# 5

# Chemical Equilibrium

5.1 For the reaction $N_2(g) + 3H_2(g) = 2NH_3(g)$, $K = 1.60 \times 10^{-4}$ at 400 °C. Calculate (a) $\Delta_r G^o$ and (b) $\Delta_r G$ when the pressures of $N_2$ and $H_2$ are maintained at 10 and 30 bar, respectively, and $NH_3$ is removed at a partial pressure of 3 bar. (c) Is the reaction spontaneous under the latter conditions?

SOLUTION

(a)  $\Delta_r G^o = - RT \ln K$
$$= - (8.314 \text{ J K}^{-1} \text{ mol}^{-1})(673 \text{ K}) \ln 1.60 \times 10^{-4} = 48.9 \text{ kJ mol}^{-1}$$

(b)  $\Delta_r G = \Delta_r G^o + RT \ln \dfrac{(P_{NH_3}/P^o)^2}{(P_{N_2}/P^o)(P_{H_2}/P^o)^3}$

$$= 48.9 + (8.314 \times 10^{-3})(673) \ln \frac{3^2}{10(30)^3} = - 8.78 \text{ kJ mol}^{-1}$$

(c)  Yes

5.2 At 1:3 mixture of nitrogen and hydrogen was passed over a catalyst at 450 °C. It was found that 2.04% by volume of ammonia was formed when the total pressure was maintained at 10.13 bar. Calculate the value of $K$ for $\dfrac{3}{2} H_2(g) + \dfrac{1}{2} N_2(g) = NH_3(g)$ at this temperature.

SOLUTION

At equilibrium $P_{H_2} + P_{N_2} + P_{NH_3} = 10.13$ bar

$P_{NH_3} = (10.13 \text{ bar})(0.0204) = 0.207$ bar

$P_{H_2} + P_{N_2} = 10.13 \text{ bar} - 0.207 \text{ bar} = 9.923$ bar

$P_{H_2} = 3P_{N_2}$    because this initial ratio is not changed by reaction

$P_{N_2} = \dfrac{9.923 \text{ bar}}{4} = 2.481$ bar

$P_{H_2} = \dfrac{3}{4}(9.923 \text{ bar}) = 7.442$ bar

$$K = \frac{(P_{NH_3}/P^o)}{(P_{H_2}/P^o)^{3/2}(P_{N_2}/P^o)^{1/2}}$$

$$= \frac{0.207}{7.442^{3/2}\,2.482^{1/2}} = 6.47 \times 10^{-3}$$

5.3    At 55 °C and 1 bar the average molar mass of partially dissociated $N_2O_4$ is 61.2 g mol$^{-1}$. Calculate (a) $\xi$ and (b) $K$ for the reaction $N_2O_4(g) = 2NO_2(g)$. (c) Calculate $\xi$ at 55 °C if the total pressure is reduced to 0.1 bar.

SOLUTION

(a)    $\xi = \dfrac{M_1 - M_2}{M_2} = \dfrac{92.0 - 61.2}{61.2} = 0.503$

(b)    $K = \dfrac{4\xi^2(P/P^o)}{1 - \xi^2} = \dfrac{4(0.503)^2}{1 - 0.503^2} = 1.36$

(c)    $\dfrac{\xi^2}{1 - \xi^2} = \dfrac{K}{4(P/P^o)} = \dfrac{1.36}{4(0.1)}$

$\xi = 0.879$

(Note that $\xi$ is the dimensionless extent of reaction.)

5.4    A 1 liter reaction vessel containing 0.233 mol of $N_2$ and 0.341 mol of $PCl_5$ is heated to 250 °C. The total pressure at equilibrium is 29.33 bar. Assuming that all the gases are ideal, calculate $K$ for the only reaction that occurs.
$PCl_5(g) = PCl_3(g) + Cl_2(g)$

SOLUTION

|  | PCl$_5$ | = | PCl$_3$ | + | Cl$_2$ |  |
|---|---|---|---|---|---|---|
| initial | 0.341 |  | 0 |  | 0 |  |
| eq. | 0.341 - $\xi$ |  | $\xi$ |  | $\xi$ | total = 0.341 + $\xi$ |

$$K = \frac{\xi^2(P/P^o)^2}{(0.341 + \xi)(0.341 - \xi)}$$

$$= \frac{\xi^2(P/P^o)}{0.341^2 - \xi^2} \quad \text{where } P = P_{PCl_5} + P_{PCl_3} + P_{Cl_2}$$

Calculate the equilibrium pressure of the reacting gases by subtracting the partial pressure of nitrogen from the total pressure.

$$P = 29.33 \text{ bar} - \frac{(0.233 \text{ mol})(0.08314 \text{ L bar K}^{-1}\text{mol}^{-1})(523 \text{ K})}{1 \text{ L}}$$

$$= 19.20 \text{ bar} = \frac{(0.341 + \xi)(0.08314)(523)}{1}$$

$\xi = 0.1005$

$$K = \frac{(0.1005)^2(19.2)}{0.341^2 - 0.1005^2} = 1.83$$

5.5 An evacuated tube containing $5.96 \times 10^{-3}$ mol L$^{-1}$ of solid iodine is heated to 973 K. The experimentally determined pressure is 0.496 bar. Assuming ideal gas behavior, calculate $K$ for $I_2(g) = 2I(g)$.
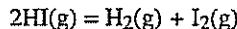
SOLUTION

$$P = \frac{n}{V} RT$$

$$0.496 \text{ bar} = (1 + \xi)(5.96 \times 10^{-3} \text{ L}^{-1}) \times (0.08314 \text{ L bar K}^{-1} \text{ mol}^{-1})(973 \text{ K})$$

$$\xi = \frac{0.496 \text{ bar}}{(5.96 \times 10^{-3} \text{ mol L}^{-1})(0.08314 \text{ L bar}^{-1} \text{ K}^{-1} \text{ mol}^{-1})(973 \text{ K})} - 1$$

$$= 0.0288$$

$$K = \frac{4\xi^2(P/P^o)}{1 - \xi^2} = \frac{4(0.0288)^2(0.496)}{1 - 0.0287^2} = 1.64 \times 10^{-3}$$

*5.7 For the reaction
$2HI(g) = H_2(g) + I_2(g)$
at 698.6 K, $K = 1.83 \times 10^{-2}$. (a) How many grams of hydrogen iodide will be formed when 10 g of iodine and 0.2 g of hydrogen are heated to this temperature in a 3 L vessel? (b) What will be the partial pressures of $H_2$, $I_2$, and HI?

SOLUTION

(a) Pressures due to reactants prior to reaction:

$$P_{I_2} = \frac{(10 \text{ g})(0.08314 \text{ L bar K}^{-1} \text{ mol}^{-1})(698.6 \text{ K})}{(254 \text{ g mol}^{-1})(3 \text{ L})} = 0.762 \text{ bar}$$

$$P_{H_2} = \frac{(0.2)(0.08314 \text{ L bar K}^{-1} \text{ mol}^{-1})(698.6 \text{ K})}{2 \times 3} = 1.936 \text{ bar}$$

$$K = \frac{(0.762 - x)(1.936 - x)}{(2x)^2} = 1.83 \times 10^{-2}$$
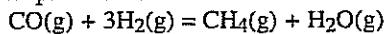
$$x = 0.730 \text{ bar}$$

(b) $P_{H_2} = 1.936 - 0.730 = 1.206$ bar

$P_{I_2} = 0.762 - 0.730 = 0.032$ bar

$P_{HI} = 1.460$ bar

5.8    Express $K$ for the reaction
       $CO(g) + 3H_2(g) = CH_4(g) + H_2O(g)$
       in terms of the equilibrium extent of reaction $\xi$ when one mole of CO is mixed with
       one mole of hydrogen.
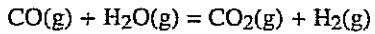
       SOLUTION

|              | C O | + | $3H_2$ | = | $CH_4$ | + | $H_2O$ | |
|--------------|-----|---|--------|---|--------|---|--------|---|
| initial      | 1   |   | 1      |   | 0      |   | 0      | |
| equilibrium  | $1 - \xi$ |   | $1 - 3\xi$ |   | $\xi$ |   | $\xi$ | total = $2 - 2\xi$ |

$$K = \frac{\left(\frac{\xi}{2-2\xi}\right)^2\left(\frac{P}{P^o}\right)^2}{\left(\frac{1-\xi}{2-2\xi}\right)\left(\frac{1-3\xi}{2-2\xi}\right)^3\left(\frac{P}{P^o}\right)^4}$$

$$K = \frac{(\xi)^2(2 - 2\xi)^2}{(1 - \xi)(1 - 3\xi)^3(P/P^o)^2}$$

5.10   In order to produce more hydrogen from "synthesis gas" (CO + $H_2$) the water gas
       shift reaction is used.

       $CO(g) + H_2O(g) = CO_2(g) + H_2(g)$

       Calculate $K$ at 1000 K and the equilibrium extent of reaction starting with an
       equimolar mixture of CO and $H_2O$.

       SOLUTION

       $\Delta G^o = - 395,886 - (- 200,275) - (- 192,590) = -3021$ J mol$^{-1}$
       $= - (8.314$ J K$^{-1}$ mol$^{-1})(1000$ K$) \ln K$

$$K = 1.44 = \frac{P_{H_2}P_{CO_2}}{P_{CO}P_{H_2O}} = \frac{\xi^2}{(1 - \xi)^2}$$

       $\xi = 0.545$

       (Note that this reaction is exothermic so that there will be a larger extent of reaction
       at lower temperatures.  In practice this reaction is usually carried out at about 700
       K.)

5.11   Calculate the extent of reaction $\xi$ of 1 mol of $H_2O(g)$ to form $H_2(g)$ and $O_2(g)$ at
       2000 K and 1 bar.  (Since the extent of reaction is small, the calculation may be
       simplified by assuming that $P_{H_2O} = 1$ bar.)

       SOLUTION

|       | $H_2O(g)$ | = | $H_2(g)$ | + | $\frac{1}{2}O_2(g)$ |
|-------|-----------|---|----------|---|---------------------|
| init. | 1         |   | 0        |   | 0                   |

eq.     $1 - \xi$         $\xi$         $\frac{1}{2}\xi$

$\Delta_r G^o = 135{,}528 \text{ J mol}^{-1}$

$\qquad = -(8.1315 \text{ J K}^{-1} \text{ mol}^{-1})(2000 \text{ K}) \ln K$

$K = 2.887 \times 10^{-4}$

$$K = \frac{\left(\frac{P_{H_2}}{P^o}\right)\left(\frac{P_{O_2}}{P^o}\right)^{1/2}}{\left(\frac{P_{H_2O}}{P^o}\right)} \quad ; \quad \frac{P_{O_2}}{P^o} = \frac{P_{H_2}}{2P^o}$$

$$\left(\frac{P_{H_2}}{P^o}\right)\left(\frac{P_{H_2}}{2P^o}\right)^{1/2} = \frac{1}{\sqrt{2}}\left(\frac{P_{H_2}}{P^o}\right)^{3/2}$$
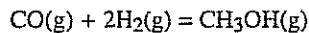
$$\xi = \left(\frac{P_{H_2}}{P^o}\right) = (\sqrt{2}\ K)^{2/3} = 0.0055$$

5.17   In the synthesis of methanol by $CO(g) + 2H_2(g) = CH_3OH(g)$ at 500 K, calculate the total pressure required for a 90% conversion to methanol if CO and $H_2$ are initially in a 1:2 ratio.  Given: $K = 6.09 \times 10^{-3}$.

SOLUTION

$$CO(g) + 2H_2(g) = CH_3OH(g)$$

initial moles          1      2       0

equil. moles 0.1          0.2 0.9     total 1.2

$$K = \frac{(P_{CH_3OH}/P^o)}{(P_{CO}/P^o)(P_{H_2}/P^o)^2} = 6.09 \times 10^{-3}$$

$$= \frac{\dfrac{0.9}{1.2}\dfrac{P}{P^o}}{\dfrac{0.1}{1.2}\dfrac{P}{P^o}\left(\dfrac{0.2}{1.2}\dfrac{P}{P^o}\right)^2}$$
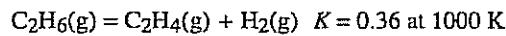
$$\frac{P}{P^o} = \sqrt{\frac{(0.9)(1.2)^2}{(0.1)(0.04)(6.09 \times 10^{-3})}} = 231$$
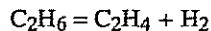
$P = 231$ bar $=$ total pressure for 90% conversion to $CH_3OH$

**5.19** When alkanes are heated up, they lose hydrogen and alkenes are produced. For example,

$$C_2H_6(g) = C_2H_4(g) + H_2(g) \quad K = 0.36 \text{ at } 1000 \text{ K}$$

If this is the only reaction that occurs when ethane is heated to 1000 K, at what total pressure will ethane be (a) 10% dissociated and (b) 90% dissociated to ethylene and hydrogen?

SOLUTION

$$C_2H_6 = C_2H_4 + H_2$$

Init.    1       0       0

Equil.   $1 - \xi$   $\xi$   $\xi$    total $= 1 + \xi$

$$K = \frac{\xi^2(P/P^o)}{(1 + \xi)(1 - \xi)} = \frac{\xi^2(P/P^o)}{1 - \xi^2}$$
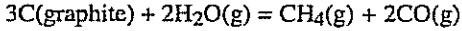
(a)   $0.36 = \dfrac{0.1^2(P/P^o)}{1 - 0.1^2} = \dfrac{0.01(P/P^o)}{0.99}$

$\dfrac{P}{P^o} = \left[ \dfrac{(0.99)(0.36)}{0.01} \right] = 35.6$

(b)   $0.36 = \dfrac{0.9^2(P/P^o)}{1 - 0.9^2} = \dfrac{0.81(P/P^o)}{0.19}$

$P = \left[ \dfrac{(0.19)(0.36)}{0.81} \right] = 0.084 \text{ bar}$

**5.23** The following reaction is nonspontaneous at room temperature and endothermic.
$$3C(\text{graphite}) + 2H_2O(g) = CH_4(g) + 2CO(g)$$
As the temperature is raised, the equilibrium constant will become equal to unity at some point. Estimate this temperature using data from Appendix C.3.

SOLUTION

At 1000 K

$\Delta_r G^o = 19.492 + 2(-200.275) - 2(-192.590) = 4.122 \text{ kJ mol}^{-1}$

$= -(8.3145 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1})(1000 \text{ K}) \ln K$

$K = 0.609$

$\Delta_r H^o = -89.849 + 2(-111.983) - 2(-247.857) = 181.899 \text{ kJ mol}^{-1}$

$\ln \dfrac{K_2}{K_1} = \dfrac{\Delta H^o}{R} \left( \dfrac{1}{T_1} - \dfrac{1}{T_2} \right)$

$\ln \dfrac{1}{0.609} = \dfrac{181\ 899 \text{ J mol}^{-1}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}} \left( \dfrac{1}{1000 \text{ K}} - \dfrac{1}{T_2} \right)$

$T_2 = \dfrac{1}{\dfrac{1}{1000 \text{ K}} - \dfrac{8.3145}{181899} \ln \dfrac{1}{0.609}} = 1023 \text{ K}$

5.28 Water vapor is passed over coal (assumed to be pure graphite in this problem) at 1000 K. Assuming that the only reaction occurring is the water gas reaction

$C(graphite) + H_2O(g) = CO(g) + H_2(g)$      $K = 2.52$

calculate the equilibrium pressures of $H_2O$, CO, and $H_2$ at a total pressure of 1 bar. [Actually the water gas shift reaction

$CO(g) + H_2O(g) = CO_2(g) + H_2(g)$

occurs in addition, but it is considerably more complicated to take this additional reaction into account.]

SOLUTION

$$K = \frac{(P_{CO}/P^o)(P_{H_2}/P^o)}{(P_{H_2O}/P^o)} = \frac{x^2}{y} = \frac{x^2}{1 - 2x} = 2.52$$

$2x + y = 1$        $x^2 = 2.52 - 5.04x$

$x^2 + 5.04x - 2.52 = 0$

$$x = \frac{-5.04 \pm \sqrt{5.04^2 + 4(2.52)}}{2} = 0.458$$

$$= \frac{P_{CO}}{P^o} = \frac{P_{H_2}}{P^o}$$

$$1 - 2x = 0.084 = \frac{P_{H_2O}}{P^o}$$

$P_{H_2O} = 0.084$ bar        $P_{CO} = 0.458$ bar        $P_{H_2} = 0.458$ bar

5.32 Mercuric oxide dissociates according to the reaction $2HgO(s) = 2Hg(g) + O_2(g)$. At 420 °C the dissociation pressure is $5.16 \times 10^4$ Pa, and at 450 °C it is $10.8 \times 10^4$ Pa. Calculate (a) the equilibrium constants, and (b) the enthalpy of dissociation per mole of HgO.

SOLUTION

(a)     $P_{Hg} = 2P_{O_2}$          $P_{Hg} = \frac{2}{3} P$      $P_{O_2} = \frac{1}{3} P$

$$K_{420} = P_{Hg}^2 P_{O_2} = \left(\frac{2}{3}\right)^2 \left(\frac{1}{3}\right) P^3$$

$$= \left(\frac{4}{27}\right) \left(\frac{5.16 \times 10^4 \text{ Pa}}{1.013 \times 10^5 \text{ Pa}}\right)^3 = 0.0196$$

$$K_{450} = \left(\frac{4}{27}\right) \left(\frac{10.8 \times 10^4 \text{ Pa}}{1.013 \times 10^5 \text{ Pa}}\right)^3 = 0.1794$$

(b)     $$\Delta_r H^o = \frac{RT_1 T_2}{T_2 - T_1} \ln \frac{K_2}{K_1}$$

$$= \frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(693 \text{ K})(723 \text{ K})}{30 \text{K}} \ln \frac{0.1794}{0.0196}$$

$$= 308 \text{ kJ mol}^{-1} \text{ for the reaction as written}$$

$$= 154 \text{ kJ mol}^{-1} \text{ of HgO(s)}$$

5.34 The dissociation of ammonium carbamate takes place according to the reaction

$(NH_2)CO(ONH_4)(s) = 2NH_3(g) + CO_2(g)$

When an excess of ammonium carbamate is placed in a previously evacuated vessel, the partial pressure generated by $NH_3$ is twice the partial pressure of the $CO_2$, and the partial pressure of $(NH_2)CO(ONH_4)$ is negligible in comparison. Show that

$$K = \left(\frac{P_{NH_3}}{P^o}\right)^2\left(\frac{P_{CO_2}}{P^o}\right) = \frac{4}{27}\left(\frac{P}{P^o}\right)^3$$

where $P$ is the total pressure.

SOLUTION
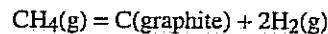
$P = P_{NH_3} + P_{CO_2} = 3P_{CO_2}$ since $P_{NH_3} = 2P_{CO_2}$

$P_{CO_2} = \frac{P}{3}$ $\qquad$ $P_{NH_3} = \frac{2}{3}P$

$$K = \left(\frac{P_{NH_3}}{P^o}\right)^2\left(\frac{P_{CO_2}}{P^o}\right) = \left(\frac{2}{3}\frac{P}{P^o}\right)^2\left(\frac{1}{3}\frac{P}{P^o}\right) = \frac{4}{27}\left(\frac{P}{P^o}\right)^3$$

5.35 At 1000 K methane at 1 bar is in the presence of hydrogen. In the presence of a sufficiently high partial pressure of hydrogen, methane does not decompose to form graphite and hydrogen. What is this partial pressure?

SOLUTION

$CH_4(g) = C(graphite) + 2H_2(g)$

$\Delta G^o = -RT \ln K = -19.46$ kJ mol$^{-1}$

$$K = 10.39 = \frac{\left(\frac{P_{H_2}}{P^o}\right)^2}{\frac{P_{CH_4}}{P^o}}$$

$P_{H_2} = P^o[(10.39)(1)]^{1/2} = 3.2$ bar

5.43 Calculate the equilibrium extent of the reaction $N_2O_4(g) = 2NO_2(g)$ at 298.15 K and a total pressure of 1 bar if the $N_2O_4(g)$ is mixed with an equal volume of $N_2(g)$ before the reaction occurs. As shown by Example 5.4, $K = 0.143$. Do you expect the same equilibrium extent of reaction as in example? If not do you expect a larger or smaller equilibrium extent of reaction?

SOLUTION

If there is initially 1 mol of $N_2O_4$, the total amount of gas at equilibrium is $2 + \xi$. Thus the expression for the equilibrium constant is

$$K = \frac{4\xi^2(P/P^o)}{(2+\xi)(1-\xi)}$$

where $P$ is the total pressure. When the total pressure is 1 bar, the equilibrium extent of reaction obtained by solving this quadratic equation with the formula

$$\xi = \frac{-b \pm (b^2 - 4ac)^{1/2}}{2a}$$

is 0.249.

This equilibrium extent of reaction is smaller than that in Example 5.3 because the partial pressure of $N_2O_4(g)$ plus $NO_2(g)$ is larger than 0.5 bar. The partial pressure of $N_2(g)$ was initially 0.5 bar, but it is less than this in the equilibrium mixture because of the expansion of the reaction mixture during the reaction at a constant pressure of 1 bar.