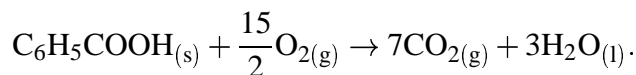


Chemistry 2000B Spring 2002 Assignment 5 Solutions

1. (a) The reaction is



Therefore

$$\begin{aligned}\Delta\bar{H}^\circ &= 7\Delta\bar{H}_f^\circ(\text{CO}_2) + 3\Delta\bar{H}_f^\circ(\text{H}_2\text{O}_{(l)}) - \Delta\bar{H}_f^\circ(\text{C}_6\text{H}_5\text{COOH}) - \frac{15}{2}\Delta\bar{H}_f^\circ(\text{O}_2) \\ &= 7(-393.509) + 3(-285.830) - (-384.8) - \frac{15}{2}(0) \text{ kJ/mol} \\ &= -3227.3 \text{ kJ/mol.} \\ n_{\text{C}_6\text{H}_5\text{COOH}} &= \frac{1.0043 \text{ g}}{122.123 \text{ g/mol}} = 8.2237 \times 10^{-3} \text{ mol.} \\ \therefore q &= n_{\text{C}_6\text{H}_5\text{COOH}}\Delta\bar{H}^\circ = (8.2237 \times 10^{-3} \text{ mol})(-3227.3 \text{ kJ/mol}) \\ &= -26.540 \text{ kJ.}\end{aligned}$$

- (b) No. A bomb calorimeter is a constant volume device. The heat produced at constant volume is not necessarily the same as the heat at constant pressure.

2. (a) The density of water is about 1 g/mL. Since ginger ale won't have exactly the same density as water at the same temperature, there is no point using a more accurate value than this. Accordingly, 300 mL of ginger ale weighs about 300 g. If there is no heat exchange with the room, we have

$$\begin{aligned}q = 0 &= \left\{ \begin{array}{c} \text{ginger ale} \\ \text{cooling to } 4^\circ\text{C} \end{array} \right\} + \left\{ \begin{array}{c} \text{glass} \\ \text{cooling to } 4^\circ\text{C} \end{array} \right\} + \left\{ \begin{array}{c} \text{ice} \\ \text{warming to } 0^\circ\text{C} \end{array} \right\} \\ &+ \left\{ \begin{array}{c} \text{ice} \\ \text{melting} \end{array} \right\} + \left\{ \begin{array}{c} \text{melted ice} \\ \text{warming to } 4^\circ\text{C} \end{array} \right\} \\ &= (300 \text{ g})(4.18 \text{ J K}^{-1} \text{ g}^{-1})(4 - 30^\circ\text{C}) + (94 \text{ J/K})(4 - 30^\circ\text{C}) \\ &+ m_{\text{ice}}(2.06 \text{ J K}^{-1} \text{ g}^{-1})[0 - (-5^\circ\text{C})] + m_{\text{ice}}(333 \text{ J/g}) \\ &+ m_{\text{ice}}(4.18 \text{ J K}^{-1} \text{ g}^{-1})(4 - 0^\circ\text{C}) \\ &= -35048 \text{ J} + (360 \text{ J/g})m_{\text{ice}}. \\ \therefore m_{\text{ice}} &= 97 \text{ g.}\end{aligned}$$

- (b) Each ice cube has a volume of $(2.7 \text{ cm})^3 = 20 \text{ cm}^3$. Since the density of ice is 0.917 g/cm^3 (p 32 of the textbook), this corresponds to 18 g per ice cube. You therefore need five ice cubes to cool your drink. Hopefully, your glass is large enough for this!

(c) As your drink begins to cool below room temperature, heat will tend to flow from the surroundings into your drink. It will therefore be necessary to add slightly more ice than calculated above.

3. (a)

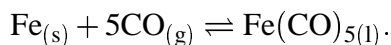
$$\begin{aligned}\Delta\bar{G}^\circ &= \Delta\bar{G}_{f(\text{COCl}_2)}^\circ - \Delta\bar{G}_{f(\text{CO})}^\circ - \Delta\bar{G}_{f(\text{Cl}_2)}^\circ \\ &= -204.6 - (-137.168) - 0 \text{ kJ/mol} = -67.4 \text{ kJ/mol.} \\ \therefore K &= e^{-\Delta\bar{G}^\circ/(RT)} \\ &= \exp\left(\frac{67.4 \times 10^3 \text{ J/mol}}{(8.314510 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})}\right) \\ &= 6.51 \times 10^{11}.\end{aligned}$$

(b) The equilibrium constant is enormous, so the reaction will proceed until just about all of the limiting reagent (chlorine) is used up. Accordingly, the equilibrium pressures of COCl_2 and of CO are 0.25 and 0.15 atm, respectively. The equilibrium pressure of chlorine can be calculated from the equilibrium relation:

$$\begin{aligned}K &= \frac{a_{\text{COCl}_2}}{(a_{\text{CO}})(a_{\text{Cl}_2})}. \\ \therefore a_{\text{Cl}_2} &= \frac{a_{\text{COCl}_2}}{K a_{\text{CO}}} = \frac{0.25}{(6.51 \times 10^{11})(0.15)} = 2.6 \times 10^{-12}.\end{aligned}$$

The equilibrium pressure of chlorine gas is therefore 2.6×10^{-12} atm.

4. The reaction is



For this reaction,

$$Q = \frac{1}{(a_{\text{CO}})^5}.$$

There are at least two ways to solve this problem:

(a) The reaction becomes spontaneous when $Q < K$. We can calculate K as follows:

$$\begin{aligned}\Delta\bar{G}^\circ &= \Delta\bar{G}_{f(\text{Fe}(\text{CO})_5)}^\circ - \Delta\bar{G}_{f(\text{Fe})}^\circ - 5\Delta\bar{G}_{f(\text{CO})}^\circ \\ &= -705.3 - 0 - 5(-137.168 \text{ kJ/mol}) = -19.5 \text{ kJ/mol.} \\ \therefore K &= e^{-\Delta\bar{G}^\circ/(RT)} \\ &= \exp\left(\frac{19.5 \times 10^3 \text{ J/mol}}{(8.314510 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})}\right) \\ &= 2.57 \times 10^3. \\ \therefore (a_{\text{CO}})^5 &> \frac{1}{2.57 \times 10^3} = 3.90 \times 10^{-4}. \\ \therefore a_{\text{CO}} &> 0.208.\end{aligned}$$

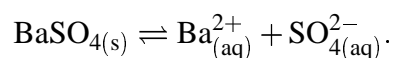
The reaction therefore becomes spontaneous when $P_{\text{CO}} > 0.208 \text{ atm}$.

- (b) The reaction becomes spontaneous when $\Delta\bar{G} < 0$. Since $\Delta\bar{G} = \Delta\bar{G}^\circ + RT \ln Q$, spontaneity requires that

$$\begin{aligned}\Delta\bar{G}^\circ &< -RT \ln Q. \\ \therefore \ln Q &< \frac{-\Delta\bar{G}^\circ}{RT}. \\ \therefore Q &< e^{-\Delta\bar{G}^\circ / RT} = K.\end{aligned}$$

The rest of the calculations are identical to those used in the first approach.

5. Solid barium sulfate dissociates in water:



The equilibrium constant for this reaction is $K_{\text{sp}} = 1.1 \times 10^{-10}$. From this equilibrium constant, we can calculate the standard free energy of reaction:

$$\begin{aligned}\Delta\bar{G}^\circ &= -RT \ln K \\ &= -(8.314510 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K}) \ln(1.1 \times 10^{-10}) \\ &= 57 \text{ kJ/mol.}\end{aligned}$$

Also, $\Delta\bar{G}^\circ = \Delta\bar{G}_{f(\text{Ba}^{2+})}^\circ + \Delta\bar{G}_{f(\text{SO}_4^{2-})}^\circ - \Delta\bar{G}_{f(\text{BaSO}_4)}^\circ$.

$$\begin{aligned}\therefore \Delta\bar{G}_{f(\text{Ba}^{2+})}^\circ &= \Delta\bar{G}^\circ - \Delta\bar{G}_{f(\text{SO}_4^{2-})}^\circ + \Delta\bar{G}_{f(\text{BaSO}_4)}^\circ \\ &= 57 - (-744.00) + (-1362.2 \text{ kJ/mol}) = -561 \text{ kJ/mol.}\end{aligned}$$