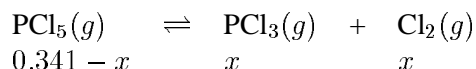


CHEMISTRY 311 PHYSICAL CHEMISTRY  
Homework Assignment # 5

1. A one liter vessel containing 0.233 mol of  $\text{N}_2$  and 0.341 mol of  $\text{PCl}_5$  is heated to  $250^\circ\text{C}$ . The total pressure at equilibrium is 29.33 bar. Assuming that all gases are ideal, calculate  $K_P$  for the only reaction that occurs:  $\text{PCl}_5(g) = \text{PCl}_3(g) + \text{Cl}_2(g)$ .

**Answer**



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

$$\begin{aligned} c_{\text{PCl}_5} &= 0.341 - x, \\ c_{\text{PCl}_3} &= c_{\text{Cl}_2} = x. \end{aligned}$$

Therefore,

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

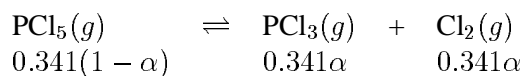
We can also directly solve for  $K_P$  once we know  $x$  using Dalton's Law of partial pressures:

$$\begin{aligned} p_{\text{PCl}_3} &= p_{\text{Cl}_2} = \frac{x}{0.341 + x + 0.233} \times 29.33 \text{ bar} = 4.362 \text{ bar} \\ p_{\text{PCl}_5} &= \frac{0.341 - x}{0.341 + x + 0.233} \times 29.33 \text{ bar} = 10.470 \text{ bar} \end{aligned}$$

Then

$$\begin{aligned} K_P &= \frac{(p_{\text{PCl}_3}/P^\circ)(p_{\text{Cl}_2}/P^\circ)}{(p_{\text{PCl}_5}/P^\circ)} \\ &= 1.82. \end{aligned}$$

An alternate way to solve is to use the extent of reaction or the degree of dissociation  $\alpha$ :



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  $\text{CO}(g) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CO}_2(g) + \text{H}_2(g)$  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  $\text{H}_2\text{O}$ .

**Answer**

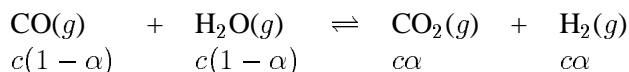
From Appendix D and data given on the course web site, we get

$$\begin{aligned} \Delta_r G^\circ &= (\Delta_f G^\circ_{\text{CO}_2} + \Delta_f G^\circ_{\text{H}_2}) - (\Delta_f G^\circ_{\text{CO}} + \Delta_f G^\circ_{\text{H}_2\text{O}(g)}) \\ &= -394.36 - 0 + 137.17 + 228.57 \text{ kJ} \\ &= -28.62 \text{ kJ}. \end{aligned}$$

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  $\alpha$  be the degree of dissociation.



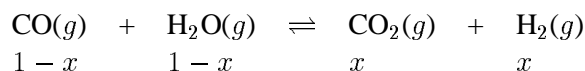
The total number of moles is  $2c(1-\alpha) + 2c\alpha = 2c$ . The partial pressures can be expressed in terms of mole-fractions and the total pressure  $P$ , as  $P_{\text{CO}} = [c(1-\alpha)/2c]P = (1-\alpha)P/2$ , and so on. The expression for  $K_P$  is

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

Solving for the degree of dissociation (or the extent of reaction)  $\alpha$ , 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  $\text{H}_2\text{O}$ , which would lead to



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  $3\text{C}(\text{graphite}) + 2\text{H}_2\text{O}(g) \rightleftharpoons \text{CH}_4(g) + 2\text{CO}(g)$ , at 1000 K. The enthalpy of reaction  $\Delta_r H^\circ = 182 \text{ kJ mol}^{-1}$ . Write an expression for  $K_P$ , showing the standard pressure  $P^\circ$  explicitly. Based on Le Chatelier's 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

$$\begin{aligned} K_P &= \frac{(P_{\text{CH}_4}/P^\circ)(P_{\text{CO}}/P^\circ)^2}{(P_{\text{H}_2\text{O}}/P^\circ)^2} \\ &= \frac{P_{\text{CH}_4} P_{\text{CO}}^2}{P_{\text{H}_2\text{O}}^2} \left( \frac{1}{P^\circ} \right). \end{aligned}$$

- (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  $\text{CH}_4$  and  $\text{CO}$ .
- (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.