19 Chemical Thermodynamics

Visualizing Concepts

19.2 (a) The process depicted is a change of state from a solid to a gas. ΔS increases because of the greater motional freedom of the particles. ΔH increases because both melting and boiling are endothermic processes. Since $\Delta G = \Delta H - T\Delta S$, and both ΔH and ΔS are positive, the sign of ΔG depends on temperature. This is true for all phase changes. If the temperature of the system is greater than the boiling point of the substance, the process is spontaneous and ΔG is negative. If the temperature is lower than the boiling point, the process is not spontaneous and ΔG is positive.

(b) If the process is spontaneous, the second law states that $\Delta S_{univ} \geq 0$. Since ΔS_{sys} increases, ΔS_{surr} must decrease. If the change occurs via a reversible pathway, $\Delta S_{univ} = 0$ and $\Delta S_{surr} = -\Delta S_{sys}$. If the pathway is irreversible, the magnitude of ΔS_{sys} is greater than the magnitude of ΔS_{surr}, but the sign of ΔS_{surr} is still negative.

19.3 In the depicted reaction, both reactants and products are in the gas phase (they are far apart and randomly placed). There are twice as many molecules (or moles) of gas in the products, so ΔS is positive for this reaction.

19.5 (a) *Analyze.* The boxes depict three different mixtures of reactants and products for the reaction $A_2 + B_2 \rightleftharpoons 2AB$.

Plan. Box 1 is an equilibrium mixture. By definition, $\Delta G = 0$ for box 1. Calculate K and $\Delta G°$ for the reaction from box 1. Boxes 2 and 3 are nonequilibrium mixtures. Calculate Q and ΔG for boxes 2 and 3.

Solve. $K = \dfrac{[AB]^2}{[A][B]}$. Use number of molecules as a measure of concentration.

Box 1: $K = \dfrac{(3)^2}{(3)(3)} = 1.$

$\Delta G = \Delta G° + RT \ln K;\ 0 = \Delta G° - RT \ln(1),\ 0 = \Delta G° - 0;\ \Delta G° = 0$

Box 2: $Q = \dfrac{(1)^2}{(4)(4)} = \dfrac{1}{16} = 0.0625 = 0.06$

$\Delta G = \Delta G° + RT \ln Q = 0 - RT \ln(0.0625) = 2.77\ RT = 3RT$

Box 3: $Q = \dfrac{(7)^2}{(1)(1)} = \dfrac{46}{1} = 49$

$\Delta G = \Delta G° + RT \ln Q = 0 - RT \ln(49) = -3.89\ RT = -4RT$

(b) The magnitudes of ΔG (ignoring sign) are: box 1, 0; box 2, 2.8 RT; box 3, 3.9 RT. The order of increasing *magnitude* of ΔG is: box 1 < box 2 < box 3.

The signs on ΔG indicate in which direction the reaction is spontaneous. The mixture in box 2 will react spontaneously in the forward direction, toward products. The mixture in box 3 will react spontaneously in the reverse direction, toward reactants. The driving force for the reverse reaction in box 3, the *magnitude* of ΔG, is greater than the driving force for the forward reaction in box 2.

19.6 (a) The minimum in the plot is the equilibrium position of the reaction, where $\Delta G = 0$.

(b) X is the difference in free energy between reactant and products in their standard states, $\Delta G°$.

Spontaneous Processes

19.8 (a) Spontaneous; a gas, in this case perfume vapor, expands to fill its container, the room.

(b) Nonspontaneous; a mixture cannot be separated without outside intervention.

(c) Nonspontaneous; an inflated balloon doesn't burst without external stress, such as a pin prick, a squeeze, or adding more gas.

(d) Spontaneous; see Figure 8.2.

(e) Spontaneous; the very polar HCl molecules readily dissolve in water to form concentrated HCl(aq).

19.10 Berthelot's suggestion is incorrect. Some examples of nonexothermic spontaneous processes are expansion of certain pressurized gases, dissolving of one liquid in another, and dissolving of many salts in water.

19.12 (a) Exothermic. If melting requires heat and is endothermic, freezing must be exothermic.

(b) At 1 atm (indicated by the term "normal" freezing point), the freezing of 1-propanol is spontaneous at temperatures below -127°C.

(c) At 1 atm, the freezing of 1-propanol is nonspontaneous at temperatures above -127°C.

(d) At 1 atm and -127°C, the normal freezing point of 1-propanol, the solid and liquid phases are in equilibrium. That is, at the freezing point, 1-propanol molecules escape to the liquid phase at the same rate as liquid 1-propanol solidifies, assuming no heat is exchanged between 1-propanol and the surroundings.

19.14 (a) A process is *irreversible* if the system cannot be returned to its original state by the same path that the forward process took place.

(b) Since the system returned to its initial state via a different path (different q_r and w_r than q_f and w_f), there is a net change in the surroundings.

(c) The condensation of a liquid will be irreversible if it occurs at any temperature other than the boiling point of the liquid, at a specified pressure.

19.16 (a) $\Delta E\ (1 \rightarrow 2) = -\Delta E\ (2 \rightarrow 1)$

(b) We can say nothing about the values of q and w because we have no information about the paths.

(c) If the changes of state are reversible, the two paths are the same and $w\ (1 \rightarrow 2) = -w\ (2 \rightarrow 1)$. This is the maximum realizable work from this system.

19.18 (a) The detonation of an explosive is definitely spontaneous, once it is initiated.

(b) The quantity q is related to ΔH. Since the detonation is highly exothermic, q is large and negative.

If only PV-work is done and P is constant, $\Delta H = q$. Although these conditions probably do not apply to a detonation, we can still predict the sign of q, based on ΔH, if not its exact magnitude.

(c) The sign (and magnitude) of w depend on the path of the process, the exact details of how the detonation is carried out. It seems clear, however, that work will be done by the system on the surroundings in almost all circumstances (buildings collapse, earth and air are moved), so the sign of w is probably negative.

(d) $\Delta E = q + w$. If q and w are both negative, then the sign of ΔE is negative, regardless of the magnitudes of q and w.

Entropy and the Second Law of Thermodynamics

19.20 (a) When a liquid freezes, the entropy of the system decreases.

(b) ΔS is negative.

(c) Entropy being a state function means that ΔS is independent of the path of the process. ΔS defined in terms of a reversible path must equal ΔS for any path.

19.22 (a) $Cs(l) \rightarrow Cs(s)$, ΔS is negative

(b) $$\Delta H = 15.0\,\text{g Cs} \times \frac{1\,\text{mol Cs}}{132.9\,\text{g Cs}} \times \frac{2.09\,\text{kJ}}{\text{mol Cs}} = 0.2359 = 0.236\,\text{kJ}$$

$$\Delta S = \frac{\Delta H}{T} = 0.2359\,\text{kJ} \times \frac{1000\,\text{J}}{1\,\text{kJ}} \times \frac{1}{(273.15 + 28.4)\text{K}} = 0.782\,\text{J/K}$$

19.24 (a) For a spontaneous process, $\Delta S_{universe} > 0$. For a reversible process, $\Delta S_{universe} = 0$.

(b) $\Delta S_{surroundings}$ is positive and greater than the magnitude of the decrease in ΔS_{system}.

(c) $\Delta S_{system} = 78$ J/K.

19.26 According to Boyle's law, $P_1V_1 = P_2V_2$ at constant n and T.

$0.900 \text{ atm} \times V_1 = 3.00 \text{ atm} \times V_2$; $V_2/V_1 = 0.900 \text{ atm}/3.00 \text{ atm} = 0.300$

$\Delta S_{sys} = nR \ln (V_2/V_1) = 0.500 \text{ mol } (8.314 \text{ J/mol•K})(\ln 0.300) = -5.0049 = -5.00 \text{ J/K}$

Check. An increase in pressure results in a decrease in volume at constant T, so we expect ΔS to be negative, and it is.

The Molecular Interpretation of Entropy

19.28 (a) ΔH_{vap} for H_2O at 25°C = 44.02 kJ/mol; at 100°C = 40.67 kJ/mol

$$\Delta S = \frac{q_{rev}}{T} = \frac{44.02 \text{ kJ}}{\text{mol}} \times \frac{1000 \text{ J}}{\text{kJ}} \times \frac{1}{298 \text{ K}} = 148 \text{ J/mol} \bullet \text{K}$$

$$\Delta S = \frac{q_{rev}}{T} = \frac{40.67 \text{ kJ}}{\text{mol}} \times \frac{1000 \text{ J}}{\text{kJ}} \times \frac{1}{373 \text{ K}} = 109 \text{ J/mol} \bullet \text{K}$$

(b) At both temperatures, the liquid → gas phase transition is accompanied by an increase in entropy, as expected. That the magnitude of the increase is greater at the lower temperature requires some explanation.

In the liquid state, there are significant hydrogen bonding interactions between H_2O molecules. This reduces the number of possible molecular positions and the number of microstates. Liquid water at 100° has sufficient kinetic energy to have broken many hydrogen bonds, so the number of microstates for $H_2O(l)$ at 100° is greater than the number of microstates for $H_2O(l)$ at 25°C. The difference in the number of microstates upon vaporization at 100°C is smaller, and the magnitude of ΔS is smaller.

19.30 (a) Solids are much more ordered than gases, so ΔS is negative.

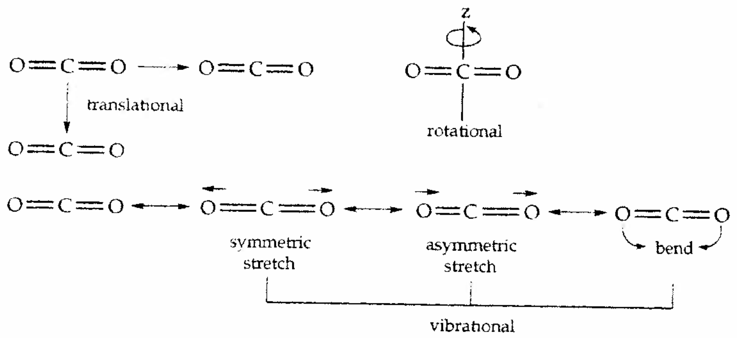
(b) ΔS is positive for Exercise 19.7 (a), (b), and (e). [At room temperature and 1 atm pressure, H_2O is a liquid, so there are more moles of gas in the products in part (e) and $\Delta S > 0$.]

19.32 (a) When temperature increases, the range of accessible molecular speeds and kinetic energies increases. This produces more microstates and an increase in entropy.

(b) When the volume of a gas increases (even at constant T), there are more possible positions for the particles, more microstates, and greater entropy.

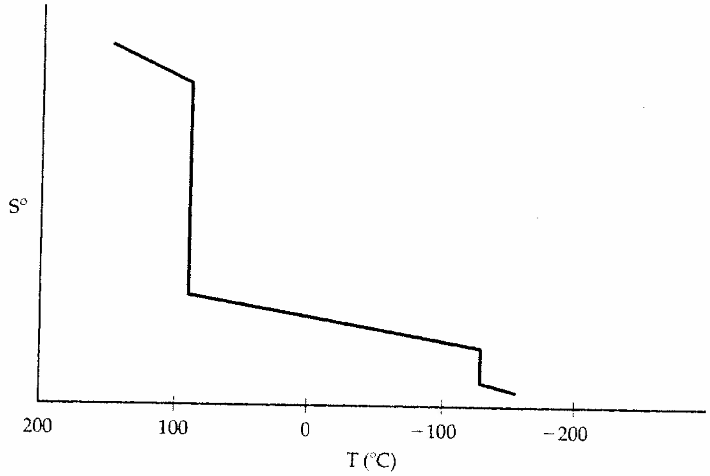
(c) When a solid dissolves in water, there are both more possible positions for the particles (ions or molecules) and more motional freedom. The number of microstates and entropy increases.

19.34 (a) Since CO_2 has more than one atom, the thermal energy can be distributed as translational, vibrational, or rotational motion.



(b) According to Boltzmann's Law, S = k lnW. The number of microstates, W, is directly proportional to entropy, S. Thus, if the number of microstates for a system increases, the entropy of the system increases.

19.36 Melting = –126.5°C; boiling = 97.4°C.



19.38 (a) 1 mol of $As_4(g)$ at 300°C, 0.01 atm (As_4 has more massive atoms in a comparable system at the same temperature.)

(b) 1 mol $H_2O(g)$ at 100°C, 1 atm (larger volume occupied by $H_2O(g)$)

(c) 0.5 mol $CH_4(g)$ at 298 K, 20-L volume (more complex molecule, more rotational and vibrational degrees of freedom)

(d) 100 g of $Na_2SO_4(aq)$ at 30°C (more motional freedom in aqueous solution)

19.40 (a) $Fe(l) \rightarrow Fe(s)$; ΔS is negative (less motional freedom)

(b) $2Li(s) + Cl_2(g) \rightarrow 2LiCl$; ΔS is negative (moles of gas decrease)

(c) $Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$; ΔS is positive (moles of gas increase)

(d) $AgNO_3(aq) + KBr(aq) \rightarrow AgBr(s) + KNO_3(aq)$; ΔS is negative (less motional freedom)

Entropy Changes in Chemical Reactions

19.42 Propylene will have a higher S° at 25°C. At this temperature, both are gases, so there are no lattice effects. Since they have the same molecular formula, only the details of their structures are different. In propylene, there is free rotation around the C—C single bond, while in cyclopropane the 3-membered ring severely limits rotation. The greater motional freedom of the propylene molecule leads to a higher absolute entropy.

19.44 (a) $CuO(s)$, 42.59 J/mol•K; $Cu_2O(s)$, 92.36 J/mol•K. Molecules in the solid state have only vibrational motion available to them. The more complex Cu_2O molecule has more vibrational degrees of freedom and a larger standard entropy.

(b) 1 mol $N_2O_4(g)$, 304.3 J/K; 2 mol $NO_2(g)$, 2(240.45) = 480.90 J/K. More particles have a greater number of arrangements.

(c) $CH_3OH(g)$, 237.6 J/mol•K; $CH_3OH(l)$, 126.8 J/mol•K. Molecules in the gas phase occupy a larger volume and have more motional freedom than molecules in the liquid state.

(d) 1 mol $PbCO_3(s)$, 131.0 J/K; 1 mol $PbO(s)$ + 1 mol $CO_2(g)$, (68.70 + 213.6) = 282.3 J/K. The second member of the pair has more total particles and half of them are in the gas phase for greater total motional freedom. Note that 1 mol of $PbCO_3(s)$ has greater entropy than 1 mol of $PbO(s)$, because of the additional ways to store energy in the more complex CO_3^{2-} anion.

19.46 (a) C(diamond), S° = 2.43 J/mol•K; C(graphite), S° = 5.69 J/mol•K. Diamond is a network covalent solid with each C atom tetrahedrally bound to four other C atoms. Graphite consists of sheets of fused planar 6-membered rings with each C atom bound in a trigonal planar arrangement to three other C atoms. The internal entropy in graphite is greater because there is translational freedom among the planar sheets of C atoms, while there is very little translational or vibrational freedom within the covalent-network diamond lattice.

(b) S° for buckminsterfullerene will be ≥ 10 J/mol•K. S° for graphite is twice S° for diamond, and S° for the fullerene should be higher than that of graphite. The 60-atom "bucky" balls have more flexibility than graphite sheets. Also, the balls have translational freedom in three dimensions, while graphite sheets have it in only two directions. Because of the ball structure, there is more empty space in the fullerene lattice than in graphite or diamond; essentially, 60 C-atoms in fullerene occupy a larger volume than 60 C-atoms in graphite or diamond. Thus, the fullerene has additional "molecular" complexity, more degrees of translational freedom, and occupies a larger volume, all features that point to a higher absolute entropy.

19.48 (a)

$$\Delta S^\circ = 2S^\circ\ NH_3(g) - S^\circ\ N_2H_4(g) - S^\circ\ H_2(g)$$

$$= 2(192.5) - 238.5 - 130.58 = +15.9\ J/K$$

ΔS° is small because there are the same number of moles of gas in the products as in reactants. The slight increase is due to the relatively small S° value of $H_2(g)$, which has fewer degrees of freedom than molecules with more than two atoms.

(b) $\Delta S° = 2S°\ AlCl_3(s) - 2S°\ Al(s) - 3S°\ Cl_2(g)$

$= 2(109.3) - 2(28.32) - 3(222.96) = -506.9\ J/K$

$\Delta S°$ is negative because the products contain fewer (no) moles of gas.

(c) $\Delta S° = S°\ MgCl_2(s) + 2S° H_2O(l) - S°\ Mg(OH)_2(s) - 2S°\ HCl(g)$

$= 89.6 + 2(69.91) - 63.24 - 2(186.69) = -207.2\ J/K$

$\Delta S°$ is negative because the products contain fewer (no) moles of gas.

(d) $\Delta S° = S°\ C_2H_6(g) + S°\ H_2(g) - 2S°\ CH_4(g)$

$= 229.5 + 130.58 - 2(186.3) = -12.5\ J/K$

$\Delta S°$ is very small because there are the same number of moles of gas in the products and reactants. The slight decrease is related to the relatively small S° value for $H_2(g)$, which has fewer degrees of freedom than molecules with more than two atoms.

Gibbs Free Energy

19.50 (a) The *standard* free energy change, $\Delta G°$, represents the free energy change for the process when all reactants and products are in their standard states. When any or all reactants or products are not in their standard states, the free energy is represented simply as ΔG. The value for ΔG thus depends on the specific states of all reactants and products.

(b) When $\Delta G = 0$, the system is at equilibrium.

(c) The sign and magnitude of ΔG give no information about rate; we cannot predict whether the reaction will occur rapidly.

19.52 (a) $\Delta H°$ is negative; the reaction is exothermic.

(b) $\Delta S°$ is positive; the reaction leads to an increase in disorder.

(c) $\Delta G° = \Delta H° - T\Delta S° = -19.5\ kJ - 298\ K\ (0.0427\ kJ/K) = -32.225 = -32.2\ kJ$

(d) At 298 K, $\Delta G°$ is negative. If all reactants and products are present in their standard states, the reaction is spontaneous (in the forward direction) at this temperature.

19.54 (a) $\Delta H° = -305.3 - [0 + 0] = -305.3\ kJ$

$\Delta S° = 97.65 - [29.9 + 222.96] = -155.21 = -155.2\ J/K$

$\Delta G° = -259.0 - [0 + 0] = -259.0\ kJ$

$\Delta G° = -305.3\ kJ - 298(-0.15521)\ kJ = -259.047 = -259.0\ kJ$

(b) $\Delta H° = -635.5 + (-393.5) - (-1207.1) = 178.1\ kJ$

$\Delta S° = 39.75 + 213.6 - (92.88) = 160.47 = 160.5\ J/K$

$\Delta G° = -604.17 + (-394.4) - (-1128.76) = 130.19 = 130.2\ kJ$

$\Delta G° = 178.1\ kJ - 298(0.16047)\ kJ = 130.28 = 130.3\ kJ$

(c) $\Delta H^\circ = 4(-1288.3) - [-2940.1 + 6(-285.83)] = -498.12 = -498.1$ kJ

$\Delta S^\circ = 4(158.2) - [228.9 + 6(69.91)] = -15.56 = -15.6$ J/K

$\Delta G^\circ = 4(-1142.6) - [-2675.2 + 6(-237.13)] = -472.42 = -472.4$ kJ

$\Delta G^\circ = -498.12$ kJ $- 298(-0.01556)$ kJ $= -493.48 = -493.5$ kJ

(The discrepancy in ΔG° values is due to experimental uncertainties in the tabulated thermodynamic data.)

(d) $\Delta H^\circ = 2(-393.5) + 4(-285.83) - [2(-238.6) + 3(0)] = -1453.1$ kJ

$\Delta S^\circ = 2(213.6) + 4(69.91) - [2(126.8) + 3(205.0)] = -161.76 = -161.8$ J/K

$\Delta G^\circ = 2(-394.4) + 4(-237.13) - [2(-166.23) + 3(0)] = -1404.86 = -1404.9$ kJ

$\Delta G^\circ = -1453.2$ kJ $- 298(-0.16176)$ kJ $= -1404.996 = -1405.0$ kJ

19.56 (a) $\Delta G^\circ = 2\Delta G^\circ\ HCl(g) - [\Delta G^\circ\ H_2(g) + \Delta G^\circ\ Cl_2(g)]$

$= 2(-95.27$ kJ$) - 0 - 0 = -190.5$ kJ, spontaneous

(b) $\Delta G^\circ = \Delta G^\circ\ MgO(s) + 2\Delta G^\circ\ HCl(g) - [\Delta G^\circ\ MgCl_2(s) + \Delta G^\circ\ H_2O(l)]$

$= -569.6 + 2(-95.27) - [-592.1 + (-237.13)] = +69.1$ kJ, nonspontaneous

(c) $\Delta G^\circ = \Delta G^\circ\ N_2H_4(g) + \Delta G^\circ\ H_2(g) - 2\Delta G^\circ\ NH_3(g)$

$= 159.4 + 0 - 2(-16.66) = +192.7$ kJ, nonspontaneous

(d) $\Delta G^\circ = 2\Delta G^\circ\ NO(g) + \Delta G^\circ\ Cl_2(g) - 2\Delta G^\circ\ NOCl(g)$

$= 2(86.71) + 0 - 2(66.3) = +40.8$ kJ, nonspontaneous

19.58 (a) ΔG° should be less negative than ΔH°. Products contain fewer moles of gas, so ΔS° is negative. $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$; $-T\Delta S^\circ$ is positive so ΔG° is less negative than ΔH°.

(b) We can estimate ΔS° using a similar reaction and then use $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ (estimate) to get a ballpark figure. There are no sulfite salts listed in Appendix C, so use a reaction such as $CO_2(g) + CaO(s) \rightarrow CaCO_3(s)$ or $CO_2(g) + BaO(s) \rightarrow BaCO_3(s)$. Or calculate both ΔS° values and use the average as your estimate.

19.60 $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

(a) $\Delta G^\circ = -844$ kJ $- 298$ K$(-0.165$ kJ/K$) = -795$ kJ, spontaneous

(b) $\Delta G^\circ = +572$ kJ $- 298$ K$(0.179$ kJ/K$) = +519$ kJ, nonspontaneous

To be spontaneous, ΔG must be negative ($\Delta G < 0$).

Thus, $\Delta H^\circ - T\Delta S^\circ < 0$; $\Delta H^\circ < T\Delta S^\circ$; $T > \Delta H^\circ/\Delta S^\circ$; $T > \dfrac{572\ \text{kJ}}{0.179\ \text{kJ/K}} = 3.20 \times 10^3$ K

19.62 At -25°C or 248 K, $\Delta G > 0$. $\Delta G = \Delta H - T\Delta S > 0$

$\Delta H - 248$ K $(95$ J/K$) > 0$; $\Delta H > +2.4 \times 10^4$ J; $\Delta H > +24$ kJ

19.64 ΔG is negative when $T\Delta S > \Delta H$ or $T > \Delta H/\Delta S$.

$\Delta H^\circ = \Delta H^\circ\ CH_4(g) + \Delta H^\circ\ CO_2(g) - \Delta H^\circ\ CH_3COOH(l)$

$= -74.8 + (-393.5) - (-487.0) = +18.7$ kJ

$\Delta S^\circ = S^\circ\ CH_4(g) + S^\circ\ CO_2(g) - S^\circ\ CH_3COOH(l) = +186.3 + 213.6 - 159.8 = +240.1\ J/K$

$$T > \frac{18.7\ kJ}{0.2401\ kJ/K} = 77.9\ K$$

The reaction is spontaneous above 77.9 K (−195°C).

19.66 (a) $\Delta H^\circ = \Delta H^\circ_f CH_3OH(g) - \Delta H^\circ_f CH_4(g) - 1/2\ \Delta H^\circ_f O_2(g)$

$= -201.2 - (-74.8) - 0 = -126.4\ kJ$

$\Delta S^\circ = S^\circ CH_3OH(g) - S^\circ CH_4(g) - 1/2\ S^\circ O_2(g)$

$= 237.6 - 186.3 - 1/2(205.0) = -51.2\ J/K = -0.0512\ kJ/K$

(b) $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$. $-T\Delta S^\circ$ is positive, so ΔG° becomes more positive as temperature increases.

(c) $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -126.4\ kJ - 298\ K(-0.0512\ kJ/K) = -111.1\ kJ$

The reaction is spontaneous at 298 K because ΔG° is negative at this temperature. In this case, ΔG° could have been calculated from ΔG°_f values in Appendix C, since these values are tabulated at 298 K.

(d) The reaction is at equilibrium when $\Delta G^\circ = 0$.

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

$T = -126.4\ kJ/-0.0512\ kJ/K = 2469 = 2470\ K$.

This temperature is so high that the reactants and products are likely to decompose. At standard conditions, equilibrium is functionally unattainable for this reaction.

19.68 (a) As in Sample Exercise 19.9, $T_{sub} = \Delta H^\circ_{sub}/\Delta S^\circ_{sub}$

Use Data from Appendix C to calculate ΔH°_{sub} and ΔS°_{sub} for $I_2(s)$.

$I_2(s) \rightarrow I_2(l)$ melting
$I_2(l) \rightarrow I_2(g)$ boiling
$I_2(s) \rightarrow I_2(g)$ sublimation

$\Delta H^\circ_{sub} = \Delta H^\circ_f I_2(g) - \Delta H^\circ_f\ I_2(s) = 62.25 - 0 = 62.25\ kJ$

$\Delta S^\circ_{sub} = S^\circ\ I_2(g) - S^\circ\ I_2(s) = 260.57 - 116.73 = 143.84\ J/K = 0.14384\ kJ/K$

$$T_{sub} = \frac{\Delta H^\circ_{sub}}{\Delta S^\circ_{sub}} = \frac{62.25\ kJ}{0.14384\ kJ/K} = 432.8\ K = 159.6^\circ C$$

(b) T_m for $I_2(s) = 386.85\ K = 113.7^\circ C$, $T_b = 457.4\ K = 184.3^\circ C$ (from WebElements™, 2005)

(c) The boiling point of I_2 is closer to the sublimation temperature. Both boiling and sublimation begin with molecules in a condensed phase (little space between molecules) and end in the gas phase (large intermolecular distances). Separation of the molecules is the main phenomenon that determines both ΔH and ΔS, so it is not surprising that the ratio of $\Delta H/\Delta S$ is similar for sublimation and boiling.

19.70 (a) $C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(l)$

$$\Delta H^\circ = 2\Delta H_f^\circ\ CO_2(g) + 2\Delta H_f^\circ\ H_2O(l) - \Delta H_f^\circ\ C_2H_4(g) - 3\Delta H_f^\circ\ O_2(g)$$

$$= 2(-393.5) + 2(-285.83) - 52.30 - 3(0) = -1410.96 = -1411.0 \text{ kJ/mol } C_2H_4 \text{ burned}$$

(b) $$w_{max} = \Delta G^\circ = 2\Delta G_f^\circ\ CO_2(g) + 2\Delta H_f^\circ\ H_2O(l) - \Delta G_f^\circ\ C_2H_4(g) - 3\Delta G_f^\circ\ O_2(g)$$

$$= 2(-394.4) + 2(-237.13) - 68.11 - 3(0) = -1331.2 \text{ kJ}$$

The system can accomplish at most 1331.2 kJ of work per mole of C_2H_4 on the surroundings.

Free Energy and Equilibrium

19.72 Consider the relationship $\Delta G = \Delta G^\circ + RT \ln Q$, where Q is the reaction quotient.

(a) $H_2(g)$ appears in the denominator of Q for this reaction. An increase in pressure of H_2 decreases Q and ΔG becomes smaller or more negative. Increasing the concentration of a reactant increases the tendency for a reaction to occur.

(b) $H_2(g)$ appears in the numerator of Q for this reaction. Increasing the pressure of H_2 increases Q and ΔG becomes more positive. Increasing the concentration of a product decreases the tendency for the reaction to occur.

(c) $H_2(g)$ appears in the denominator of Q for this reaction. An increase in pressure of H_2 decreases Q and ΔG becomes smaller or more negative.

19.74 (a) $\Delta G^\circ = 2\Delta G^\circ\ HF(g) - [\Delta G^\circ\ H_2(g) + \Delta G^\circ\ F_2(g)] = 2(-270.70) - [0 + 0] = -541.40$ kJ

(b) $\Delta G = \Delta G^\circ + RT \ln P^2_{HF} / P_{H_2} \times P_{F_2}$

$$= -541.40 + \frac{8.314 \times 10^{-3}\ \text{kJ}}{\text{K} \bullet \text{mol}} \times 298\ \text{K} \ln[(0.36)^2/8.0 \times 4.5] = -555.34 = -555\ \text{kJ}$$

19.76 $\Delta G^\circ = -RT \ln K$; $\ln K = -\Delta G^\circ / RT$; at 298 K, RT = 2.4776 = 2.478 kJ

(a) $\Delta G^\circ = \Delta G^\circ\ NaOH(s) + \Delta G^\circ\ CO_2(g) - \Delta G^\circ\ NaHCO_3(s)$

$$= -379.5 + (-394.4) - (-851.8) = +77.9 \text{ kJ}$$

$$\ln K = \frac{-\Delta G^\circ}{RT} = \frac{-77.9\ \text{kJ}}{2.478\ \text{kJ}} = -31.442 = -31.4; \quad K = 2 \times 10^{-14}$$

$$K = P_{CO_2} = 2 \times 10^{-14}$$

(b) $\Delta G^\circ = 2\Delta G^\circ\ HCl(g) + \Delta G^\circ\ Br_2(g) - 2\Delta G^\circ\ HBr(g) - \Delta G^\circ\ Cl_2(g)$

$$= 2(-95.27) + 3.14 - 2(-53.22) - 0 = -80.96 \text{ kJ}$$

$$\ln K = \frac{-(-80.96)}{2.4776} = +32.68; \quad K = 1.6 \times 10^{14}$$

$$K = \frac{P^2_{HCl} \times P_{Br_2}}{P^2_{HBr} \times P_{Cl_2}} = 1.6 \times 10^{14}$$

(c) From Exercise 19.55(a), $\Delta G°$ at 298 K = -140.0 kJ.

$$\ln K = \frac{-\Delta G°}{RT} = \frac{-(-140.0)}{2.4776} = 56.51; \quad K = 3.5 \times 10^{24}$$

$$K = \frac{P^2_{SO_3}}{P^2_{SO_2} \times P_{O_2}} = 3.5 \times 10^{24}$$

19.78 $K = P_{CO_2}$. Calculate $\Delta G°$ at the two temperatures using $\Delta G° = \Delta H° - T\Delta S°$ and then calculate K and P_{CO_2}.

$\Delta H° = \Delta H°$ PbO(s) + $\Delta H°$ $CO_2(g)$ - $\Delta H°$ $PbCO_3(s)$

= -217.3 - 393.5 + 699.1 = 88.3 kJ

$\Delta S°$ = S° PbO(s) + S° $CO_2(g)$ - S° $PbCO_3(s)$

= 68.70 + 213.6 - 131.0 = 151.3 J/K or 0.1513 kJ/K

(a) $\Delta G° = \Delta H° - T\Delta S°$. At 393 K, $\Delta G°$ = 88.3 kJ - 393 K(0.1513 kJ/K) = 28.84

= 28.8 kJ

$$\ln K = \frac{-\Delta G°}{RT} = \frac{-28.84 \times 10^3\ J}{8.314\ J/K \times 393\ K} = -8.82631 = -8.83$$

$$K = P_{CO_2} = 1.5 \times 10^{-4}\ atm$$

(b) $\Delta G° = \Delta H° - T\Delta S°$. At 753 K, $\Delta G°$ = 88.3 kJ - 753 K (0.1513 kJ) = -25.629

= -25.6 kJ

$$\ln K = \frac{-(-25.629 \times 10^3\ J)}{8.314\ J/K \times 753\ K} = 4.0938 = 4.09; \quad K = P_{CO_2} = 60\ atm$$

19.80 (a) $CH_3NH_2(aq) + H_20(l) \rightleftharpoons CH_3NH_3^+(aq) + OH^-(aq)$

(b) $\Delta G° = -RT \ln K_b = -(8.314 \times 10^{-3})(298) \ln (4.4 \times 10^{-4}) = 19.148 = 19.1$ kJ

(c) $\Delta G = 0$ at equilibrium

(d) $\Delta G = \Delta G° + RT \ln Q$; $[OH^-] = 1 \times 10^{-14}/1.5 \times 10^{-8} = 6.7 \times 10^{-7}$

$$= 19.148 + (8.314 \times 10^{-3})(298) \ln \frac{(5.5 \times 10^{-4})(6.67 \times 10^{-7})}{0.120} = -29.43 = -29\ kJ$$

Additional Exercises

19.81 (a) False. The essential question is whether the reaction proceeds far to the right before arriving at equilibrium. The position of equilibrium, which is the essential aspect, is not only dependent on ΔH but on the entropy change as well.

(b) True.

(c) True.

(d) False. Nonspontaneous processes in general require that work be done to force them to proceed. Spontaneous processes occur without application of work.

(e) False. Such a process **might** be spontaneous, but would not necessarily be so. Spontaneous processes are those that are exothermic and/or that lead to increased disorder in the system.

19.83 There is no inconsistency. The second law states that in any spontaneous process there is an increase in the entropy of the universe. While there may be a decrease in entropy of the system, as in the present case, this decrease is more than offset by an increase in entropy of the surroundings.

19.84 If $NH_4NO_3(s)$ dissolves spontaneously in water, $\Delta G = \Delta H - T\Delta S$. If ΔG is negative and ΔH is positive, the sign of ΔS must be positive. Furthermore, $T\Delta S > \Delta H$ at room temperature.

19.85 At the normal boiling point of a liquid, $\Delta G = 0$ and $\Delta H_{vap} = T\Delta S_{vap}$; $T = \Delta H_{vap}/\Delta S_{vap}$. By Trouton's rule, $\Delta S_{vap} = 88$ J/mol•K. The process of vaporization is:

(a) $Br_2(l) \rightleftharpoons Br_2(g)$

$$\Delta H_{vap} = \Delta H_f^\circ\ Br_2(g) - \Delta H_f^\circ\ Br_2(l) = 30.71\ kJ - 0 = 30.71\ kJ$$

$$T_b = \frac{\Delta H_{vap}}{\Delta S_{vap}} = \frac{30.71\ kJ}{88\ J/mol \bullet K} \times \frac{1000\ J}{kJ} = 349 = 3.5 \times 10^2\ K$$

(b) According to WebElements™ 2005, the normal boiling pont of $Br_2(l)$ is 332 K. Trouton's rule provides a good"ballpark" estimate.

19.87 (a) (i) $2RbCl(s) + 3O_2(g) \rightarrow 2RbClO_3(s)$

$$\Delta H^\circ = 2\Delta H^\circ\ RbClO_3(s) - 3\Delta H^\circ\ O_2(g) - 2\Delta H^\circ\ RbCl(s)$$

$$= 2(-392.4) - 3(0) - 2(-430.5) = +76.2\ kJ$$

$$\Delta S^\circ = 2(152) - 3(205.0) - 2(92) = -495\ J/K = -0.495\ kJ/K$$

$$\Delta G^\circ = 2(-292.0) - 3(0) - 2(-412.0) = +240.0\ kJ$$

(ii) $C_2H_2(g) + 4Cl_2(g) \rightarrow 2CCl_4(l) + H_2(g)$

$$\Delta H^\circ = 2\Delta H^\circ\ CCl_4(l) + \Delta H^\circ\ H_2(g) - \Delta H^\circ\ C_2H_2(g) - 4\Delta H^\circ\ Cl_2(g)$$

$$= 2(-139.3) + 0 - (226.7) - 4(0) = -505.3\ kJ$$

$$\Delta S^\circ = 2(214.4) + 130.58 - (200.8) - 4(222.96) = -533.3\ J/K = -0.5333\ kJ/K$$

$$\Delta G^\circ = 2(-68.6) + 0 - (209.2) - 4(0) = -346.4\ kJ$$

(iii) $TiCl_4(l) + 2H_2O(l) \rightarrow TiO_2(s) + 4HCl(aq)$

$$\Delta H^\circ = \Delta H^\circ\ TiO_2(s) + 4\Delta H^\circ\ HCl(aq) - \Delta H^\circ\ TiCl_4(l) - 2\Delta H^\circ\ H_2O(l)$$

$$= -944.7 + 4(-167.2) - (-804.2) - 2(-285.83) = -237.6\ kJ$$

$$\Delta S^\circ = 50.29 + 4(56.5) - 221.9 - 2(69.91) = -85.43\ J/K = -0.0854\ kJ/K$$

$$\Delta G^\circ = -889.4 + 4(-131.2) - (-728.1) - 2(-237.13) = -211.8\ kJ$$

(b) (i) ΔG° is (+), nonspontaneous

(ii) ΔG° is (–), spontaneous

(iii) ΔG° is (–), spontaneous

(c) In each case the manner in which free energy change varies with temperature depends mainly on ΔS: $\Delta G = \Delta H - T\Delta S$. When ΔS is substantially positive, ΔG becomes more negative as temperature increases. When ΔS is substantially negative, ΔG becomes more positive as temperature increases.

(i) ΔS° is negative, ΔG° becomes more positive with increasing temperature.

(ii) ΔS° is negative, ΔG° becomes more positive with increasing temperature. (The reaction will become nonspontaneous at some temperature.)

(iii) ΔS° is negative, ΔG° becomes more positive with increasing temperature. (The reaction will become nonspontaneous at some temperature.)

19.88 $\Delta G = \Delta G^\circ + RT \ln Q$

(a) $$Q = \frac{P^2_{NH_3}}{P_{N_2} \times P^3_{H_2}} = \frac{(1.2)^2}{(2.6)(5.9)^3} = 2.697 \times 10^{-3} = 2.7 \times 10^{-3}$$

$$\Delta G^\circ = 2\Delta G^\circ\ NH_3(g) - \Delta G^\circ\ N_2(g) - 3\Delta G^\circ\ H_2(g)$$

$$= 2(-16.66) - 0 - 3(0) = -33.32\ kJ$$

$$\Delta G = -33.32\ kJ + \frac{8.314 \times 10^{-3}\ kJ}{K \bullet mol} \times 298\ K \times \ln(2.69 \times 10^{-3})$$

$$\Delta G = -33.32 - 14.66 = -47.98 = -48.0\ kJ$$

(b) $$Q = \frac{P^3_{N_2} \times P^4_{H_2O}}{P^2_{N_2H_4} \times P^2_{NO_2}} = \frac{(0.5)^3(0.3)^4}{(5.0 \times 10^{-2})^2(5.0 \times 10^{-2})^2} = 162 = 2 \times 10^2$$

$$\Delta G^\circ = 3\Delta G^\circ\ N_2(g) + 4\Delta G^\circ\ H_2O(g) - 2\Delta G^\circ\ N_2H_4(g) - 2\Delta G^\circ\ NO_2(g)$$

$$= 3(0) + 4(-228.57) - 2(159.4) - 2(51.84) = -1336.8\ kJ$$

$$\Delta G = -1336.8\ kJ + 2.478 \ln 162 = -1324.2 = -1.32 \times 10^3\ kJ$$

(c) $$Q = \frac{P_{N_2} \times P^2_{H_2}}{P_{N_2H_4}} = \frac{(1.5)(2.5)^2}{0.5} = 18.75 = 2 \times 10^1$$

$$\Delta G^\circ = \Delta G^\circ\ N_2(g) + 2\Delta G^\circ\ H_2(g) - \Delta G^\circ\ N_2H_4(g)$$

$$= 0 + 2(0) - 159.4 = -159.4\ kJ$$

$$\Delta G = -159.4\ kJ + 2.478 \ln 18.75 = -152.1 = -152\ kJ$$