CHAPTER 13: CHEMICAL EQUILIBRIUM

17. No, equilibrium is a dynamic process. Both reactions:

\[ \text{H}_2\text{O} + \text{CO} \rightarrow \text{H}_2 + \text{CO}_2 \text{ and } \text{H}_2 + \text{CO}_2 \rightarrow \text{H}_2\text{O} + \text{CO} \]

are occurring, but at equal rates. Thus, \(^{14}\text{C}\) atoms will be distributed between CO and CO\(_2\).

20. \[ a. \quad K_p = \frac{P_{\text{NO}_2} \times P_{\text{O}_2}}{P_{\text{NO}} \times P_{\text{O}_3}} \quad b. \quad K_p = \frac{P_{\text{O}_2} \times P_{\text{O}}}{P_{\text{O}_3}} \]

\[ c. \quad K_p = \frac{P_{\text{CO}_2} \times P_{\text{O}_2}}{P_{\text{CO}} \times P_{\text{O}_3}} \quad d. \quad K_p = \frac{P_{\text{O}_2}^3}{P_{\text{O}_3}^2} \]

21. \[ K = 278 = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]} \text{ for } 2 \text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2 \text{SO}_3(g) \]

When a reaction is reversed, then \(K_{\text{new}} = \frac{1}{K_{\text{original}}}\). When a reaction is multiplied through by a value of \(n\), then \(K_{\text{new}} = (K_{\text{original}})^n\).

\[ a. \quad \text{SO}_2(g) + \frac{1}{2} \text{O}_2(g) \rightleftharpoons \text{SO}_3(g), \quad K' = \frac{[\text{SO}_3]}{[\text{SO}_2][\text{O}_2]^{1/2}} = K^{1/2} = (278)^{1/2} = 16.7 \]

\[ b. \quad 2 \text{SO}_3(g) \rightleftharpoons 2 \text{SO}_2(g) + \text{O}_2(g), \quad K'' = \frac{[\text{SO}_2]^2[\text{O}_2]}{[\text{SO}_3]^2} = \frac{1}{K} = \frac{1}{278} = 3.60 \times 10^{-3} \]

\[ c. \quad \text{SO}_3(g) \rightleftharpoons \text{SO}_2(g) + \frac{1}{2} \text{O}_2(g), \quad K''' = \frac{[\text{SO}_2][\text{O}_2]^{1/2}}{[\text{SO}_3]} = \left(\frac{1}{K}\right)^{1/2} = 6.00 \times 10^{-2} \]

\[ d. \quad 4 \text{SO}_2(g) + 2 \text{O}_2(g) \rightleftharpoons 4 \text{SO}_3(g), \quad K'''' = \frac{[\text{SO}_3]^4}{[\text{SO}_2]^4[\text{O}_2]^2} = K^2 = 7.73 \times 10^4 \]

23. \[ K = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]} = \frac{(4.7 \times 10^{-4} M)^2}{(0.041 M)(0.0078 M)} = 6.9 \times 10^{-4} \]

27. \[ K_p = \frac{P_{\text{NO}}^2 \times P_{\text{Cl}_2}^2}{P_{\text{NOClo}}^2} = \frac{(1.25 \times 10^{-2} \text{ atm})^2(0.300 \text{ atm})}{(1.20 \text{ atm})^2} = 3.26 \times 10^{-5} \text{ atm} \]

29. \[ K_p = K(RT)^{\Delta n} \text{ where } \Delta n = \text{sum of gaseous product coefficients} - \text{sum of gaseous reactant coefficients}. \text{ For this reaction, } \Delta n = 4 - 2 = 2. \]

\[ K_p = \frac{2.6 \times 10^{-5} \text{ mol}^2}{\text{L}^2} \times \left(\frac{0.08206 \text{ L atm}}{\text{mol K}} \times 400 \text{ K}\right)^2 = 2.8 \times 10^{-2} \text{ atm}^2 \]
32. a. \( K_p = \frac{1}{(P_{O_2})^3} \)  
   b. \( K_p = \frac{1}{P_{CO_2}} \)  
   c. \( K_p = \frac{P_{CO} \times P_{H_2}}{P_{H_2O}} \)  
   d. \( K_p = \frac{P_{O_2}^3}{P_{H_2O}^2} \)  

34. \( C(s) + CO_2(g) \rightleftharpoons 2 CO(g) \)  
   \[ K_p = \frac{P_{CO}^2}{P_{CO_2}^2} = \frac{(2.6 \text{ atm})^2}{2.9 \text{ atm}} = 2.3 \text{ atm} \]

38. As in Exercise 13.37, determine \( Q \) for each reaction and compare this value to \( K_p (= 0.0900) \) to determine which direction the reaction shifts to reach equilibrium.
   
   a. \( Q = \frac{P_{HCl}^2}{P_{H_2O} \times P_{ClO}} = \frac{(1.00 \text{ atm})^3}{(1.00 \text{ atm}) (1.00 \text{ atm})} = 1.00 \)  
      \( Q > K_p \) so the reaction shifts left to reach equilibrium.
   
   b. \( Q = \frac{(21.0 \text{ torr})^2}{(200. \text{ torr}) (49.8 \text{ torr})} = 4.43 \times 10^{-2} < K_p \)  
      Reaction will proceed to the right to reach equilibrium. Note: Since \( Q \) and \( K_p \) are unitless, we can use any pressure units to determine \( Q \).
   
   c. \( Q = \frac{(20.0 \text{ torr})^2}{(296 \text{ torr}) (15.0 \text{ torr})} = 0.0901 = K_p \); at equilibrium

39. \( CaCO_3(s) = CaO(s) + CO_2(g) \)  
   \( K_p = P_{CO_2} = 1.04 \text{ atm} \)
   
   a. \( Q = P_{CO_2} \); We only need the partial pressure of \( CO_2 \) to determine \( Q \) since solids do not appear in equilibrium expressions (or \( Q \) expressions). At this temperature all \( CO_2 \) will be in the gas phase. \( Q = 2.55 \text{ atm} \) so \( Q > K_p \); Reaction will shift to the left to reach equilibrium; the mass of \( CaO \) will decrease.
   
   b. \( Q = 1.04 \text{ atm} = K_p \) so the reaction is at equilibrium; mass of \( CaO \) will not change.
   
   c. \( Q = 1.04 \text{ atm} = K_p \) so the reaction is at equilibrium; mass of \( CaO \) will not change.
   
   d. \( Q = 0.211 \text{ atm} < K_p \); The reaction will shift to the right to reach equilibrium; the mass of \( CaO \) will increase.

42. \( K_p = \frac{P_{HI}^2}{P_{H_2} \times P_{I_2}} = 45.9 \); \( \frac{(4.00 \text{ atm})^2}{0.200 \text{ atm} \times P_{I_2}} \); \( P_{I_2} = 1.74 \text{ atm} \)
Q = 1.00 which is less than K. Reaction shifts to the right to reach equilibrium. Summarizing the equilibrium problem in a table:

\[
\begin{align*}
& \text{SO}_2(g) + \text{NO}_2(g) \rightleftharpoons \text{SO}_3(g) + \text{NO}(g) \quad K = 2.50 \\
\text{Initial} & \quad 1.00\, M & 1.00\, M & 1.00\, M & 1.00\, M \\
\text{x mol/L of SO}_2 \text{ reacts to reach equilibrium} & -x & -x & +x & +x \\
\text{Change} & \quad 1.00 - x & 1.00 - x & 1.00 + x & 1.00 + x \\
\text{Equil.} & \quad 1.00 - x & 1.00 - x & 1.00 + x & 1.00 + x 
\end{align*}
\]

Plug the equilibrium concentrations into the equilibrium constant expression:

\[
K = \frac{[\text{SO}_3][\text{NO}]}{[\text{SO}_2][\text{NO}_2]} = 2.50 = \frac{(1.00 + x)^2}{(1.00 - x)^2}; \quad \text{Take the square root of both sides and solve for } x:
\]

\[
\frac{1.00 + x}{1.00 - x} = 1.58, \quad 1.00 + x = 1.58 - 1.58x, \quad 2.58x = 0.58, \quad x = 0.22\, M
\]

The equilibrium concentrations are:

\[
[\text{SO}_3] = [\text{NO}] = 1.00 + x = 1.00 + 0.22 = 1.22\, M; \quad [\text{SO}_2] = [\text{NO}_2] = 1.00 - x = 0.78\, M
\]