CHEMISTRY 311 PHYSICAL CHEMISTRY
Homework Assignment # 5

1. A one liter 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 gases are ideal, calculate K_P for the only reaction that occurs: $PCl_5(g) = PCl_3(g) + Cl_2(g)$.

Answer

$$\begin{array}{llll} \mathrm{PCl_5}(g) & \rightleftharpoons & \mathrm{PCl_3}(g) & + \quad \mathrm{Cl_2}(g) \\ 0.341-x & & x & \quad\;\; x \end{array}$$

Total number of moles at equilibrium (including nitrogen) $= 0.341 + x + 0.233 = 0.574 + x$ mol.

From ideal gas law, we have

$$\begin{aligned} 29.33 \text{ bar } &= (0.574 + x)RT/V \\ &= \frac{(0.574 + x) \times 0.083145 \text{ L bar K}^{-1} \text{ mol}^{-1} \times 523.15 \text{ K}}{1.0 \text{ L}}, \end{aligned}$$

from which we get $x = 0.10029$. Now, the concentrations are calculated as

$$\begin{aligned} c_{\mathrm{PCl_5}} &= 0.341 - x, \\ c_{\mathrm{PCl_3}} &= c_{\mathrm{Cl_2}} = x. \end{aligned}$$

Therefore,

$$\begin{aligned} K_C = \frac{x^2}{0.341 - x} &= \frac{(0.10029)^2}{(0.341 - 0.10029)} = 0.0418 \\ K_P &= K_c \left(\frac{RT}{P^\circ}\right)^1 = 1.82. \end{aligned}$$

We can also directly solve for K_P once we know x using Dalton's Law of partial pressures:

$$\begin{aligned} p_{\mathrm{PCl_3}} = p_{\mathrm{Cl_2}} = \frac{x}{0.341 + x + 0.233} \times 29.33 \text{ bar } &= 4.362 \text{ bar} \\ p_{\mathrm{PCl_5}} = \frac{0.341 - x}{0.341 + x + 0.233} \times 29.33 \text{ bar } &= 10.470 \text{ bar} \end{aligned}$$

Then

$$\begin{aligned} K_P &= \frac{(p_{\mathrm{PCl_3}}/P^\circ)(p_{\mathrm{Cl_2}}/P^\circ)}{(p_{\mathrm{PCl_5}}/P^\circ)} \\ &= 1.82. \end{aligned}$$

An alternate way to solve is to use the extent of reaction or the degree of dissociation α:

$$\begin{array}{llll} \mathrm{PCl_5}(g) & \rightleftharpoons & \mathrm{PCl_3}(g) & + \quad \mathrm{Cl_2}(g) \\ 0.341(1-\alpha) & & 0.341\alpha & \quad\;\; 0.341\alpha \end{array}$$

So, at equilibrium, there are $[0.341(1 - \alpha) + 2 \times 0.341\alpha] = 0.341(1 + \alpha)$ moles of gases We are given that

$$0.341(1 + \alpha)\frac{RT}{V} = 29.33 \text{ bar}.$$

This gives $\alpha = 0.2941$. Now,

$$K_C = \frac{(0.341\alpha)^2}{0.341(1-\alpha)} = 0.0418.$$
$$K_P = K_C\left(\frac{RT}{P^\circ}\right)^1 = 1.82.$$

2. Find the free energy of reaction for CO(g) + H_2O(g) $\rightleftharpoons$ CO_2(g) + H_2(g) using standard free energies of formation. Calculate the value of the equilibrium constant at 1000 K and the extent of reaction at equilibrium if we start with an equimolar mixture of CO and H_2O.

   Answer

   From Appendix D and data given on the course web site, we get

$$\begin{aligned}\Delta_r G^\circ &= (\Delta_f G^\circ_{CO_2} + \Delta_f G^\circ_{H_2}) - \left(\Delta_f G^\circ_{CO} + \Delta_f G^\circ_{H_2O(g)}\right)\\ &= -394.36 - 0 + 137.17 + 228.57 \text{ kJ}\\ &= -28.62 \text{ kJ.}\end{aligned}$$

   Since $\Delta_r G^\circ = -RT\ln K_P$,we get

$$\begin{aligned}K_P &= e^{-\Delta_r G^\circ/(RT)}\\ &= \exp\left(\frac{28620}{8.3145\times 1000}\right)\\ &= 31.225.\end{aligned}$$

   Let us assume that we start with c moles each of the reactants, and let α be the degree of dissociation.

$$\begin{array}{ccccccc} CO(g) & + & H_2O(g) & \rightleftharpoons & CO_2(g) & + & H_2(g)\\ c(1-\alpha) & & c(1-\alpha) & & c\alpha & & c\alpha \end{array}$$

The total number of moles is $2c(1-\alpha)+2c\alpha = 2c$. The partial pressures can be expressed in terms of mole-fractions and the total pressure P, as $P_{CO} = [c(1-\alpha)/2c]P = (1-\alpha)P/2$, and so on. The expression for K_P is

$$K_P = \frac{\alpha^2}{(1-\alpha)^2} \text{ (all pressure terms and } c\text{'s will cancel).}$$

Solving for the degree of dissociation (or the extent of reaction) α, we get

$$\begin{aligned}\sqrt{K_P} &= \frac{\alpha}{1-\alpha} = \sqrt{31.225}.\\ \alpha &= 0.8482.\end{aligned}$$

Alternately, we could start with 1 mole each of CO and H_2O, which would lead to

$$\begin{array}{ccccccc} CO(g) & + & H_2O(g) & \rightleftharpoons & CO_2(g) & + & H_2(g)\\ 1-x & & 1-x & & x & & x \end{array}$$

and

$$K_P = \frac{x^2}{(1-x)^2}.$$

This also leads to the same result as above, i.e., $x = 0.8482$.

3. Consider the equilibrium 3C(graphite) + $2H_2O(g) \rightleftharpoons CH_4(g) + 2CO(g)$, at 1000 K. The enthalpy of reaction $\Delta_r H^\circ$ = 182 kJ mol^{-1}. Write an expression for K_P, showing the standard pressure P° explicitly. Based on Le Chateliers principle, what will be the effect of (a) raising the temperature at a constant pressure of 1 bar, (b) raising the pressure to 5 bar at constant temperature of 1000 K, (c) adding graphite at a constant pressure of 1 bar.

Answer

The expression for K_P in terms of the partial pressures and the standard pressure is

$$\begin{aligned} K_P &= \frac{(P_{\mathrm{CH_4}}/P^\circ)(P_{\mathrm{CO}}/P^\circ)^2}{(P_{\mathrm{H_2O}}/P^\circ)^2} \\ &= \frac{P_{\mathrm{CH_4}} P_{\mathrm{CO}}^2}{P_{\mathrm{H_2O}}^2} \left(\frac{1}{P^\circ}\right). \end{aligned}$$

(a) Since the reaction is endothermic in the forward direction, Le Chatelier's Principle predicts that increasing the temperature will cause the equilibrium to shift to the right, i.e., form more CH_4 and CO.

(b) Increasing the pressure will cause the equilibrium to shift to the side with fewer moles of *gases*, which is the reactant side. Therefore the equilibrium will shift to the left.

(c) Since solid graphite is not involved in the definition of K_P, as long as *some* graphite is present, the quantity of graphite has no influence on the equilibrium position.