Chemistry 2e
16: Thermodynamics
16.1: Spontaneity

1. What is a spontaneous reaction?

Solution

A reaction has a natural tendency to occur and takes place without the continual input of energy from an external source.

3. Indicate whether the following processes are spontaneous or nonspontaneous.

(a) Liquid water freezing at a temperature below its freezing point
(b) Liquid water freezing at a temperature above its freezing point
(c) The combustion of gasoline
(d) A ball thrown into the air
(e) A raindrop falling to the ground
(f) Iron rusting in a moist atmosphere

Solution

(a) spontaneous; (b) nonspontaneous; (c) spontaneous; (d) nonspontaneous; (e) spontaneous; (f) spontaneous

5. Many plastic materials are organic polymers that contain carbon and hydrogen. The oxidation of these plastics in air to form carbon dioxide and water is a spontaneous process; however, plastic materials tend to persist in the environment. Explain.

Solution

Although the oxidation of plastics is spontaneous, the rate of oxidation is very slow. Plastics are therefore kinetically stable and do not decompose appreciably even over relatively long periods of time.

Chemistry 2e
16: Thermodynamics
16.2: Entropy

7. In Figure 16.8, all of the possible distributions and microstates are shown for four different particles shared between two boxes. Determine the entropy change, Δ*S*, for the system when it is converted from distribution (b) to distribution (d).

Solution

There are four initial microstates and four final microstates.

$$\Delta S = k \ln \frac{w_f}{w_i} = 1.38 \times 10^{-23}\ \text{J/K} \times \ln \frac{4}{4} = 0$$

9. Consider a system similar to the one in Figure 16.8, except that it contains six particles instead of four. What is the probability of having all the particles in only one of the two boxes in the case? Compare this with the similar probability for the system of four particles that we have derived to be equal to $\frac{1}{8}$. What does this comparison tell us about even larger systems?

Solution

A system of N particles will have 2^N microstates, since each of the particles can be in one of the two states (on the left or on the right), and its probability to be in one of them is independent of positions of the other particles. Therefore, there are $2^6 = 64$ possible microstates for six particles. Only two of them correspond to all the particles being in one box (one for the right box and one for the left box). Thus, the probability for all the particles to be on one side is $\frac{2}{64} = \frac{1}{32}$. This probability is noticeably lower than the $\frac{1}{8}$ result for the four-particle system. The conclusion we can make is that the probability for all the particles to stay in only one part of the system will decrease rapidly as the number of particles increases, and, for instance, the probability for all molecules of gas to gather in only one side of a room at room temperature and pressure is negligible since the number of gas molecules in the room is very large.

11. Consider the system shown in Figure 16.9. What is the change in entropy for the process where the energy is initially associated with particles A and B, and the energy is distributed between two particles in different boxes (one in A-B, the other in C-D)?

Solution

There is only one initial state. For the final state, the energy can be contained in pairs A-C, A-D, B-C, or B-D. Thus, there are four final possible states.

$$\Delta S = k \ln\left(\frac{W_f}{W_i}\right) = 1.38 \times 10^{-23}\ \text{J/K} \times \ln\left(\frac{4}{1}\right) = 1.91 \times 10^{-23}\ \text{J/K}$$

13. At room temperature, the entropy of the halogens increases from I_2 to Br_2 to Cl_2. Explain.

Solution

The masses of these molecules would suggest the opposite trend in their entropies. The observed trend is a result of the more significant variation of entropy with a physical state. At room temperature, I_2 is a solid, Br_2 is a liquid, and Cl_2 is a gas.

15. Indicate which substance in the given pairs has the higher entropy value. Explain your choices.

(a) $C_2H_5OH(l)$ or $C_3H_7OH(l)$

(b) $C_2H_5OH(l)$ or $C_2H_5OH(g)$

(c) 2H(*g*) or H(*g*)

Solution

(a) $C_3H_7OH(l)$ as it is a larger molecule (more complex and more massive), and so more microstates describing its motions are available at any given temperature. (b) $C_2H_5OH(g)$ as it is in the gaseous state. (c) 2H(*g*), since entropy is an extensive property, and so two H atoms (or two moles of H atoms) possess twice as much entropy as one atom (or one mole of atoms).

17. Predict the sign of the enthalpy change for the following processes. Give a reason for your prediction.

(a) $\text{Na}^+(aq) \ + \ \text{Cl}^-(aq) \ \longrightarrow \ \text{NaCl}(s)$

(b) $2\text{Fe} + \frac{3}{2}\text{O}_2 \rightarrow \text{Fe}_2\text{O}_2$

(c) $2\text{C}_6\text{H}_{14}(l) \ + \ 19\text{O}_2(g) \ \longrightarrow \ 14\text{H}_2\text{O}(g) \ + \ 12\text{CO}_2(g)$

Solution

(a) Negative. The relatively ordered solid precipitating decreases the number of mobile ions in solution. (b) Negative. There is a net loss of three moles of gas from reactants to products. (c) Positive. There is a net increase of seven moles of gas from reactants to products.

19. Write the balanced chemical equation for the combustion of benzene, $C_6H_6(l)$, to give carbon dioxide and water vapor. Would you expect ΔS to be positive or negative in this process?

Solution

$$\text{C}_6\text{H}_6(l) + 7.5\text{O}_2(g) \longrightarrow 3\text{H}_2\text{O}(g) + 6\text{CO}_2(g)$$

There are 7.5 moles of gas initially, and 3 + 6 = 9 moles of gas in the end. Therefore, it is likely that the entropy increases as a result of this reaction, and ΔS is positive.

Chemistry 2e
16: Thermodynamics
16.3: The Second and Third Laws of Thermodynamics

21. Calculate ΔS° for the following changes.

(a) $\text{SnCl}_4(l) \longrightarrow \text{SnCl}_4(g)$

(b) $\text{CS}_2(g) \longrightarrow \text{CS}_2(l)$

(c) $\text{Cu}(s) \longrightarrow \text{Cu}(g)$

(d) $\text{H}_2\text{O}(l) \longrightarrow \text{H}_2\text{O}(g)$

(e) $2\text{H}_2(g) + \text{O}_2(g) \longrightarrow 2\text{H}_2\text{O}(l)$

(f) $2\text{HCl}(g) + \text{Pb}(s) \longrightarrow \text{PbCl}_2(s) + \text{H}_2(g)$

(g) $\text{Zn}(s) + \text{CuSO}_4(s) \longrightarrow \text{Cu}(s) + \text{ZnSO}_4(s)$

Solution

(a)

$$\Delta S^\text{o} = \sum \nu \Delta S^\text{o}(\text{products}) - \sum \nu \Delta S^\text{o}(\text{reactants})$$

$$= 1\Delta S^\circ \text{SnCl}_4(g) - 1\Delta S^\circ \text{SnCl}_4(l)$$

$$= \left[1\text{ mol}\left(366\ \frac{\text{J}}{\text{mol K}}\right)\right] - \left[1\text{ mol}\left(259\ \frac{\text{J}}{\text{mol K}}\right)\right] = 107\text{ J/K}$$

(b)

$$\Delta S^\text{o} = \sum \nu \Delta S^\text{o}(\text{products}) - \sum \nu \Delta S^\text{o}(\text{reactants})$$

$$= 1\Delta S^\circ \text{Cs}_2(l) - 1\Delta S^\circ \text{Cs}_2(g)$$

$$= \left[1\text{ mol}\left(151.3\ \frac{\text{J}}{\text{mol K}}\right)\right] - \left[1\text{ mol}\left(237.7\ \frac{\text{J}}{\text{mol K}}\right)\right] = -86.4\text{ J/K}$$

(c)

$$\Delta S^\text{o} = \sum \nu \Delta S^\text{o}(\text{products}) - \sum \nu \Delta S^\text{o}(\text{reactants})$$

$$= 1\Delta S^\circ \text{Cu}(g) - 1\Delta S^\circ \text{Cu}(s)$$

$$= \left[1\text{ mol}\left(166.3\ \frac{\text{J}}{\text{mol K}}\right)\right] - \left[1\text{ mol}\left(33.15\ \frac{\text{J}}{\text{mol K}}\right)\right] = 133.2\text{ J/K}$$

(d)

$$\Delta S^\text{o} = \sum \nu \Delta S^\text{o}(\text{products}) - \sum \nu \Delta S^\text{o}(\text{reactants})$$

$$= 1\Delta S^\circ \text{H}_2\text{O}(g) - 1\Delta S^\circ \text{H}_2\text{O}(l)$$

$$= \left[1\text{ mol}\left(188.8\ \frac{\text{J}}{\text{mol K}}\right)\right] - \left[1\text{ mol}\left(70.0\ \frac{\text{J}}{\text{mol K}}\right)\right] = 118.8\text{ J/K}$$

(e)

$$\Delta S^{\circ} = \sum \nu \Delta S^{\circ}(\text{products}) - \sum \nu \Delta S^{\circ}(\text{reactants})$$

$$= 2\Delta S^{\circ}\mathrm{H_2O}(l) - \left[1\Delta S^{\circ}\mathrm{O_2}(g) + 2\Delta S^{\circ}\mathrm{H_2}(g)\right] \quad ;$$

$$= \left[2\text{ mol}\left(70.0\ \frac{\text{J}}{\text{mol K}}\right)\right] - \left[1\text{ mol}\left(205.2\ \frac{\text{J}}{\text{mol K}}\right) + 2\text{ mol}\left(130.7\ \frac{\text{J}}{\text{mol K}}\right)\right] = -326.6\text{ J/K}$$

(f)

$$\Delta S^{\circ} = \sum \nu \Delta S^{\circ}(\text{products}) - \sum \nu \Delta S^{\circ}(\text{reactants})$$

$$= \left[1\Delta S^{\circ}\mathrm{PbCl_2}(s) + 1\Delta S^{\circ}\mathrm{H_2}(g)\right] - \left[1\Delta S^{\circ}\mathrm{Pb}(s) + 2\Delta S^{\circ}\mathrm{HCl}(g)\right]$$

$$= \left[1\text{ mol}\left(136.0\ \frac{\text{J}}{\text{mol K}}\right) + 1\text{ mol}\left(130.7\ \frac{\text{J}}{\text{mol K}}\right)\right] -$$

$$\left[1\text{ mol}\left(64.81\ \frac{\text{J}}{\text{mol K}}\right) + 2\text{ mol}\left(186.9\ \frac{\text{J}}{\text{mol K}}\right)\right] = -171.9\text{ J/K}$$

(g)

$$\Delta S^{\circ} = \sum \nu \Delta S^{\circ}(\text{products}) - \sum \nu \Delta S^{\circ}(\text{reactants})$$

$$= \left[1\Delta S^{\circ}\mathrm{Cu}(s) + 1\Delta S^{\circ}\mathrm{ZnSO_4}(s)\right] - \left[1\Delta S^{\circ}\mathrm{Zn}(s) + 1\Delta S^{\circ}\mathrm{CuSO_4}(s)\right]$$

$$= \left[1\text{ mol}\left(33.15\ \frac{\text{J}}{\text{mol K}}\right) + 1\text{ mol}\left(110.5\ \frac{\text{J}}{\text{mol K}}\right)\right] -$$

$$\left[1\text{ mol}\left(41.6\ \frac{\text{J}}{\text{mol K}}\right) + 1\text{ mol}\left(109.2\ \frac{\text{J}}{\text{mol K}}\right)\right] = -7.2\text{ J/K}$$

23. Determine the entropy change for the combustion of gaseous propane, C_3H_8, under the standard conditions to give gaseous carbon dioxide and water.

Solution

The reaction is $\mathrm{C_3H_8}(g) + 5\mathrm{O_2}(g) \longrightarrow 3\mathrm{CO_2}(g) + 4\mathrm{H_2O}(g)$.

$$\Delta S^{\circ} = \sum \nu \Delta S^{\circ}(\text{products}) - \sum \nu \Delta S^{\circ}(\text{reactants})$$

$$= \left[3\Delta S^{\circ}\mathrm{CO_2}(g) + 4\Delta S^{\circ}\mathrm{H_2O}(g)\right] - \left[1\Delta S^{\circ}\mathrm{C_3H_8}(g) + 5\Delta S^{\circ}\mathrm{O_2}(g)\right]$$

$$= \left[3\text{ mol}\left(213.6\ \frac{\text{J}}{\text{mol K}}\right) + 4\text{ mol}\left(69.91\ \frac{\text{J}}{\text{mol K}}\right)\right] -$$

$$\left[1\text{ mol}\left(269.9\ \frac{\text{J}}{\text{mol K}}\right) + 5\text{ mol}\left(205.03\ \frac{\text{J}}{\text{mol K}}\right)\right] = 100.6\text{ J/K}$$

25. Using the relevant S° values listed in Appendix G, calculate ΔS° for the following changes:

(a) $\mathrm{N_2}(g) + 3\mathrm{H_2}(g) \longrightarrow 2\mathrm{NH_3}(g)$

(b) $\mathrm{N_2}(g) + \frac{5}{2}\mathrm{O_2}(g) \longrightarrow \mathrm{N_2O_5}(g)$

Solution

(a) $\Delta S^\circ_{\text{sys}} = \sum \nu \Delta S^\circ(\text{products}) - \sum \nu \Delta S^\circ(\text{reactants})$

$$\Delta S^\circ_{\text{sys}} = \left(2\Delta S^\circ \text{NH}_3\right) - \left(1\Delta S^\circ \text{N}_2 + 3\Delta S^\circ \text{H}_2\right)$$

$$\Delta S^\circ_{\text{sys}} = \left[2\text{ mol}\left(192.8\frac{\text{J}}{\text{mol K}}\right)\right] - \left[1\text{ mol}\left(191.6\frac{\text{J}}{\text{mol K}}\right) + 3\text{ mol}\left(130.7\frac{\text{J}}{\text{mol K}}\right)\right];$$

$$= -198.1\text{ J/K}$$

(b) $\Delta S^\circ_{\text{sys}} = \sum \nu \Delta S^\circ(\text{products}) - \sum \nu \Delta S^\circ(\text{reactants})$

$$\Delta S^\circ_{\text{sys}} = \left(2\Delta S^\circ \text{N}_2\text{O}_5\right) - \left(1\Delta S^\circ \text{N}_2 + \frac{5}{2} \times \Delta S^\circ \text{O}_2\right)$$

$$\Delta S^\circ_{\text{sys}} = \left[1\text{ mol}\left(355.7\frac{\text{J}}{\text{mol K}}\right)\right] - \left[1\text{ mol}\left(191.6\frac{\text{J}}{\text{mol K}}\right) + \frac{5}{2}\text{ mol}\left(205.2\frac{\text{J}}{\text{mol K}}\right)\right]$$

$$= -348.9\text{ J/K}$$

27. By calculating ΔS_{univ} at each temperature, determine if the melting of 1 mole of NaCl(*s*) is spontaneous at 500 °C and at 700 °C.

$$S^\circ_{\text{NaCl}(s)} = 72.11\frac{\text{J}}{\text{mol}\cdot\text{K}} \qquad S^\circ_{\text{NaCl}(l)} = 95.06\frac{\text{J}}{\text{mol}\cdot\text{K}} \qquad \Delta H^\circ_{\text{fusion}} = 27.95\text{ kJ/mol}$$

What assumptions are made about the thermodynamic information (entropy and enthalpy values) used to solve this problem?

Solution

The process is $\text{NaCl}(s) \longrightarrow \text{NaCl}(l)$.

At 500 °C, the following is true:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \frac{q_{\text{surr}}}{T} = (95.06 - 72.11)\frac{\text{J}}{\text{mol}\cdot\text{K}} + \frac{-27.95 \times 10^3\,\frac{\text{J}}{\text{mol}}}{500 + 273.15} = -13.2\frac{\text{J}}{\text{mol}\cdot\text{K}}$$

At 700 °C, the following is true:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \frac{q_{\text{surr}}}{T} = (95.06 - 72.11)\frac{\text{J}}{\text{mol}\cdot\text{K}} + \frac{-27.95 \times 10^3\,\frac{\text{J}}{\text{mol}}}{700 + 273.15} = -5.8\frac{\text{J}}{\text{mol}\cdot\text{K}}$$

As $\Delta S_{\text{univ}} < 0$ at each of these temperatures, melting is not spontaneous at either of them. The given values for entropy and enthalpy are for NaCl at 298 K. It is assumed that these do not change significantly at the higher temperatures used in the problem.

29. Use the standard entropy data in Appendix G to determine the change in entropy for each of the reactions listed in Exercise 34. All the processes occur at the standard conditions and 25 °C.

Solution

(a) $\Delta S^\circ = \sum \nu \Delta S^\circ(\text{products}) - \sum \nu \Delta S^\circ(\text{reactants})$

$$\Delta S^\circ = \left[1\text{ mol}\left(213.8\ \frac{\text{J}}{\text{mol}\cdot\text{K}}\right)\right] - \left[1\text{ mol}\left(5.740\ \frac{\text{J}}{\text{mol}\cdot\text{K}}\right) + 1\text{ mol}\left(205.2\ \frac{\text{J}}{\text{mol}\cdot\text{K}}\right)\right] = 2.86\text{ J/K}$$

(b) $\Delta S^\circ = \sum \nu \Delta S^\circ(\text{products}) - \sum \nu \Delta S^\circ(\text{reactants})$

$$\Delta S^\circ = \left[2\ \text{mol}\left(210.8\ \frac{\text{J}}{\text{mol}\cdot\text{K}}\right)\right] - \left[1\ \text{mol}\left(191.6\ \frac{\text{J}}{\text{mol}\cdot\text{K}}\right) + 1\ \text{mol}\left(205.2\ \frac{\text{J}}{\text{mol}\cdot\text{K}}\right)\right] = 24.8\ \text{J/K}$$

(c) $\Delta S^\circ = \sum v\Delta S^\circ(\text{products}) - \sum v\Delta S^\circ(\text{reactants})$

$$\Delta S^\circ = \left[1\ \text{mol}\left(120.9\ \frac{\text{J}}{\text{mol}\cdot\text{K}}\right)\right] - \left[2\ \text{mol}\left(33.15\ \frac{\text{J}}{\text{mol}\cdot\text{K}}\right) + 1\ \text{mol}\left(167.82\ \frac{\text{J}}{\text{mol}\cdot\text{K}}\right)\right]$$

$$= -113.2\ \text{J/K}$$

(d) $\Delta S^\circ = \sum v\Delta S^\circ(\text{products}) - \sum v\Delta S^\circ(\text{reactants})$

$$\Delta S^\circ = \left[1\ \text{mol}\left(83.4\ \frac{\text{J}}{\text{mol}\cdot\text{K}}\right)\right] - \left[1\ \text{mol}\left(38.1\ \frac{\text{J}}{\text{mol}\cdot\text{K}}\right) + 1\ \text{mol}\left(70.0\ \frac{\text{J}}{\text{mol}\cdot\text{K}}\right)\right] = -24.7\ \text{J/K}$$

(e) $\Delta S^\circ = \sum v\Delta S^\circ(\text{products}) - \sum v\Delta S^\circ(\text{reactants})$

$$\Delta S^\circ = \left[2\ \text{mol}\left(27.3\ \frac{\text{J}}{\text{mol}\cdot\text{K}}\right) + 3\ \text{mol}\left(213.8\ \frac{\text{J}}{\text{mol}\cdot\text{K}}\right)\right] -$$

$$\left[1\ \text{mol}\left(81.40\ \frac{\text{J}}{\text{mol}\cdot\text{K}}\right) + 3\ \text{mol}\left(197.7\ \frac{\text{J}}{\text{mol}\cdot\text{K}}\right)\right] = 15.5\ \text{J/K}$$

(f) $\Delta S^\circ = \sum v\Delta S^\circ(\text{products}) - \sum v\Delta S^\circ(\text{reactants})$

$$\Delta S^\circ = \left[1\ \text{mol}\left(106.5\ \frac{\text{J}}{\text{mol}\cdot\text{K}}\right) + 2\ \text{mol}\left(188.8\ \frac{\text{J}}{\text{mol}\cdot\text{K}}\right)\right] - \left[1\ \text{mol}\left(194.14\ \frac{\text{J}}{\text{mol}\cdot\text{K}}\right)\right] = 290.0\ \text{J/K}$$

Chemistry 2e
16: Thermodynamics
16.4: Free Energy

31. A reactions has $\Delta H^\circ = 100\ \text{kJ/mol}$ and $\Delta S^\circ = 250\ \text{J/mol}\cdot\text{K}$. Is the reaction spontaneous at room temperature? If not, under what temperature conditions will it become spontaneous?

Solution

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

$$\Delta G^\circ = 100 - 298.15 \times 250 \frac{\text{J}}{\text{mol}\cdot\text{K}}\left(\frac{1\ \text{kJ}}{1000\ \text{J}}\right) = 25.5\ \text{kJ/mol}$$

The $\Delta G^\circ > 0$, so the reaction is nonspontaneous at room temperature.

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

$$0 = 100 - T\left[250\frac{\text{J}}{\text{mol}\cdot\text{K}}\left(\frac{1\ \text{kJ}}{1000\ \text{J}}\right)\right]$$

$T = 400$ K

Above 400 K, ΔG will become negative, and the reaction will become spontaneous.

33. Use the standard free energy of formation data in Appendix G to determine the free energy change for each of the following reactions, which are run under standard state conditions and 25 °C. Identify each as either spontaneous or nonspontaneous at these conditions.

(a) $\text{MnO}_2(s) \longrightarrow \text{Mn}(s) + \text{O}_2(g)$

(b) $\text{H}_2(g) + \text{Br}_2(l) \longrightarrow 2\text{HBr}(g)$

(c) $\text{Cu}(s) + \text{S}(g) \longrightarrow \text{CuS}(s)$

(d) $2\text{LiOH}(s) + \text{CO}_2(g) \longrightarrow \text{Li}_2\text{CO}_3(s) + \text{H}_2\text{O}(g)$

(e) $\text{CH}_4(g) + \text{O}_2(g) \longrightarrow \text{C}(s,\ \text{graphite}) + 2\text{H}_2\text{O}(g)$

(f) $\text{CS}_2(g) + 3\text{Cl}_2(g) \longrightarrow \text{CCl}_4(g) + \text{S}_2\text{Cl}_2(g)$

Solution

(a) $\Delta G^\circ = \sum \nu\Delta G_\text{f}^\circ(\text{products}) - \sum \nu\Delta G_\text{f}^\circ(\text{reactants})$

$$\Delta G^\circ = \left[1\ \text{mol}\left(0\ \text{kJ/mol}\right) + 1\ \text{mol}\left(0\ \text{kJ/mol}\right)\right] - \left[1\ \text{mol}\left(-465.1\ \text{kJ/mol}\right)\right] = 465.1$$

nonspontaneous

(b) $\Delta G^\circ = \sum \nu\Delta G_\text{f}^\circ(\text{products}) - \sum \nu\Delta G_\text{f}^\circ(\text{reactants})$

$$\Delta G^\circ = \left[2\ \text{mol}\left(-53.43\ \text{kJ/mol}\right)\right] - \left[1\ \text{mol}\left(0\ \text{kJ/mol}\right) + 1\ \text{mol}\left(0\ \text{kJ/mol}\right)\right] = -106.86\ \text{kJ}$$

spontaneous

(c) $\Delta G^\circ = \sum \nu\Delta G_\text{f}^\circ(\text{products}) - \sum \nu\Delta G_\text{f}^\circ(\text{reactants})$

$$\Delta G^\circ = \left[1\ \text{mol}\left(-53.6\ \text{kJ/mol}\right)\right] - \left[1\ \text{mol}\left(0\ \text{kJ/mol}\right) + 1\ \text{mol}\left(238.25\ \text{kJ/mol}\right)\right] = -291.9\ \text{kJ}$$

spontaneous

(d) $\Delta G^\circ = \sum \nu \Delta G_\text{f}^\circ(\text{products}) - \sum \nu \Delta G_\text{f}^\circ(\text{reactants})$

$$\Delta G^\circ = \left[1\text{ mol}\left(-1132.19\text{ kJ/mol}\right) + 1\text{ mol}\left(-228.59\text{ kJ/mol}\right)\right] - \left[2\text{ mol}\left(-441.5\text{ kJ/mol}\right) + 1\text{ mol}\left(-394.36\text{ kJ/mol}\right)\right] = -83.4\text{ kJ}$$

spontaneous

(e) $\Delta G^\circ = \sum \nu \Delta G_\text{f}^\circ(\text{products}) - \sum \nu \Delta G_\text{f}^\circ(\text{reactants})$

$$\Delta G^\circ = \left[1\text{ mol}\left(0\text{ kJ/mol}\right) + 2\text{ mol}\left(-228.59\text{ kJ/mol}\right)\right] - \left[1\text{ mol}\left(-50.5\text{ kJ/mol}\right) + 1\text{ mol}\left(0\text{ kJ/mol}\right)\right] = -406.7\text{ kJ}$$

spontaneous

(f) $\Delta G^\circ = \sum \nu \Delta G_\text{f}^\circ(\text{products}) - \sum \nu \Delta G_\text{f}^\circ(\text{reactants})$

$$\Delta G^\circ = \left[1\text{ mol}\left(-58.2\text{ kJ/mol}\right) + 1\text{ mol}\left(-29.25\text{ kJ/mol}\right)\right] - \left[1\text{ mol}\left(66.8\text{ kJ/mol}\right) + 3\text{ mol}\left(0\text{ kJ/mol}\right)\right] = -154.3\text{ kJ}$$

spontaneous

35. Given:

$$\text{P}_4(s) + 5\text{O}_2(g) \longrightarrow \text{P}_4\text{O}_{10}(s) \qquad \Delta G^\circ = -2697.0\text{ kJ/mol}$$

$$2\text{H}_2(g) + \text{O}_2(g) \longrightarrow 2\text{H}_2\text{O}(g) \qquad \Delta G^\circ = -457.18\text{ kJ/mol}$$

$$6\text{H}_2\text{O}(g) + \text{P}_4\text{O}_{10}(s) \longrightarrow 4\text{H}_3\text{PO}_4(l) \qquad \Delta G^\circ = -428.66\text{ kJ/mol}$$

(a) Determine the standard free energy of formation, ΔG_f°, for phosphoric acid.

(b) How does your calculated result compare to the value in Appendix G? Explain.

Solution

(a) The standard free energy of formation is the standard free energy change for $\frac{1}{4}\text{P}_4(s) + \frac{3}{2}\text{H}_2(g) + 2\text{O}_2(g) \longrightarrow \text{H}_3\text{PO}_4(l)$. We can use a Hess's law-like approach. Note that adding the first reaction plus three times the second reaction plus the third reaction gives, after cancelling terms

$$\text{P}_4(s) + 6\text{H}_2(g) + 8\text{O}_2(g) \longrightarrow 4\text{H}_3\text{PO}_4(l)$$

$$\Delta G_\text{rxn}^\circ = \left[\left(-2697.0\right) + 3\left(-457.18\right) + \left(-428.66\right)\right]\text{ kJ/mol} = -4497.2\text{ kJ/mol}$$

Dividing this result by four gives the equation of interest. The standard free energy of formation is –1124.3kJ/mol. (b) The calculation agrees with the value in Appendix G because free energy is a state function (just like the enthalpy and entropy), so its change depends only on the initial and final states, not the path between them.

37. Consider the decomposition of red mercury(II) oxide under standard state conditions.

$$2\text{HgO}(s,\text{ red}) \longrightarrow 2\text{Hg}(l) + \text{O}_2(g)$$

(a) Is the decomposition spontaneous under standard state conditions?

(b) Above what temperature does the reaction become spontaneous?

Solution

(a) Using the data in Appendix G, determine ΔG°_{298}:

$$\Delta G^\circ = 2\Delta G^\circ_\text{f}\left(\text{Hg}(l)\right) + \Delta G^\circ_\text{f}\left(\text{O}_2(g)\right) - 2\Delta G^\circ_\text{f}\left(\text{HgO}(s,\ \text{red})\right)$$

$$= \left\{2(0) + 0 - 2(-58.5)\right\}\ \text{kJ/mol} = 117.0\ \text{kJ/mol}$$

From its value at 298.15 K, the reaction is nonspontaneous; (b) requires the ratio of the standard enthalpy change to the standard entropy change:

$$\Delta H^\circ = 2\Delta H^\circ_\text{f}\left(\text{Hg}(l)\right) + \Delta H^\circ_\text{f}\left(\text{O}_2(g)\right) - 2\Delta H^\circ_\text{f}\left(\text{HgO}(s,\ \text{red})\right)$$

= [2(0) + 0 – 2(–90.83)]kJ/mol = 181.66 kJ/mol

$$\Delta S^\circ = 2S^\circ\left(\text{Hg}(l)\right) + S^\circ\left(\text{O}_2(g)\right) - 2S^\circ\left(\text{HgO}(s,\ \text{red})\right)$$

= [2(75.9) + 205.0 – 2(70.29)]J/K•mol = 216.42 J/K•mol

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{181.66 \times 10^3\ \text{J/mol}}{216.42\ \text{J/K·mol}} = 839\ \text{K} = 566\ °\text{C}$$

Above 566 °C the process is spontaneous.

39. Calculate $\Delta G°$ for each of the following reactions from the equilibrium constant at the temperature given.

(a) $N_2(g) + O_2(g) \longrightarrow 2NO(g)$ T = 2000 °C $K_P = 4.1 \times 10^{-4}$

(b) $H_2(g) + I_2(g) \longrightarrow 2HI(g)$ T = 400 °C $K_P = 50.0$

(c) $CO_2(g) + H_2(g) \longrightarrow CO(g) + H_2O(g)$ T = 980 °C $K_P = 1.67$

(d) $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$ T = 900 °C $K_P = 1.04$

(e) $HF(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + F^-(aq)$ T = 25 °C $K_P = 7.2 \times 10^{-4}$

(f) $AgBr(s) \longrightarrow Ag^+(aq) + Br^-(aq)$ T = 25 °C $K_P = 3.3 \times 10^{-13}$

Solution

(a) $\Delta G° = -RT \ln K_P = -(8.314\ \text{J K}^{-1})(2273.15\ \text{K})(\ln 4.1 \times 10^{-4}) = 147\ \text{kJ} = 1.5 \times 10^2\ \text{kJ}$
(b) $\Delta G° = -(8.314\ \text{J K}^{-1})(673.15\ \text{K})(\ln 50.0) = -21{,}893\ \text{J} = -21.9\ \text{kJ}$
(c) $\Delta G° = -(8.314\ \text{J K}^{-1})(1253.15\ \text{K})(\ln 1.67) = -5.34\ \text{kJ}$
(d) $\Delta G° = -(8.314\ \text{J K}^{-1})(1173.15\ \text{K})(\ln 1.04) = -0.383\ \text{kJ}$
(e) $\Delta G° = -(8.314\ \text{J K}^{-1})(298.15\ \text{K})(\ln 7.2 \times 10^{-4}) = 17{,}937\ \text{J} = 18\ \text{kJ}$
(f) $\Delta G° = -(8.314\ \text{J K}^{-1})(298.15\ \text{K})(\ln 3.3 \times 10^{-13}) = 71{,}240\ \text{J} = 71\ \text{kJ}$

41. Calculate the equilibrium constant at 25°C for each of the following reactions from the value of $\Delta G°$ given.

(a) $O_2(g) + 2F_2(g) \longrightarrow 2OF_2(g)$ $\Delta G° = -9.2\ \text{kJ}$

(b) $I_2(s) + Br_2(l) \longrightarrow 2IBr(g)$ $\Delta G° = 7.3\ \text{kJ}$

(c) $2LiOH(s) + CO_2(g) \longrightarrow Li_2CO_3(s) + H_2O(g)$ $\Delta G° = -79\ \text{kJ}$

(d) $N_2O_3(g) \longrightarrow NO(g) + NO_2(g)$ $\Delta G° = -1.6\ \text{kJ}$

(e) $SnCl_4(l) \longrightarrow SnCl_4(l)$ $\Delta G° = 8.0\ \text{kJ}$

Solution

Equilibrium constants are calculated from $\ln K = \frac{-\Delta G°}{RT}$. Note that K is a function of T and thus changes as T changes.

$$\text{(a)}\ \ln K = -\left[\frac{-9.2 \times 10^{3}\ \text{J}}{\left(8.314\ \text{J mol}^{-1}\ \text{K}^{-1} \times 298.15\ \text{K}\right)}\right] = 3.71,\ K = 41;$$

$$\text{(b)}\ \ln K = \frac{-7300\ \text{J}}{\left(8.314\ \text{J mol}^{-1}\ \text{K}^{-1} \times 298.15\ \text{K}\right)} = -2.945,\ K = 0.053;$$

$$\text{(c)}\ \ln K = -\left[\frac{-79 \times 10^{3}\ \text{J}}{\left(8.314\ \text{J mol}^{-1}\ \text{K}^{-1} \times 298.15\ \text{K}\right)}\right] = 31.870,\ K = 6.9 \times 10^{13};$$

$$\text{(d)}\ \ln K = -\left[\frac{-1.6 \times 10^{3}\ \text{J}}{\left(8.314\ \text{J mol}^{-1}\ \text{K}^{-1} \times 298.15\ \text{K}\right)}\right] = 0.645,\ K = 1.9;$$

$$\text{(e)}\ \ln K = \frac{-8 \times 10^{3}\ \text{J}}{\left(8.314\ \text{J mol}^{-1}\ \text{K}^{-1} \times 298.15\ \text{K}\right)} = -3.227,\ K = 0.04$$

43. Calculate the equilibrium constant at the temperature given.

(a) $O_2(g) + 2F_2(g) \longrightarrow 2F_2O(g) \qquad (T = 100\ °C)$

(b) $I_2(s) + Br_2(l) \longrightarrow 2IBr(g) \qquad (T = 0.0\ °C)$

(c) $2LiOH(s) + CO_2(g) \longrightarrow Li_2CO_3(s) + H_2O(g) \qquad (T = 575\ °C)$

(d) $N_2O_3(g) \longrightarrow NO(g) + NO_2(g) \qquad (T = -10.0\ °C)$

(e) $SnCl_4(l) \longrightarrow SnCl_4(g) \qquad (T = 200\ °C)$

Solution

In each of the following, the value of ΔG is not given at the temperature of the reaction. Therefore, we must calculate ΔG from the values $\Delta H°$ and ΔS and then calculate ΔG from the relation $\Delta G = \Delta H° - T\Delta S°$.

$$\text{(a)}\ \Delta H° = 2\Delta H^{°}_{f_{OF_2(g)}} - \Delta H^{°}_{f_{O_2(g)}} - 2\Delta H^{°}_{f_{F_2(g)}} = 2\ \text{mol}\left(24.7\ \text{kJ mol}^{-1}\right) - 0 - 2(0)$$

$$= 49.4\ \text{kJ} = 4.94 \times 10^{4}\ \text{J}$$

$$\Delta S° = 2\Delta S^{°}_{OF_2(g)} - \Delta S^{°}_{O_2(g)} - 2\Delta S^{°}_{F_2(g)} = 2(247.43) - 205.2 - 2(202.8) = -115.94\ \text{J}$$

$$\Delta G = \Delta H° - T\Delta S° = 49{,}400\ \text{J} - 373.15(-115.94\ \text{J}) = 92{,}663\ \text{J}$$

$$\ln K = \frac{\Delta G}{-RT} = \frac{92{,}663}{-8.314 \times 373.15} = -29.868, \qquad K = 1.07\ \text{x}\ 10^{-13}$$

$$\text{(b)}\ \Delta H^{°} = 2\Delta H^{°}_{f_{IBr(g)}} - \Delta H^{°}_{f_{I_2(s)}} - \Delta H^{°}_{f_{Br_2(l)}} = 2(40{,}840\ \text{J}) = 81{,}680\ \text{J}$$

$$\Delta S° = 2\Delta S^{°}_{IBr(g)} - \Delta S^{°}_{I_2(s)} - \Delta S^{°}_{Br_2(l)} = 2(258.66) - 116.14 - 152.23 = 248.95$$

$$\Delta G = 81{,}680 - 273.15(248.95) = 1.368 \times 10^{4}\ \text{J}$$

$$\ln K = \frac{13{,}680}{-8.314(273.15)} = -6.024, \qquad K = 2.42 \times 10^{-3}$$

(c) $\Delta H° = \Delta H^{\circ}_{\mathrm{f}_{\mathrm{Li_2CO_3}(s)}} + \Delta H^{\circ}_{\mathrm{f}_{\mathrm{H_2O}(g)}} - 2\Delta H^{\circ}_{\mathrm{f}_{\mathrm{LiOH}(g)}} - \Delta H^{\circ}_{\mathrm{f}_{\mathrm{CO_2}(g)}} = -1216.04 - 241.82 - 2(-487.5) - (-393.51)$

$= -89.35\ \mathrm{kJ}$

$\Delta S° = \Delta S^{\circ}_{\mathrm{f}_{\mathrm{Li_2CO_3}(s)}} + \Delta S^{\circ}_{\mathrm{f}_{\mathrm{H_2O}(g)}} - 2(\Delta S^{\circ}_{\mathrm{f}_{\mathrm{LiOH}(g)}}) - \Delta S^{\circ}_{\mathrm{f}_{\mathrm{CO_2}(g)}} = 90.17 + 188.8 - 2(42.8) - 213.8$

$= -20.43\ \mathrm{J\ K^{-1}}$

$\Delta G = \Delta H° - T\Delta S^{\circ}, \qquad T = 575\ °\mathrm{C} + 273.15 = 848.15\ \mathrm{K}$

$\Delta G = -89{,}350 - 848.15(-20.43) = -7.2022 \times 10^{-4}$

$$\ln K = \frac{\Delta G}{-RT} = \frac{-7.2022 \times 10^{4}}{-8.314 \times 848.15} = 10.2138, \qquad K = 2.72 \times 10^{4} J$$

(d) $\Delta H° = \Delta H^{\circ}_{\mathrm{f}_{\mathrm{NO}(g)}} + \Delta H^{\circ}_{\mathrm{f}_{\mathrm{NO_2}(g)}} - \Delta H^{\circ}_{\mathrm{f}_{\mathrm{N_2O}(g)}} = 90.25 + 33.2 - 83.72 = 39.73\ \mathrm{kJ}$

$\Delta S° = \Delta S^{\circ}_{\mathrm{NO}(g)} + \Delta S^{\circ}_{\mathrm{f}_{\mathrm{NO_2}(g)}} - \Delta S^{\circ}_{\mathrm{N_2O_3}(g)} = 210.8 + 240.1 - 312.17 = 138.73\ \mathrm{J\ K^{-1}}$

$\Delta G = \Delta H° - T\Delta S° = 39{,}730 - 263.15(138.73) = 3223.2\ \mathrm{J}$

$$\ln K = \frac{\Delta G}{-RT} = \frac{3223.2}{-8.314 \times 263.15} = -1.4732, \qquad K = 0.229$$

(e) $\Delta H° = \Delta H^{\circ}_{\mathrm{f}_{\mathrm{SnCl_4}(g)}} - \Delta H^{\circ}_{\mathrm{f}_{\mathrm{SnCl_4}(l)}} = -471.5\ \mathrm{kJ\ mol^{-1}} - (-511.3\ \mathrm{kJ\ mol^{-1}}) = 39.8\ \mathrm{kJ\ mol^{-1}}$

$\Delta S° = \Delta S^{\circ}_{\mathrm{SnCl_4}(g)} - \Delta S^{\circ}_{\mathrm{SnCl_4}(l)} = 365.8\mathrm{J\ K^{-1}\ mol^{-1}} - 258.6\mathrm{J\ K^{-1}\ mol^{-1}} = 107.2\ \mathrm{J\ K^{-1}\ mol^{-1}}$

$\Delta G = \Delta H^{\circ} - T\Delta S^{\circ} = 39{,}800 - 473.15(107.2) = -10{,}922\ \mathrm{J}$

$$\ln K = \frac{-10{,}922}{-8.314 \times 473.15} = 2.7764, \qquad K = 16.1$$

45. Consider the following reaction at 298 K:

$$\mathrm{N_2O_4}(g) \rightleftharpoons 2\mathrm{NO_2}(g) \qquad K_P = 0.142$$

What is the standard free energy change at this temperature? Describe what happens to the initial system, where the reactants and products are in standard states, as it approaches equilibrium.

Solution

The standard free energy change is $\Delta G^{\circ} = -RT \ln K = 4.84\ \mathrm{kJ/mol}$. When reactants and products are in their standard states (1 bar or 1 atm), $Q = 1$. As the reaction proceeds toward equilibrium, the reaction shifts left (the amount of products drops while the amount of reactants increases): $Q < 1$, and ΔG becomes less positive as it approaches zero. At equilibrium, $Q = K$, and $\Delta G = 0$.

47. Under what conditions is $\mathrm{N_2O_3}(g) \longrightarrow \mathrm{NO}(g) + \mathrm{NO_2}(g)$ spontaneous?

Solution

This reaction will become spontaneous when ΔG goes from positive to negative, or at the point where $\Delta G = 0$. $\Delta G° = \Delta H° - T\Delta S° \qquad T = \dfrac{\Delta H}{\Delta S}$

Calculate $\Delta H°$ and $\Delta S°$:

$$\Delta H^\circ = \Delta H^\circ_{\text{NO}(g)} + \Delta H^\circ_{\text{NO}_2(g)} - \Delta H^\circ_{\text{N}_2\text{O}_3(g)} = (90.25 + 33.2 - 83.72)\text{ kJ} = 39.73\text{ kJ}$$

$$\Delta S^\circ = S^\circ_{\text{NO}(g)} + S^\circ_{\text{NO}_2(g)} - S^\circ_{\text{N}_2\text{O}_3(g)} = (210.65 + 239.9 - 312.2)\text{ J K}^{-1} = 138.35\ J\text{ K}^{-1}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 39.73\text{ kJ} - (298.15\text{ K})(0.13835\text{ kJ K}^{-1}) = -1.519\text{ kJ}$$

Thus this reaction is spontaneous at 298 K because Δ*G* is negative at this temperature, and because *T*Δ*S*° term is negative, Δ*G* will become progressively more negative as the temperature increases above 298 K. Thus the temperature at which Δ*G* first becomes negative must lie at a temperature lower than 298 K. We can find this temperature by substituting into $T = \dfrac{\Delta H}{\Delta S}$.

$$T = \frac{\Delta H}{\Delta S} = \frac{39{,}700\text{ J}}{138.35\text{ J K}^{-1}} = 287\text{ K}$$

The reaction will be spontaneous at temperatures greater than 287 K.

49. Hydrogen sulfide is a pollutant found in natural gas. Following its removal, it is converted to sulfur by the reaction $2\text{H}_2\text{S}(g) + \text{SO}_2(g) \rightleftharpoons \frac{3}{8}\text{S}_8(s,\text{ rhombic}) + 2\text{H}_2\text{O}(l)$. What is the equilibrium constant for this reaction? Is the reaction endothermic or exothermic?

Solution

Find Δ*G*° for the reaction, and from Δ*G*° find *K*.

$$\begin{aligned}\Delta G^\circ &= 3\Delta G^\circ_{\text{S}(s)} + 2\Delta G^\circ_{\text{H}_2\text{O}(g)} - 2\Delta G^\circ_{\text{H}_2\text{S}(g)} - \Delta G^\circ_{\text{SO}_2(s)} = 3(0) + 2(-228.59) - 2(-33.6) - (-300.19)\\ &= -89.79\text{ kJ}\end{aligned}$$

$$\Delta G^\circ = -RT\ln K = -2.303RT\log K$$

$$K = \text{antilog}\left(\frac{-\Delta G}{2.303RT}\right) = \left[\frac{89{,}790}{2.303(8.314)(298.15)}\right] = \text{antilog }15.729 = 5.35 \times 10^{15}$$

The process is exothermic.

51. In the laboratory, hydrogen chloride (HCl(*g*)) and ammonia (NH_3(*g*)) often escape from bottles of their solutions and react to form the ammonium chloride (NH_4Cl(*s*)), the white glaze often seen on glassware. Assuming that the number of moles of each gas that escapes into the room is the same, what is the maximum partial pressure of HCl and NH_3 in the laboratory at room temperature? (Hint: The partial pressures will be equal and are at their maximum value when at equilibrium.)

Solution

The equilibrium may be written as

$$\text{NH}_4\text{Cl}(s) \rightleftharpoons \text{HCl}(g) + \text{NH}_3(g) \qquad K_P = P_{\text{NH}_3}P_{\text{HCl}} = x^2$$

to help simplify the mathematics. Use the standard free energy change to determine the equilibrium constant for the reaction: $\Delta G^\circ = 91.1\text{ kJ/mol}$, $K_P = 1.1 \times 10^{-16}$. At equilibrium, the partial pressures are equal so that $x = \sqrt{K_P} = 1.0 \times 10^{-8}\text{ atm}$. This is the maximum pressure of the gases under the stated conditions.

53. Carbon dioxide decomposes into CO and O_2 at elevated temperatures. What is the equilibrium partial pressure of oxygen in a sample at 1000 °C for which the initial pressure of CO_2 was 1.15 atm?

Solution

The reaction is $2CO_2(g) \longrightarrow 2CO(g) + O_2(g)$.

$\Delta H°$ = (2 mol)(–110.52 kJ mol^{-1}) + (1 mol)(0) – (2 mol)(–393.51 kJ mol^{-1}) = 565.98 kJ;
$\Delta S°$ = (2 mol)(197.56 J $K^{-1}mol^{-1}$) + (1 mol)(205.03 J $K^{-1}mol^{-1}$) – (2 mol)(–393.51 kJ mol^{-1}) = 172.95 J K^{-1};
$\Delta G°$ = (565,980 J) – (1273 K)(172.95 J K^{-1}) = 345,810 J;

$$\log K = \frac{345,810 \text{ J}}{(-2.303)(8.314 \text{ J K}^{-1})(1273\ K)} = -14.1975$$

$$K = 6.494 \times 10^{-15} = \frac{(P_{CO})^2 (P_{O_2})}{(P_{CO_2})} = \frac{(2x)^2 (x)}{(1.15 - 2x)^2} \approx \frac{(2x)^2 (x)}{(1.15)^2}$$

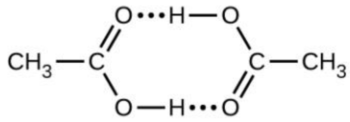
$$4x^3 = 8.59 \times 10^{-15}$$

$$x = 1.29 \times 10^{-5} \text{ atm} = P_{O_2}$$

55. Acetic acid, CH_3CO_2H, can form a dimer, $(CH_3CO_2H)_2$, in the gas phase.

$$2CH_3CO_2H(g) \longrightarrow (CH_3CO_2H)_2(g)$$

The dimer is held together by two hydrogen bonds with a total strength of 66.5 kJ per mole of dimer.



At 25 °C, the equilibrium constant for the dimerization is 1.3×10^3 (pressure in atm). What is $\Delta S°$ for the reaction?

Solution

The equilibrium constant allows the calculation of ΔG°.

$$\Delta G^\circ = -RT \ln K = -2.303RT \log K = -2.303\left(8.314 \text{ J K}^{-1} \text{ mol}^{-1}\right)\left(298.2\ K\right)\left(\log 1.3 \times 10^3\right)$$

$$= -17.78 \text{ kJ mol}^{-1} = 1.8 \text{ kJ mol}^{-1} \text{ (2 significant figures)}$$

The strength of the bond (66.5 kJ) means that it requires 66.5 kJ to pull 1 mol of bonds apart. In other words, $\Delta H^\circ = -66.5$ kJ. The values of ΔG° and ΔH° allow us to calculate $\Delta S°$ by use of the equation

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

$$\Delta S^\circ = -\frac{\Delta G^\circ - \Delta H^\circ}{T} = -\frac{(-17,780 \text{ J}) - (-66,500 \text{ J})}{298.2 \text{ K}} = -163 \text{ J K}^{-1} = -0.16 \text{ kJ}$$

56. Determine $\Delta G°$ for the following reactions.

(a) Antimony pentachloride decomposes at 448 °C. The reaction is:

$$SbCl_5(g) \longrightarrow SbCl_3(g) + Cl_2(g)$$

An equilibrium mixture in a 5.00 L flask at 448 °C contains 3.85 g of $SbCl_5$, 9.14 g of $SbCl_3$, and 2.84 g of Cl_2.

(b) Chlorine molecules dissociate according to this reaction:

$$Cl_2(g) \longrightarrow 2Cl(g)$$

1.00% of Cl_2 molecules dissociate at 975 K and a pressure of 1.00 atm.

Solution

(a) Find the equilibrium constant by first calculating the number of moles of each component.
molar masses: $SbCl_5$ = 299.11 g mol$^{–1}$
$SbCl_3$ = 228.11 g mol$^{–1}$
Cl_2 = 70.9054 g mol$^{–1}$

$$\text{mol SbCl}_5 \;=\; \frac{3.85\text{ g}}{299.01\,g\text{ mol}^{-1}} \;=\; 0.0129\text{ mol}$$

$$\text{mol SbCl}_3 \;=\; \frac{9.14\text{ g}}{228.11\text{ g mol}^{-1}} \;=\; 0.0401\text{ mol}$$

$$\text{mol Cl}_2 \;=\; \frac{2.84\text{ g}}{70.9054\text{ g mol}^{-1}} \;=\; 0.0401\text{ mol}$$

$$K \;=\; \frac{[\text{SbCl}_3][Cl_2]}{[\text{SbCl}_5]} \;=\; \frac{\left(\dfrac{0.0401\text{ mol}}{5.00\text{ L}}\right)\left(\dfrac{0.0401\text{ mol}}{5.00\text{ L}}\right)}{\left(\dfrac{0.0129\text{ mol}}{5.00\text{ L}}\right)} \;=\; 0.0249\text{ mol L}^{-1}$$

At 448 °C = 721.15 K,

$$\Delta G° \;=\; -RT\ln K \;=\; -(8.314\text{ J K}^{-1})(721.15\text{ K})(\ln 0.0249) \;=\; 2.21 \times 10^4\text{ J} \;=\; 22.1\text{ kJ}$$

(b) Determine the value of K and then determine the value of $\Delta G°$ from the value of K. Molar concentrations are required to find K. The concentration of Cl_2 at 1.00 atm and 975 K is determined from the ideal gas law, $PV = nRT$

$$\frac{n}{V} \;=\; \frac{P}{RT} \;=\; \frac{1.00\text{ atm}}{0.08206\dfrac{\text{L atm}}{\text{K mol}}(975\text{ K})} \;=\; 0.0125\,M$$

Since the Cl_2 gas is 1.00% dissociated, the concentration of Cl_2 is 0.9900 × 0.0125 M = 0.0124 M. The concentration of Cl_2 is 2 × 0.0100 × 0.0124 = 0.000250 M (we have to use the factor of two since each dissociated Cl_2 molecule produces two Cl particles).

$$K \;=\; \frac{[\text{Cl}]^2}{[\text{Cl}_2]} \;=\; \frac{0.000250^2}{0.0124} = 5.04\times10^{-6}$$

Using this result, $\Delta G^o = –RT \ln K$ = –8.314 J/mol K × 975 K ln(5.04 × 10$^{–6}$) = 98,900 J/mol = 98.9 kJ/mol.

58. Determine the standard free energy change, ΔG_f°, for the formation of $S^{2–}(aq)$ given that the ΔG_f° for $Ag^+(aq)$ and $Ag_2S(s)$ are 77.1 kJ/mole and –39.5 kJ/mole respectively, and the solubility product for $Ag_2S(s)$ is 8 × 10$^{–51}$.

Solution

The reaction of interest is: $\text{Ag}_2\text{S}(s) \rightleftharpoons 2\text{Ag}^+(aq) + \text{S}^{2-}(aq) \qquad K_{\text{sp}} = 8 \times 10^{-51}$

$$\Delta G^\circ = -RT\ln K$$

$$\Delta G^\circ = -8.314 \times 298.15 \cdot \ln 8 \times 10^{-51}$$

$$\Delta G^\circ = 286\text{ kJ}$$

$$\Delta G^\circ = \sum \nu\Delta G_f^\circ(\text{products}) - \sum \nu\Delta G_f^\circ(\text{reactants})$$

$$286 = \left[1\text{ mol}\left(\Delta G_f^\circ S^{2-}\text{ kJ/mol}\right) + 2\text{ mol}\left(77.1\text{ kJ/mol}\right)\right] - \left[1\text{ mol}\left(-39.5\text{ kJ/mol}\right)\right]$$

$$\Delta G_f^\circ S^{2-} = 90\text{ kJ/mol}$$

60. The evaporation of one mole of water at 298 K has a standard free energy change of 8.58 kJ.

$$\text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{O}(g) \qquad \Delta G^\circ = 8.58\text{ kJ}$$

(a) Is the evaporation of water under standard thermodynamic conditions spontaneous?
(b) Determine the equilibrium constant, K_P, for this physical process.
(c) By calculating ΔG, determine if the evaporation of water at 298 K is spontaneous when the partial pressure of water, $P_{\text{H}_2\text{O}}$, is 0.011 atm.
(d) If the evaporation of water were always nonspontaneous at room temperature, wet laundry would never dry when placed outside. In order for laundry to dry, what must be the value of $P_{\text{H}_2\text{O}}$ in the air?

Solution
(a) Under standard thermodynamic conditions, the temperature is 298 K, and the pressure of water vapor would be 1 atm (or 1 bar). Under these conditions, the evaporation is nonspontaneous as indicated by $\Delta G^\circ > 0$. (b) $\Delta G^\circ = -RT \ln K$, $8.58 \times 10^3 = -8.314 \times 2981.15 \ln K$, $K_P = 0.031$; (c) $Q = P_{\text{H}_2\text{O}} = 0.011\text{ atm}$, $\Delta G = \Delta G^\circ_{298} + RT \ln Q$, $\Delta G = 8.58 \times 10^3 + (8.314 \times 298 \times \ln 0.011) = -2.6$ kJ, Under these conditions, the evaporation of water is spontaneous; (d) $P_{\text{H}_2\text{O}}$ must always be less than K_P or less than 0.031 atm. 0.031 atm represents air saturated with water vapor at 25 °C, or 100% humidity.

62. One of the important reactions in the biochemical pathway glycolysis is the reaction of glucose-6-phosphate (G6P) to form fructose-6-phosphate (F6P):

$$\text{G6P} \rightleftharpoons \text{F6P} \qquad \Delta G^\circ = 1.7\text{ kJ}$$

(a) Is the reaction spontaneous or nonspontaneous under standard thermodynamic conditions?
(b) Standard thermodynamic conditions imply the concentrations of G6P and F6P to be 1 *M*, however, in a typical cell, they are not even close to these values. Calculate ΔG when the concentrations of G6P and F6P are 120 μ*M* and 28 μ*M* respectively, and discuss the spontaneity of the forward reaction under these conditions. Assume the temperature is 37 °C.

Solution
(a) Nonspontaneous as $\Delta G^\circ > 0$; (b) $\Delta G = \Delta G^\circ + RT \ln Q$,

$$\Delta G = 1.7 \times 10^3 + \left(8.314 \times 310 \times \ln\frac{28}{120}\right) = -2.1\text{ kJ}$$

. The forward reaction to produce F6P is spontaneous under these conditions.

64. When ammonium chloride is added to water and stirred, it dissolves spontaneously and the resulting solution feels cold. Without doing any calculations, deduce the signs of ΔG, ΔH, and ΔS for this process, and justify your choices.

Solution
ΔG is negative as the process is spontaneous. ΔH is positive as with the solution becoming cold, the dissolving must be endothermic. ΔS must be positive as this drives the process, and it is expected for the dissolution of any soluble ionic compound.

66. What happens to ΔG° (becomes more negative or more positive) for the following chemical reactions when the partial pressure of oxygen is increased?

(a) $\mathrm{S}(s) + \mathrm{O_2}(g) \longrightarrow \mathrm{SO_2}(g)$

(b) $2\mathrm{SO_2}(g) + \mathrm{O_2}(g) \longrightarrow 2\mathrm{SO_3}(g)$

(c) $\mathrm{HgO}(s) \longrightarrow \mathrm{Hg}(l) + \mathrm{O_2}(g)$

Solution

(a) Increasing $P_{\mathrm{O_2}}$ will shift the equilibrium toward the products, which increases the value of K. ΔG° therefore becomes more negative.

(b) Increasing $P_{\mathrm{O_2}}$ will shift the equilibrium toward the products, which increases the value of K. ΔG° therefore becomes more negative.

(c) Increasing $P_{\mathrm{O_2}}$ will shift the equilibrium the reactants, which decreases the value of K. ΔG° therefore becomes more positive.