Chapter 18: 9, 13, 14, 19, 23, 25, 31, 43, 57, 59, 91

9.  
   a.  \( \text{Li}(\ell) \); the liquid form of any substance has a larger entropy than the solid form
   
   b.  \( \text{CH}_3\text{OCH}_3(\ell) \); the presence of the OH group in the \( \text{C}_2\text{H}_5\text{OH} \) molecule allows for hydrogen bonding between molecules and therefore the liquid of \( \text{C}_2\text{H}_5\text{OH} \) would have a more ordered state
   
   c.  \( \text{Xe}(\text{g}) \); Xe has a higher molar mass
   
   d.  \( \text{CO}_2(\text{g}) \); \( \text{CO}_2 \) has a higher molar mass and is a more complicated molecule
   
   e.  \( \text{O}_3(\text{g}) \); \( \text{O}_3 \) has a higher molar mass and is a more complicated molecule
   
   f.  \( \text{N}_2\text{O}_4(\text{g}) \); \( \text{N}_2\text{O}_4 \) has a higher molar mass and is a more complicated molecule

13.  
   a.  \( \Delta S > 0 \); increase in number of moles of gas and solid decomposing to form a solid and a gas
   
   b.  \( \Delta S < 0 \); decrease in number of moles of gas and the gas form of any substance has a larger entropy than the liquid form
   
   c.  \( \Delta S > 0 \); increase in number of moles of gas
   
   d.  \( \Delta S > 0 \); increase in number of moles of gas

14.  
   a.  \( \Delta S < 0 \); decrease in number of moles of gas and gas reacting with a liquid to form a solid
   
   b.  \( \Delta S > 0 \); increase in number of moles of gas and solid decomposing to form a liquid and a gas
   
   c.  \( \Delta S > 0 \); increase in number of moles of gas
   
   d.  \( \Delta S < 0 \); decrease in number of moles of gas and gas reacting with a solid to form a solid

19.  
   Reaction A:

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

   Therefore, the reaction is not spontaneous at 25 °C. Now calculate the temperature at which \( \Delta G = 0 \).

   \[ T = \frac{\Delta H}{\Delta S} = \frac{10,500 \text{ J/mol}}{30 \text{ J/K} \cdot \text{mol}} = 350 \text{ K} \]

   Reaction A is spontaneous above 350 K.
Reaction B:

\[ \Delta G = \Delta H - T \Delta S = 1\,800 \text{ J/mol} - (298 \text{ K})(-113 \text{ J/K mol}) = +3.55 \times 10^4 \text{ J/mol} \]

Therefore, the reaction is not spontaneous at 25 °C. Since both terms are positive, there is no temperature at which their sum is negative. The reaction is not spontaneous at any temperature.

23. \( \Delta G^\circ = 2.60 \text{ kJ/mol} \)

\[
K_p = e^{-\frac{\Delta G^\circ}{RT}} = \exp \left[ \frac{-2.600 \text{ J/mol}}{(8.314 \text{ J/K mol})(298 \text{ K})} \right] = e^{-1.05} = 0.35
\]

25. \( K_{sp} = 1.6 \times 10^{-14} \)

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

31. \( \text{H}_2\text{O}(\ell) \leftrightarrow \text{H}_2\text{O}(g) \quad K_p = P_{\text{H}_2\text{O}} \quad \text{and} \quad \Delta G^\circ = -RT \ln K_p \)

\[
K_p = e^{-\frac{\Delta G^\circ}{RT}} = \exp \left[ \frac{-8.600 \text{ J/mol}}{(8.314 \text{ J/K mol})(298 \text{ K})} \right] = e^{-3.47} = 0.031
\]

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

57. a. \( \Delta S > 0; \) increase in number of moles of gas

b. \( \Delta S < 0; \) decrease in number of moles of gas

c. \( \Delta S > 0; \) increase in number of moles of gas and solid decomposing to form a gases

d. \( \Delta S > 0; \) increase in number of moles of gas and liquid decomposing to form a liquid and a gas
59. At the normal boiling point, the liquid and gas phases are in equilibrium and therefore the free energy change is zero. The cross over temperature then corresponds to the normal boiling point.

\[
\begin{align*}
\text{Hg} & \xrightarrow{} \text{Hg} \\
\Delta H^\circ & = 0 \quad 60.78 \\
S^\circ & = 77.4 \quad 174.7
\end{align*}
\]

\[
\Delta H^\circ = [(1)(60.78) - (1)(0)]kJ = 60.78 kJ = 607,780 J
\]

\[
\Delta S^\circ = [(1)(174.7) - (1)(77.4)]J/K = 97.3 J/K
\]

\[
\Delta G = \Delta H - T\Delta S = 0 \implies T = \frac{607,780 J}{97.3 J/K} = 625 K = 352 \, ^\circ C
\]

The implicit assumption is that the \( \Delta H^\circ \) and \( \Delta S^\circ \) the values, which are valid at 298 K, do not change with a change in temperature. The true boiling point is 356.6 °C, which indicates that the \( \Delta H^\circ \) and \( \Delta S^\circ \) do change slightly with temperature.

91. (d) will not lead to an increase in entropy of the system. The gas is returned to its original state. The entropy of the system does not change because \( S \) is a state function.