Problem Set 2

4.5

Living systems are not isolated systems; they interact with their surroundings. The second law does apply to living systems, requiring that decreases in the entropy of a living system be accompanied by an increase in entropy of the surroundings such that the entropy change of system and surroundings is positive.

4.19

(a) Negative, since a gas, which is a highly disordered phase, is being transformed into a more ordered solid.
(b) Negative, since two moles of gas are becoming one, so more ordered.
(c) Positive, since an ordered solid is being transformed into two moles of gas.
(d) Near zero, since each side of the equation has two moles of gas.

4.20

(a) \[ \Delta_rS^\circ = 2S^\circ[\text{Fe}_2\text{O}_3(s)] - 4S^\circ[\text{Fe}(s)] - 3S^\circ[\text{O}_2(g)] \]
\[ = 2(90.0 \text{ J K}^{-1} \text{ mol}^{-1}) - 4(27.2 \text{ J K}^{-1} \text{ mol}^{-1}) - 3(205.0 \text{ J K}^{-1} \text{ mol}^{-1}) \]
\[ = -543.8 \text{ J K}^{-1} \text{ mol}^{-1} \]

(b) \[ \Delta_rS^\circ = S^\circ[\text{O}_2(g)] - 2S^\circ[\text{O}(g)] \]
\[ = 205.0 \text{ J K}^{-1} \text{ mol}^{-1} - 2(161.0 \text{ J K}^{-1} \text{ mol}^{-1}) \]
\[ = -117.0 \text{ J K}^{-1} \text{ mol}^{-1} \]

(c) \[ \Delta_rS^\circ = S^\circ[\text{NH}_3(g)] + S^\circ[\text{HCl}(g)] - S^\circ[\text{NH}_4\text{Cl}(s)] \]
\[ = 192.5 \text{ J K}^{-1} \text{ mol}^{-1} - 186.5 \text{ J K}^{-1} \text{ mol}^{-1} - 94.6 \text{ J K}^{-1} \text{ mol}^{-1} \]
\[ = 284.4 \text{ J K}^{-1} \text{ mol}^{-1} \]

(d) \[ \Delta_rS^\circ = 2S^\circ[\text{HCl}(g)] - S^\circ[\text{H}_2(g)] - S^\circ[\text{Cl}_2(g)] \]
\[ = 2(186.5 \text{ J K}^{-1} \text{ mol}^{-1}) - (130.6 \text{ J K}^{-1} \text{ mol}^{-1}) - (223.0 \text{ J K}^{-1} \text{ mol}^{-1}) \]
\[ = 19.4 \text{ J K}^{-1} \text{ mol}^{-1} \]

These results agree with the predictions in Problem 5.25.

4.32

We will have one mole of \( \text{NO}_2^- \)(aq) to oxidize. Then according to the chemical equation \( \text{NO}_2^- \)(aq) + (1/2)\( \text{O}_2 \)(g) → \( \text{NO}_3^- \)(aq),

\[ \Delta_rG^\circ = \Delta_rG^\circ[\text{NO}_3^- \text{(aq)}] - \Delta_rG^\circ[\text{NO}_2^- \text{(aq)}] - (1/2)\Delta_rG^\circ[\text{O}_2 \text{(g)}] \]
\[ = (-110.5 \text{ kJ mol}^{-1}) - (-34.6 \text{ kJ mol}^{-1}) - (1/2)0 \text{ kJ mol}^{-1} \]
\[ = -75.9 \text{ kJ mol}^{-1} \]

Since 1 mole of \( \text{NO}_2^- \) is oxidized, the Gibbs energy released is 75.9 kJ.
4.47

This is a one-component system, \( c = 1 \), with 4 phases. Many substances can be found in one of 4 or more phases. For example, carbon exists as diamond, graphite, liquid and vapor phases. The problem with the phase diagram is the appearance of a quadruple point. At the quadruple point, \( p = 4 \). Therefore, using the phase rule, we find at the quadruple point \( f = c - p + 2 = 1 - 4 + 2 = -1 \) degrees of freedom. Since the degrees of freedom cannot be negative, this phase diagram is nonphysical.

(If the system had more than one component, for example, \( c = 2 \), then a quadruple point would be possible, since then \( f = c - p + 2 = 2 - 4 + 2 = 0 \), which is fine. But we were told that this is a one-component system, so the phase diagram is not physical.)

4.66

For the process \( \text{CH}_4(\text{inert solvent}) \rightarrow \text{CH}_4(\text{aq}) \),

\[
\Delta H^\circ = 2.0 \text{ kJ mol}^{-1} - 13.5 \text{ kJ mol}^{-1} = -11.5 \text{ kJ mol}^{-1}
\]

\[
\Delta G^\circ = -14.5 \text{ kJ mol}^{-1} + 26.5 \text{ kJ mol}^{-1} = 12.0 \text{ kJ mol}^{-1}
\]

Since \( \Delta G^\circ > 0 \), the process is not spontaneous when the reactant and product are in their standard states. Notice that since

\[
\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ
\]

the negative enthalpy change is not enough to overcome the apparently costly loss of entropy under standard conditions. The \( T \Delta S^\circ \) term is apparently more negative than is \( \Delta H^\circ \), giving a positive \( \Delta G^\circ \). Transferring a nonpolar molecule like \( \text{CH}_4 \) to an aqueous environment turns out to lead to more ordering of water molecules and lower entropy. We shall see this again when we discuss protein stability.