B}{P_A} = \frac{1.00 - x}{1.00 + x} = 0.333,\ \ 1.00 - x = 0.333 + (0.333)x,\ \ x = 0.50 \text{ atm}$$

$P_B = 1.00 - 0.50 = 0.50$ atm; $P_A = 1.00 + 0.50 = 1.50$ atm

c. $\Delta G = \Delta G° + RT \ln Q = \Delta G° + RT \ln(P_B/P_A)$

$\Delta G = 2722 \text{ J} + (8.3145)(298) \ln(0.50/1.50) = 2722 \text{ J} - 2722 \text{ J} = 0$ (carrying extra sig. figs.)

102. From Exercise 71, $\ln K = \frac{-\Delta H°}{RT} + \frac{\Delta S°}{R}$. For K at two temperatures T_1 and T_2, the equation can be manipulated to give (see Exercise 71): $\ln\frac{K_2}{K_1} = \frac{\Delta H°}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

$$\ln\left(\frac{3.25 \times 10^{-2}}{8.84}\right) = \frac{\Delta H°}{8.3145 \text{ J/K} \bullet \text{mol}}\left(\frac{1}{298 \text{ K}} - \frac{1}{348 \text{ K}}\right)$$

$-5.61 = (5.8 \times 10^{-5} \text{ mol/J})(\Delta H°)$, $\Delta H° = -9.7 \times 10^4$ J/mol

For K = 8.84 at T = 25°C:

$$\ln 8.84 = \frac{-(-9.7 \times 10^4 \text{ J/mol})}{(8.3145 \text{ J/K} \bullet \text{mol})(298 \text{ K})} + \frac{\Delta S°}{8.3145 \text{ J/K} \bullet \text{mol}},\ \ \frac{\Delta S°}{8.3145} = -37$$

$\Delta S° = -310$ J/K•mol

We get the same value for ΔS° using $K = 3.25 \times 10^{-2}$ at T = 348 K data.

$\Delta G° = -RT \ln K$; when K = 1.00, then ΔG° = 0 since ln 1.00 = 0. Assuming ΔH° and ΔS° do not depend on temperature:

$$\Delta G° = 0 = \Delta H° - T\Delta S°,\ \ \Delta H° = T\Delta S°,\ \ T = \frac{\Delta H°}{\Delta S°} = \frac{-9.7 \times 10^4 \text{ J/mol}}{-310 \text{ J/K} \bullet \text{mol}} = 310 \text{ K}$$

103. $K = P_{CO_2}$; to ensure Ag_2CO_3 from decomposing, P_{CO_2} should be greater than K.

From Exercise 71, $\ln K = \frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$. For two conditions of K and T, the equation is:

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

Let T_1 = 25°C = 298 K, $K_1 = 6.23 \times 10^{-3}$ torr; T_2 = 110.°C = 383 K, K_2 = ?

$$\ln\frac{K_2}{6.23 \times 10^{-3}\ \text{torr}} = \frac{79.14 \times 10^3\ \text{J/mol}}{8.3145\ \text{J/K} \bullet \text{mol}}\left(\frac{1}{298\ \text{K}} - \frac{1}{383\ \text{K}}\right)$$

$$\ln\frac{K_2}{6.23 \times 10^{-3}} = 7.1,\quad \frac{K_2}{6.23 \times 10^{-3}} = e^{7.1} = 1.2 \times 10^3,\quad K_2 = 7.5\ \text{torr}$$

To prevent decomposition of Ag_2CO_3, the partial pressure of CO_2 should be greater than 7.5 torr.

104. From the problem, $\chi^L_{C_6H_6} = \chi^L_{CCl_4} = 0.500$. We need the pure vapor pressures (P°) in order to calculate the vapor pressure of the solution. Using the thermodynamic data:

$$C_6H_6(l) \rightleftharpoons C_6H_6(g) \quad K = P_{C_6H_6} = P^\circ_{C_6H_6} \text{ at } 25°C$$

$$\Delta G^\circ_{rxn} = \Delta G^\circ_{f,\,C_6H_6(g)} - \Delta G^\circ_{f,\,C_6H_6(l)} = 129.66\ \text{kJ/mol} - 124.50\ \text{kJ/mol} = 5.16\ \text{kJ/mol}$$

$$\Delta G^\circ = -RT\ln K,\ \ln K = \frac{-\Delta G^\circ}{RT} = \exp\frac{-5.16 \times 10^3\ \text{J/mol}}{(8.3145\ \text{J/K} \bullet \text{mol})(298\ \text{K})} = -2.08$$

$$K = P^\circ_{C_6H_6} = e^{-2.08} = 0.125\ \text{atm}$$

For CCl_4: $\Delta G^\circ_{rxn} = \Delta G^\circ_{f,\,CCl_4(g)} - \Delta G^\circ_{f,\,CCl_4(l)} = -60.59\ \text{kJ/mol} - (-65.21\ \text{kJ/mol})$
$= 4.62\ \text{kJ/mol}$

$$K = P^\circ_{CCl_4} = \exp\left(\frac{-\Delta G^\circ}{RT}\right) = \exp\left(\frac{-4620\ \text{J/mol}}{8.3145\ \text{J/K} \bullet \text{mol} \times 298\ \text{K}}\right) = 0.155\ \text{atm}$$

$P_{C_6H_6} = \chi^L_{C_6H_6} P^\circ_{C_6H_6} = 0.500(0.125\ \text{atm}) = 0.0625\ \text{atm}$; $P^\circ_{CCl_4} = 0.500(0.155\ \text{atm})$
$= 0.0775\ \text{atm}$

$$\chi^V_{C_6H_6} = \frac{P_{C_6H_6}}{P_{tot}} = \frac{0.0625\ \text{atm}}{0.0625\ \text{atm} + 0.0775\ \text{atm}} = \frac{0.0625}{0.1400} = 0.446$$

$$\chi^V_{CCl_4} = 1.000 - 0.446 = 0.554$$

105. Use the thermodynamic data to calculate the boiling point of the solvent.

At boiling point: $\Delta G = 0 = \Delta H - T\Delta S,\ T = \dfrac{\Delta H}{\Delta S} = \dfrac{33.90 \times 10^3\ \text{J/mol}}{95.95\ \text{J/K} \bullet \text{mol}} = 353.3\ \text{K}$

$\Delta T = K_b m,\ (355.4\ \text{K} - 353.3\ \text{K}) = 2.5\ \text{K kg/mol}(m),\ m = \dfrac{2.1}{2.5} = 0.84\ \text{mol/kg}$

$\text{Mass solvent} = 150.\ \text{mL} \times \dfrac{0.879\ \text{g}}{\text{mL}} \times \dfrac{1\ \text{kg}}{1000\ \text{g}} = 0.132\ \text{kg}$

$\text{Mass solute} = 0.132\ \text{kg solvent} \times \dfrac{0.84\ \text{mol solute}}{\text{kg solvent}} \times \dfrac{142\ \text{g}}{\text{mol}} = 15.7\ \text{g} = 16\ \text{g solute}$

106. $\Delta S_{surr} = -\Delta H/T = -q_P/T$

q = heat loss by hot water = moles × molar heat capacity × ΔT

$q = 1.00 \times 10^3\ \text{g}\ H_2O \times \dfrac{1\ \text{mol}\ H_2O}{18.02\ \text{g}} \times \dfrac{75.4\ \text{J}}{\text{K mol}} \times (298.2 - 363.2) = -2.72 \times 10^5\ \text{J}$

$\Delta S_{surr} = \dfrac{-(-2.72 \times 10^5\ \text{J})}{298.2\ \text{K}} = 912\ \text{J/K}$

107.

	HX	⇌ H⁺	+ X⁻
Initial	0.10 *M*	~0	0
Equil.	0.10 – *x*	*x*	*x*

$K_a = \dfrac{[H^+][X^-]}{[HX]}$

From problem, $x = [H^+] = 10^{-5.83} = 1.5 \times 10^{-6}$; $K_a = \dfrac{(1.5 \times 10^{-6})^2}{0.10 - 1.5 \times 10^{-6}} = 2.3 \times 10^{-11}$

$\Delta G° = -RT \ln K = -8.3145\ \text{J/K}\bullet\text{mol}(298\ \text{K}) \ln(2.3 \times 10^{-11}) = 6.1 \times 10^4\ \text{J/mol} = 61\ \text{kJ/mol}$

108. $NaCl(s) \rightleftharpoons Na^+(aq) + Cl^-(aq) \qquad K = K_{sp} = [Na^+][Cl^-]$

$\Delta G° = [(-262\ \text{kJ}) + (-131\ \text{kJ})] - (-384\ \text{kJ}) = -9\ \text{kJ} = -9000\ \text{J}$

$\Delta G° = = -RT \ln K_{sp},\ K_{sp} = \exp\left[\dfrac{-(-9000\ \text{J})}{8.3145\ \text{J/K} \bullet \text{mol} \times 298\ \text{K}}\right] = 38 = 40$

	NaCl(s) ⇌	Na⁺(aq) +	Cl⁻(aq)
Initial	s = solubility (mol/L)	0	0
Equil.		*s*	*s*

$K_{sp} = 40$

$K_{sp} = 40 = s(s),\ s = (40)^{1/2} = 6.3 = 6\ M = [Cl^-]$

Integrative Problems

109. Because the partial pressure of C(g) decreased, the net change that occurs for this reaction to reach equilibrium is for products to convert to reactants.

	$A(g)$	+	$2\ B(g)$	⇌	$C(g)$
Initial	0.100 atm		0.100 atm		0.100 atm
Change	$+x$		$+2x$	←	$-x$
Equil.	$0.100 + x$		$0.100 + 2x$		$0.100 - x$

From the problem, $P_C = 0.040 \text{ atm} = 0.100 - x,\ x = 0.060 \text{ atm}$

The equilibrium partial pressures are: $P_A = 0.100 + x = 0.100 + 0.060 = 0.160$ atm, $P_B = 0.100 + 2((0.60) = 0.220$ atm, and $P_C = 0.040$ atm

$$K = \frac{0.040}{0.160(0.220)^2} = 5.2$$

$$\Delta G° = -RT \ln K = -8.3145 \text{ J/K•mol}(298 \text{ K}) \ln(5.2) = -4.1 \times 10^3 \text{ J/mol} = -4.1 \text{ kJ/mol}$$

110. $\Delta G° = \Delta H° - T\Delta S° = -28.0 \times 10^3 \text{ J} - 298 \text{ K}(-175 \text{ J/K}) = 24{,}200 \text{ J}$

$$\Delta G° = -RT \ln K,\ \ln K = \frac{-\Delta G^{o}}{RT} = \frac{-24{,}000 \text{ J}}{8.3145 \text{ J/K} \bullet \text{mol} \times 298 \text{ K}} = -9.767$$

$$K = e^{-9.767} = 5.73 \times 10^{-5}$$

	B	+	H_2O	⇌	BH^+	+	OH^-	$K = K_b = 5.73 \times 10^{-5}$
Initial	$0.125\ M$				0		~0	
Change	$-x$				$+x$		$+x$	
Equil.	$0.125 - x$				x		x	

$$K_b = 5.73 \times 10^{-5} = \frac{[BH^+][OH^-]}{[B]} = \frac{x^2}{0.125 - x} \approx \frac{x^2}{0.125},\ x = [OH^-] = 2.68 \times 10^{-3}\ M$$

$pH = -\log(2.68 \times 10^{-3}) = 2.572$; $pOH = 14.000 - 2.572 = 11.428$; assumptions good

Marathon Problem

111. a. $\Delta S°$ will be negative because there is a decrease in the number of moles of gas.

b. Because $\Delta S°$ is negative, $\Delta H°$ must be negative for the reaction to be spontaneous at some temperatures. Therefore, ΔS_{surr} is positive.

c. $Ni(s) + 4\ CO(g) \rightleftharpoons Ni(CO)_4(g)$

$\Delta H° = -607 - [4(-110.5)] = -165$ kJ; $\Delta S° = 417 - [4(198) + (30.)] = -405$ J/K

d. $\Delta G° = 0 = \Delta H° - T\Delta S°, \quad T = \dfrac{\Delta H^o}{\Delta S^o} = \dfrac{-165 \times 10^3\ J}{-405\ J/K} = 407\ K$ or 134°C

e. $T = 50.°C + 273 = 323\ K$

$\Delta G^o_{323} = -165\ kJ - (323\ K)(-0.405\ kJ/K) = -34\ kJ$

$\ln K = \dfrac{-\Delta G^o}{RT} = \dfrac{-(-34{,}000\ J)}{8.3145\ J/K \bullet mol(323\ K)} = 12.66, \ K = e^{12.66} = 3.1 \times 10^5$

f. $T = 227°C + 273 = 500.\ K$

$\Delta G^o_{500} = -165\ kJ - (500.\ K)(-0.405\ kJ/K) = 38\ kJ$

$\ln K = \dfrac{-38{,}000\ J}{(8.3145\ J/K \bullet mol)(500.\ K)} = -9.14, \ K = e^{-9.14} = 1.1 \times 10^{-4}$

g. The temperature change causes the value of the equilibrium constant to change from a large value favoring formation of $Ni(CO)_4$ to a small value favoring the decomposition of $Ni(CO)_4$ into pure Ni and CO. This is exactly what is wanted in order to purify a nickel sample.

h. $Ni(CO)_4(l) \rightleftharpoons Ni(CO)_4(g) \qquad K = P_{Ni(CO)_4}$

At 42°C (the boiling point): $\Delta G° = 0 = \Delta H° - T\Delta S°$

$\Delta S° = \dfrac{\Delta H^o}{T} = \dfrac{29.0 \times 10^3\ J}{315\ K} = 92.1\ J/K$

At 152°C: $\Delta G^o_{152} = \Delta H° - T\Delta S° = 29.0 \times 10^3\ J - 425\ K(92.1\ J/K) = -10{,}100\ J$

$\Delta G° = -RT \ln K, \ \ln K = \dfrac{-(-10{,}100\ J)}{8.3145\ J/K \bullet mol(425\ K)} = 2.858, \ K_p = e^{2.858} = 17.4$

A maximum pressure of 17.4 atm can be attained before $Ni(CO)_4(g)$ will liquify.