Chemistry 2000 Spring 2001 Section B Assignment 2 Solutions

1. Since this is a liquid, the mole fractions are the appropriate measures of activity. Fortunately, we are given the data in exactly the right form: If 6.42% of the molecules are in the chair form $X_{\text{chair}} = 0.0642$. Moreover, the rest (93.58%) must be in the boat form, i.e. $X_{\text{boat}} = 0.9358$. The equilibrium constant is

$$K = \frac{a_{\text{boat}}}{a_{\text{chair}}} = \frac{X_{\text{boat}}}{X_{\text{chair}}} = \frac{0.9358}{0.0642} = 14.6.$$

2. We need to determine the reaction ratio *Q*:

$$Q = \frac{a_{\text{NOBr}}^2}{(a_{\text{NO}})^2(a_{\text{Br}_2})} = \frac{(P_{\text{NOBr}}/P^\circ)^2}{(P_{\text{NO}}/P^\circ)^2(P_{\text{Br}_2}/P^\circ)} = \frac{(0.969)^2}{(0.105)^2(0.400)} = 213.$$

Since *Q* is larger than *K*, there is excess product. Accordingly, NOBr will react to form NO and bromine.

3. (a) We can solve this problem by working out how the initial and final pressures are related:

$$\begin{array}{c|cccc} & P_{\text{CO}} \text{ (atm)} & P_{\text{Cl}_2} \text{ (atm)} & P_{\text{COCl}_2} \text{ (atm)} \\ \hline \text{initial} & 0.3 & 0.3 & 0 \\ \hline \text{final equilibrium} & 0.3 - P_{\text{COCl}_2} & 0.3 - P_{\text{COCl}_2} & P_{\text{COCl}_2} \\ \end{array}$$

For this reaction,

$$K = \frac{a_{\text{COCl}_2}}{(a_{\text{CO}})(a_{\text{Cl}_2})} = \frac{(P_{\text{COCl}_2})P^{\circ}}{(P_{\text{CO}})(P_{\text{Cl}_2})}$$

$$\therefore 0.20 = \frac{P_{\text{COCl}_2}}{(0.3 - P_{\text{COCl}_2})(0.3 - P_{\text{COCl}_2})}$$

$$\therefore P_{\text{COCl}_2} = 0.20(0.3 - P_{\text{COCl}_2})^2$$

$$= 0.018 - 0.12P_{\text{COCl}_2} + 0.20P_{\text{COCl}_2}^2$$

$$\therefore 0 = 0.20P_{\text{COCl}_2}^2 - 1.12P_{\text{COCl}_2} + 0.018$$

$$\therefore P_{\text{COCl}_2} = 5.58 \text{ or } 0.016 \text{ atm}$$

Only the second solution makes any physical sense. Thus, $P_{\text{COCl}_2} = 0.016$ atm.

(b)

$$n = \frac{PV}{RT}$$

$$P = (0.016 \text{ atm})(101325 \text{ Pa/atm}) = 1633 \text{ Pa}$$

$$V = (10 \text{ L}) \left(\frac{1 \text{ m}^3}{1000 \text{ L}}\right) = 0.01 \text{ m}^3$$

$$T = 600 + 273.15 \text{ K} = 873 \text{ K}$$

$$\therefore n = \frac{(1633 \text{ Pa})(0.01 \text{ m}^3)}{(8.314510 \text{ J} \text{ K}^{-1} \text{mol}^{-1})(873 \text{ K})} = 2.2 \times 10^{-3} \text{ mol}$$

4.

$$K = \frac{a_{\text{H}_2\text{CO}_3}}{(a_{\text{CO}_2})(a_{\text{H}_2\text{O}})}$$

We are given K and the pressure of carbon dioxide (from which we can easily compute its activity). We want to solve for the activity of H_2CO_3 (from which we can obtain the concentration). We still need to know the activity of the solvent, i.e. its mole fraction.

$$n_{\text{H}_2\text{O}} = \frac{150\,\text{g}}{18.0152\,\text{g/mol}} = 8.33\,\text{mol}$$

$$n_{\text{NaCl}} = \frac{18\,\text{g}}{58.443\,\text{g/mol}} = 0.31\,\text{mol}$$

$$\therefore X_{\text{H}_2\text{O}} = \frac{n_{\text{H}_2\text{O}}}{n_{\text{H}_2\text{O}} + n_{\text{Na}^+} + n_{\text{Cl}^-}} = \frac{8.33\,\text{mol}}{8.33 + 0.31 + 0.31\,\text{mol}} = 0.931$$

$$\therefore a_{\text{H}_2\text{CO}_3} = K(a_{\text{CO}_2})(a_{\text{H}_2\text{O}}) = (3.36 \times 10^{-2}) \left(\frac{33\,\text{Pa}}{101325\,\text{Pa}}\right) (0.931) = 1.0 \times 10^{-5}$$

$$\therefore [\text{H}_2\text{CO}_3] = 1.0 \times 10^{-5}\,\text{mol/L}$$