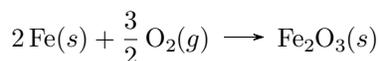


Suggested Problems: Chapter 12

12.13: Entropy is a measure of the extent to which energy is stored in atomic or molecular motion. These are all diatomic molecules with just a single bond between the atoms. They differ, however, in their phase at room temperature, with Cl_2 present as a gas, Br_2 present as a liquid, and I_2 present as a solid. A molecule in a gas phase has a much wider distribution of possible kinetic energies and, therefore, a higher entropy; thus, the entropy for Cl_2 is greater than that for Br_2 and I_2 , and the entropy for I_2 is smaller than that for Cl_2 and Br_2 .

12.15: For (a), where both compounds are in the same phase, we turn our attention to the number of bonds, because the greater the number of bonds, the more ways there are to store energy into vibrational and translational motion. A molecule of $\text{C}_3\text{H}_7\text{OH}$ has more atoms and more bonds than a molecule of $\text{C}_2\text{H}_5\text{OH}$ and, therefore, has a greater entropy. For (b), where the two compounds have the same formula and, therefore, the same number of bond domains, we turn our attention to phase. For the same reason outlined above for **Problem 12.13**, we predict that $\text{C}_2\text{H}_5\text{OH}(g)$ has a greater entropy than does $\text{C}_2\text{H}_5\text{OH}(l)$. For (c) values of entropy have units of $\text{kJ/mol}_{\text{rxn}}$ and, therefore, the absolute amount of entropy depends on stoichiometry; thus, if we have more hydrogen atoms, as we do for $2\text{H}(g)$, then we have more entropy.

12.17: For (a), the reaction goes from a less condensed phase (ions dissolved in water) to a more condensed phase (precipitated solid), which leads us to predict that the change in entropy is negative. For (b), we first must note that the reaction as given is not balanced; the authors likely meant this reaction to be



Here we have a reaction that results in the loss of gas phase molecules, which leads us to predict that the change in entropy is negative. For (c), the reaction converts 19 moles of gas phase oxygen molecules to a combined 26 moles of gas phase molecules of water and carbon dioxide, which leads us to predict that the change in entropy is positive.

12.25: For (a), ΔS° is

$$\Delta S^\circ = [2 \times S_{\text{NH}_3(g)}^\circ] - [S_{\text{N}_2(g)}^\circ + 3 \times S_{\text{H}_2(g)}^\circ]$$

$$\Delta S^\circ = [2 \times 192.8] - [191.6 + 3 \times 130.7] = -198.1 \text{ J/K}$$

For (b), ΔS is

$$\Delta S^\circ = [S_{\text{N}_2\text{O}_5(g)}^\circ] - [S_{\text{N}_2(g)}^\circ + \frac{5}{2} \times S_{\text{O}_2(g)}^\circ]$$

$$\Delta S^\circ = [355.7] - [191.6 + \frac{5}{2} \times 205.2] = -348.9 \text{ J/K}$$

12.31: To determine if the reaction is favorable (recall that we are avoiding the term *spontaneous*), we calculate ΔG° and look to see if its value is less than zero; thus,

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

$$\Delta G^\circ = 100 \text{ kJ/mol}_{\text{rxn}} - 298 \text{ K} \times 0.250 \text{ kJ/mol}_{\text{rxn}} = 25.5 \text{ kJ/mol}_{\text{rxn}}$$

To find the critical temperature, we set $\Delta G^\circ = 0$ in the equation $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ and solve for T ; thus

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{100 \text{ kJ/mol}_{\text{rxn}}}{0.250 \text{ kJ/K} \cdot \text{mol}_{\text{rxn}}} = 400 \text{ K}$$

Any temperature greater than 400 K will ensure that ΔG° is less than zero and that the reaction is favorable.

12.33: Because we wish to know if these reactions are thermodynamically favorable at room temperature, we can use the tabulated values for free energies of formation without needing to first calculate ΔH° or ΔS° . For (a) we have

$$\Delta G^\circ = [\Delta G_{f,\text{Mn}(s)}^\circ + \Delta G_{f,\text{O}_2(g)}^\circ] - [\Delta G_{f,\text{MnO}_2(s)}^\circ]$$

$$\Delta G^\circ = [0 + 0] - [-465.1] = +465.1 \text{ kJ/mol}_{\text{rxn}}$$

For (b) we have

$$\Delta G^\circ = [2 \times \Delta G_{f,\text{HBr}(g)}^\circ] - [\Delta G_{f,\text{H}_2(g)}^\circ + \Delta G_{f,\text{Br}_2(l)}^\circ]$$

$$\Delta G^\circ = [2 \times (-53.43)] - [0 + 0] = -106.86 \text{ kJ/mol}_{\text{rxn}}$$

For (c) we have

$$\Delta G^\circ = [\Delta G_{f,\text{CuS}(s)}^\circ] - [\Delta G_{f,\text{Cu}(s)}^\circ + \Delta G_{f,\text{S}(g)}^\circ]$$

$$\Delta G^\circ = [-53.6] - [0 + 238.25] = -291.85 \text{ kJ/mol}_{\text{rxn}}$$

For (d) we have

$$\Delta G^\circ = [\Delta G_{f,\text{Li}_2\text{CO}_3(s)}^\circ + \Delta G_{f,\text{H}_2\text{O}(g)}^\circ] - [2 \times \Delta G_{f,\text{LiOH}(s)}^\circ + \Delta G_{f,\text{CO}_2(g)}^\circ]$$

$$\Delta G^\circ = [-1132.19 + (-228.59)] - [2 \times (-441.5) + (-394.36)] = -83.4 \text{ kJ/mol}_{\text{rxn}}$$

For (e) we have

$$\Delta G^\circ = [\Delta G_{f,\text{C}(s,\text{graphite})}^\circ + 2 \times \Delta G_{f,\text{H}_2\text{O}(g)}^\circ] - [\Delta G_{f,\text{CH}_4(g)}^\circ + \Delta G_{f,\text{O}_2(g)}^\circ]$$

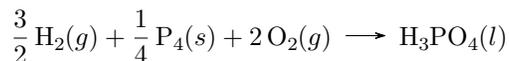
$$\Delta G^\circ = [0 + 2 \times (-228.59)] - [-50.5 + 0] = -406.7 \text{ kJ/mol}_{\text{rxn}}$$

For (f) we have

$$\Delta G^\circ = [\Delta G_{f,\text{CCl}_4(g)}^\circ + \Delta G_{f,\text{S}_2\text{Cl}_2(g)}^\circ] - [\Delta G_{f,\text{CS}_2(g)}^\circ + 3 \times \Delta G_{f,\text{Cl}_2(g)}^\circ]$$

$$\Delta G^\circ = [-58.2 + (-29.25)] - [66.8 + 3 \times 0] = -154.25 \text{ kJ/mol}_{\text{rxn}}$$

12.35: The heat of formation reaction for any species is a reaction in which one mole of the species is made from its elements in their standard form at room temperature. For phosphoric acid, $\text{H}_3\text{PO}_4(l)$, this reaction is



We can add together the three given reactions to arrive at this reaction if we multiply the coefficients of the first reaction by $\frac{1}{4}$, multiply the coefficients of the second reaction by $\frac{3}{4}$, and multiply the coefficients of the third reaction by $\frac{1}{4}$. If we do this to the reactions, then we also must do it to each reaction's ΔG° ; thus

$$\Delta G_{f, \text{H}_3\text{PO}_4(l)} = \left(\frac{1}{4} \times -2697.0 \right) + \left(\frac{3}{4} \times -457.18 \right) + \left(\frac{1}{4} \times -428.66 \right) = -1124.3 \text{ kJ/mol}_{\text{rxn}}$$

This result agrees with the value in Appendix G, as it must because free energy is a state function.

12.37: For (a), we examine the reaction's ΔG°

$$\Delta G^\circ = [2 \times \Delta G_{f, \text{Hg}(l)}^\circ + \Delta G_{f, \text{O}_2(g)}^\circ] - [2 \times \Delta G_{f, \text{HgO}(l)}^\circ] = [2 \times 0 + 0] - [2 \times -58.5] = +117 \text{ kJ/mol}_{\text{rxn}}$$

finding that it is positive, which means the reaction is not favorable at room temperature.

To find the critical temperature in (b), we first need to calculate ΔH° and ΔS° ; these are

$$\Delta H^\circ = [2 \times \Delta H_{f, \text{Hg}(l)}^\circ + \Delta H_{f, \text{O}_2(g)}^\circ] - [2 \times \Delta H_{f, \text{HgO}(l)}^\circ] = [2 \times 0 + 0] - [2 \times -90.83] = +181.66 \text{ kJ/mol}_{\text{rxn}}$$

$$\Delta S^\circ = [2 \times S_{\text{Hg}(l)}^\circ + S_{\text{O}_2(g)}^\circ] - [2 \times S_{\text{HgO}(l)}^\circ] = [2 \times 75.9 + 205.2] - [2 \times 70.29] = +216.42 \text{ J/K mol}_{\text{rxn}}$$

The critical temperature is when ΔG° is zero, or

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{181.66 \text{ kJ/mol}_{\text{rxn}}}{0.21642 \text{ kJ/K} \cdot \text{mol}_{\text{rxn}}} = 839 \text{ K}$$

and the reaction is favorable at any temperature greater than 839 K.