15.1: The Concept of Equilibrium

Conceptual Problems

1. What is meant when a reaction is described as “having reached equilibrium”? What does this statement mean regarding the forward and reverse reaction rates? What does this statement mean regarding the amounts or concentrations of the reactants and the products?

2. Is it correct to say that the reaction has “stopped” when it has reached equilibrium? Explain your answer and support it with a specific example.

3. Why is chemical equilibrium described as a dynamic process? Describe this process in the context of a saturated solution of $NaCl$ in water. What is occurring on a microscopic level? What is happening on a macroscopic level?

4. Which of these systems exists in a state of chemical equilibrium?
   a. oxygen and hemoglobin in the human circulatory system
   b. iodine crystals in an open beaker
   c. the combustion of wood
   d. the amount of $^{14}C$ in a decomposing organism

Conceptual Answer

1. When a reaction is described as "having reached equilibrium" this means that the forward reaction rate is now equal to the reverse reaction rate. In regards to the amounts or concentrations of the reactants and the products, there is no change due to the forward reaction rate being equal to the reverse reaction rate.

2. It is not correct to say that the reaction has "stopped" when it has reached equilibrium because it is not necessarily a static process where it can be assumed that the reaction rates cancel each other out to equal zero or be "stopped" but rather a dynamic process in which reactants are converted to products at the same rate products are converted to reactants. For example, a soda has carbon dioxide dissolved in the liquid and carbon dioxide between the liquid and the cap that is constantly being exchanged with each other. The system is in equilibrium and the reaction taking place is: $CO_2(g) + 2H_2O(l) \rightleftharpoons H_2CO_3(aq)$.

3. Chemical equilibrium is described as a dynamic process because there is a movement in which the forward and
reverse reactions occur at the same rate to reach a point where the amounts or concentrations of the reactants and products are unchanging with time. Chemical equilibrium can be described in a saturated solution of NaCl as on the microscopic level (Na\(^{+}\) and Cl\(^{-}\) ions continuously leave the surface of an NaCl crystal to enter the solution, while at the same time Na\(^{+}\) and Cl\(^{-}\) ions in solution precipitate on the surface of the crystal. At the macroscopic level, the salt can be seen to dissolve or not dissolve depending whether chemical equilibrium was established.

4.

a. Exists in a state of equilibrium as the chemical reaction that occurs in the body is: \(\text{Hb(aq)} + 4\text{H}_2\text{O(l)} \rightleftharpoons \text{Hb(O}_2\text{)_4(aq)}\).

b. Exists in a state of equilibrium as the chemical reaction occurs is: \(\text{H}_2\text{(g)} + \text{I}_2\text{(g)} \rightleftharpoons 2\text{HI(g)}\)

c. Does not exist in a state of equilibrium as it is not a reversible process. The chemical reaction that takes place is: \(6\text{C}\_{10}\text{H}_{15}\text{O}_7\text{(s)} + \text{heat} \rightleftharpoons \text{C}\_{50}\text{H}_{10}\text{O}(s) + 10\text{CH}_2\text{O(g)}\).

d. Does not exist in a state of chemical equilibrium as it is not a reversible process. The chemical reaction that takes place is: \(\text{CH}_2\text{O(g)} + \text{O}_2\text{(g)} \rightleftharpoons \text{H}_2\text{O(l)} + \text{CO}_2\text{(g)} + \text{nutrients}\).

15.2: The Equilibrium Constant

Conceptual Problems

1. For an equilibrium reaction, what effect does reversing the reactants and products have on the value of the equilibrium constant?

2. Which of the following equilibriums are homogeneous and which are heterogeneous?
   a. \(2\text{HF(g)} \rightleftharpoons \text{H}_2\text{(g)} + \text{F}_2\text{(g)}\)
   b. \(\text{C(s)} + 2\text{H}_2\text{(g)} \rightleftharpoons \text{CH}_4\text{(g)}\)
   c. \(\text{H}_2\text{C=CH}_2\text{(g)} + \text{H}_2\text{(g)} \rightleftharpoons \text{C}_2\text{H}_6\text{(g)}\)
   d. \(2\text{Hg(l)} + \text{O}_2\text{(g)} \rightleftharpoons 2\text{HgO}(s)\)

3. Classify each equilibrium system as either homogeneous or heterogeneous.
   a. \(\text{NH}_4\text{CO}_2\text{NH}_2\text{(s)} \rightleftharpoons 2\text{NH}_3\text{(g)} + \text{CO}_2\text{(g)}\)
   b. \(\text{C(s)} + \text{O}_2\text{(g)} \rightleftharpoons \text{CO}_2\text{(g)}\)
   c. \(2\text{Mg}(s) + \text{O}_2\text{(g)} \rightleftharpoons 2\text{MgO}(s)\)
   d. \(\text{AgCl(s)} \rightleftharpoons \text{Ag}^{+}\text{(aq)} + \text{Cl}^-\text{(aq)}\)

4. If an equilibrium reaction is endothermic, what happens to the equilibrium constant if the temperature of the reaction is increased? if the temperature is decreased?

5. Industrial production of \(\text{NO}\) by the reaction \(\text{N}_2\text{(g)} + \text{O}_2\text{(g)} \rightleftharpoons 2\text{NO}\text{(g)}\) is carried out at elevated temperatures to drive the reaction toward the formation of the product. After sufficient product has formed, the reaction mixture is quickly cooled. Why?
6. How would you differentiate between a system that has reached chemical equilibrium and one that is reacting so slowly that changes in concentration are difficult to observe?

7. What is the relationship between the equilibrium constant, the concentration of each component of the system, and the rate constants for the forward and reverse reactions?

8. Write the equilibrium constant expressions for \( K \) and \( K_p \) for each reaction.
   a. \( CO\,(g) + H_2O\,(g) \rightleftharpoons CO_2\,(g)+H_2\,(g) \)
   b. \( PCl_3\,(g)+Cl_2\,(g) \rightleftharpoons PCl_5\,(g) \)
   c. \( 2\,O\,(g) \rightleftharpoons 3\,O_2\,(g) \)

9. Write the equilibrium constant expressions for \( K \) and \( K_p \) as appropriate for each reaction.
   a. \( 2\,NO\,(g)+O_2\,(g) \rightleftharpoons 2\,NO_2\,(g) \)
   b. \( \dfrac{1}{2}\,H_2\,(g)+12\,I_2\,(g) \rightleftharpoons HI\,(g) \)
   c. \( cis-stilbene\,(soln) \rightleftharpoons trans-silbene\,(soln) \)

10. Why is it incorrect to state that pure liquids, pure solids, and solvents are not part of an equilibrium constant expression?

11. Write the equilibrium constant expressions for \( K \) and \( K_p \) for each equilibrium reaction.
   a. \( 2\,S\,(s)+3\,O_2\,(g) \rightleftharpoons 2\,SO_3\,(g) \)
   b. \( C\,(s) + CO_2\,(g) \rightleftharpoons 2\,CO\,(g) \)
   c. \( 2\,ZnS\,(s)+3\,O_2\,(g) \rightleftharpoons 2\,ZnO\,(s)+2\,SO_2\,(g) \)

12. Write the equilibrium constant expressions for \( K \) and \( K_p \) for each equilibrium reaction.
   a. \( 2\,HgO\,(s) \rightleftharpoons 2\,Hg\,(l)+O_2\,(g) \)
   b. \( H_2\,(g)+I_2\,(g) \rightleftharpoons 2\,HI\,(g) \)
   c. \( NH_4CO_2NH_{2}\,(s) \rightleftharpoons 2\,NH_{3}\,(g)+CO_{2}\,(g) \)

13. At room temperature, the equilibrium constant for the reaction \( 2\,A\,(g) \rightleftharpoons B\,(g) \) is 1. What does this indicate about the concentrations of \( A \) and \( B \) at equilibrium? Would you expect \( K \) and \( K_p \) to vary significantly from each other? If so, how would their difference be affected by temperature?

14. For a certain series of reactions, if \( \dfrac{[OH^-][HCO_3^-]}{[CO_3^{2-}]} = K_1 \) and \( \dfrac{[OH^-][H_2CO_3]}{[HCO_3^-]} = K_2 \), what is the equilibrium constant expression for the overall reaction? Write the overall equilibrium equation.

15. In the equation for an enzymatic reaction, \( ES \) represents the complex formed between the substrate \( S \) and the enzyme protein \( E \). In the final step of the following oxidation reaction, the product \( P \) dissociates from the \( ESO_2 \) complex, which regenerates the active enzyme:

\[
\begin{align*}
&E + S \rightleftharpoons ES \ \ \ \ \ K_1 \\
&ES + O_2 \rightleftharpoons ESO_2 \ \ \ \ K_2 \\
&[ESO_2] \rightleftharpoons E + P \ \ \ \ K_3
\end{align*}
\]

Give the overall reaction equation and show that \( K = K_1 \times K_2 \times K_3 \).

**Conceptual Answers**

1. By reversing the reactants and products for an equilibrium reaction, the equilibrium constant becomes: \( K' = \dfrac{1}{K} \).
2.  
   a. This equilibrium is homogeneous as all substances are in the same state.  
   b. This equilibrium is heterogeneous as not all substances are in the same state.  
   c. This equilibrium is homogeneous as all substances are in the same state.  
   d. This equilibrium is heterogeneous as not all substances are in the same state.  

3.  
   a. This equilibrium is heterogeneous as not all substances are in the same state.  
   b. This equilibrium is heterogeneous as not all substances are in the same state.  
   c. This equilibrium is heterogeneous as not all substances are in the same state.  
   d. This equilibrium is heterogeneous as not all substances are in the same state.  

4. According to Le Chatelier’s principle, equilibrium will shift in the direction to counteract the effect of a constraint (such as concentration of a reactant, pressure, and temperature). Thus, in an endothermic reaction, the equilibrium shifts to the right-hand side when the temperature is increased which increases the equilibrium constant and the equilibrium shifts to the left-hand side when the temperature is decreased which decreases the equilibrium constant.  

5. After sufficient industrial production of \(\text{NO}\) by the reaction of \(\text{N}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{NO}(g)\) at elevated temperatures to drive the reaction toward the formation of the product, the reaction mixture is cooled quickly because it quenches the reaction and prevents the system from reverting to the low-temperature equilibrium composition that favors the reactants.  

6. To differentiate between a system that has reached equilibrium and one that is reacting slowly that changes in concentrations are difficult to observe we can use Le Chatelier’s principle to observe any shifts in the reaction upon addition of a constraint (such as concentration, pressure, or temperature).  

7. The relationship between the equilibrium constant, the concentration of each component of a system, and the rate constants for the forward and reverse reactions considering a reaction of a general form: \((aA+bB \rightleftharpoons cC+dD)\) is \(K = \dfrac{[C]^c[D]^d}{[A]^a[B]^b} = \dfrac{k_f}{k_r}\).  

8.  
   a.  
   \(K = \dfrac{[CO_2][H_2]}{[CO][H_2O]}\)  
   \(K_p = \dfrac{P_{(CO_2)}(P_{(H_2)}}{(P_{(CO)})(P_{(H_2O)})}\)  
   b.
\( K = \frac{[PCl_5]}{[PCl_3][Cl_2]} \)
\( K_p = \frac{(P_{PCl_5})}{(P_{Cl_3})(P_{Cl_2})} \)

c.
\( K = \frac{[O_2]^3}{[O_3]^2} \)
\( K_p = \frac{(P_{O_2})^3}{(P_{O_3})^2} \)

9.

a.
\( K = \frac{[NO_2]^2}{[NO][O_2]} \)
\( K_p = \frac{(P_{NO_2})^2}{(P_{NO})(P_{O_2})} \)

b.
\( K = \frac{[HI]}{[H_2]^\frac{1}{2}[O_2]} \)
\( K_p = \frac{(P_{HI})}{(P_{H_2})^\frac{1}{2}(P_{O_2})} \)

c.
\( K = \frac{trans-stilbene}{cis-stilbene} \)
\( K_p = \frac{(P_{trans-stilbene})}{(P_{cis-stilbene})} \)

10. It is incorrect to state that pure liquids, pure solids, and solvents are not part of an equilibrium constant expression because they are not reactive enough or cause a change in the concentrations of the ions or the species that exist in the gas phase.

11.

a.
\( K = \frac{[SO_3]^2}{[O_2]^3} \)
\( K_p = \frac{(P_{SO_3})^2}{(P_{O_2})^3} \)

b.
\( K = \frac{[CO]^2}{[CO_2]} \)
\( K_p = \frac{(P_{CO})^2}{(P_{CO_2})} \)

c.
\[ K = \left( \frac{[SO_2]^2}{[O_2]^3} \right) \]
\[ K_p = \left( \frac{(P_{SO_2})^2}{(P_{O_2})^3} \right) \]

12.

a. \[ K = [O_2] \]
\[ K_p = (P_{O_{2}}) \]

b. \[ K = \left( \frac{[HI]^2}{[H_2]} \right) \]
\[ K_p = \left( \frac{(P_{HI})^2}{(P_{H_2})} \right) \]

c. \[ K = [NH_3]^2[CO_2] \]
\[ K_p = (P_{(NH_3)})^2(P_{(CO_2)}) \]

13.
\[ K = \frac{[B]}{[A]^2} \rightarrow 1 = \frac{[B]}{[A]^2} \rightarrow [A]^2 = [B] \rightarrow [A] = \sqrt{B} \]

\( K \) and \( K_p \) vary by \( RT \), but it largely depends on \( T \) as \( R \) is constant. A raise or decrease in temperature would cause a difference.

\[ K_p = K(RT)^{-\Delta n} = K(RT)^{-1} = \frac{K}{RT} \]

\( \Delta n = (\text{total moles of gas on the product side})-(\text{total moles on the reactant side}) = 1-2 = -1 \)

14.
\[ K = \frac{[K_1][K_2]}{[K_3]} = \frac{[OH^-][HCO_3^-]}{[CO_3^{2-}]}, \frac{[OH^-][H_2CO_3]}{[HCO_3^-]} = \frac{[HCO_3^-]^2}{[CO_3^{2-}][H_2CO_3]} \]
\[ CO_3^{2-}(g)+H_2CO_3(g) \rightleftharpoons 2HCO_3^-(g) \]

15.
\[ K = K_1 \cdot K_2 \cdot K_3 = \frac{[ES][E][S]}{[E][S][O_2]}, \frac{[ESO_2][E][S]}{[ES][O_2][S]}, \frac{[E][P]}{[ESO_2][S][O_2]} \]
\[ S+O_2 \rightleftharpoons P \]
Numerical Problems

1. Explain what each of the following values for $K$ tells you about the relative concentrations of the reactants versus the products in a given equilibrium reaction: $K = 0.892$; $K = 3.25 \times 10^8$; $K = 5.26 \times 10^{-11}$. Are products or reactants favored at equilibrium?

2. Write the equilibrium constant expression for each reaction. Are these equilibrium constant expressions equivalent? Explain.
   a. $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$
   b. $\frac{1}{2}\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons \text{NO}_2(\text{g})$

3. Write the equilibrium constant expression for each reaction.
   a. $\frac{1}{2}\text{N}_2(\text{g})+\frac{3}{2}\text{H}_2(\text{g}) \rightleftharpoons \text{NH}_3(\text{g})$
   b. $\frac{1}{3}\text{N}_2(\text{g})+\text{H}_2(\text{g}) \rightleftharpoons \frac{2}{3}\text{NH}_3(\text{g})$

   How are these two expressions mathematically related to the equilibrium constant expression for
   $\text{N}_2(\text{g})+3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$?

4. Write an equilibrium constant expression for each reaction.
   a. $\text{C}(\text{s}) + 2\text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}_2(\text{g})+2\text{H}_2(\text{g})$
   b. $\text{SbCl}_3(\text{g})+\text{Cl}_2(\text{g}) \rightleftharpoons \text{SbCl}_5(\text{g})$
   c. $2\text{O}_3(\text{g}) \rightleftharpoons 3\text{O}_2(\text{g})$

5. Give an equilibrium constant expression for each reaction.
   a. $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$
   b. $\frac{1}{2}\text{H}_2(\text{g})+\frac{1}{2}\text{I}_2(\text{g}) \rightleftharpoons \text{HI}(\text{g})$
   c. $\text{CaCO}_3(\text{s}) + 2\text{HOCl}(\text{aq}) \rightleftharpoons \text{Ca}^{2+}(\text{aq}) + 2\text{OCl}^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) + \text{CO}_2(\text{g})$

6. Calculate $K$ and $K_p$ for each reaction.
   a. $2\text{NOBr}(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})+\text{Br}_2(\text{g})$: at 727°C, the equilibrium concentration of $\text{NO}(\text{g})$ is 1.29 M, $\text{Br}_2(\text{g})$ is 10.52 M, and $\text{NOBr}(\text{g})$ is 0.423 M.
   b. $\text{C}(\text{s}) + \text{CO}_2(\text{g}) \rightleftharpoons 2\text{CO}(\text{g})$: at 1,200 K, a 2.00 L vessel at equilibrium has partial pressures of 93.5 atm $\text{CO}_2(\text{g})$ and 76.8 atm $\text{CO}(\text{g})$, and the vessel contains 3.55 g of carbon.

7. Calculate $K$ and $K_p$ for each reaction.
   a. $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$: at the equilibrium temperature of $-40^\circ\text{C}$, a 0.150 M sample of $\text{N}_2\text{O}_4(\text{g})$ undergoes a decomposition of 0.456%.
   b. $\text{CO}(\text{g})+2\text{H}_2(\text{g}) \rightleftharpoons \text{CH}_3\text{OH}(\text{g})$: an equilibrium is reached at $227^\circ\text{C}$ in a 15.5 L reaction vessel with a total pressure of $6.71 \times 10^2$ atm. It is found to contain 37.8 g of hydrogen gas, 457.7 g of carbon monoxide, and 7,193 g of methanol.

8. Determine $K$ and $K_p$ (where applicable) for each reaction.
   a. $2\text{H}_2\text{S}(\text{g}) \rightleftharpoons 2\text{H}_2(\text{g})+\text{S}_2(\text{g})$: at 1065°C, an equilibrium mixture consists of 1.00
\(10^{-3}\) M \(H_2\), \(1.20 \times 10^{-3}\) M \(S_2\), and \(3.32 \times 10^{-3}\) M \(H_2S\).

b. \((Ba(OH)_{2})(s) \rightleftharpoons 2OH^-(aq)+Ba^{2+}(aq)\): at 25°C, a 250 mL beaker contains 0.330 mol of barium hydroxide in equilibrium with 0.0267 mol of barium ions and 0.0534 mol of hydroxide ions.

9. Determine \(K\) and \(K_p\) for each reaction.

a. \((2\,NOCl,(g) \rightleftharpoons 2\,NO,(g)+Cl_2,(g))\): at 500 K, a 24.3 mM sample of \((NOCl)\) has decomposed, leaving an equilibrium mixture that contains 72.7% of the original amount of \((NOCl)\).

b. \((Cl_2,(g)+PCl_3,(g) \rightleftharpoons PCl_5,(g))\): at 250°C, a 500 mL reaction vessel contains 16.9 g of \((Cl_2)\) gas, 0.500 g of \((PCl_3)\), and 10.2 g of \((PCl_5)\) at equilibrium.

10. The equilibrium constant expression for a reaction is \(\dfrac{[CO_2]^2}{[SO_2]^2[O_2]}\). What is the balanced chemical equation for the overall reaction if one of the reactants is \((Na_2CO\,(3),(s))\)?

11. The equilibrium constant expression for a reaction is \(\dfrac{[NO][H\,(2)O]^\dfrac{3}{2}}{[NH_3][O_2]^\dfrac{5}{4}}\). What is the balanced chemical equation for the overall reaction?

12. Given \(K =\dfrac{k_f}{k_r}\), what happens to the magnitude of the equilibrium constant if the reaction rate of the forward reaction is doubled? What happens if the reaction rate of the reverse reaction for the overall reaction is decreased by a factor of 3?

13. The value of the equilibrium constant for \([2\,H_2,(g)+S_2,(g) \rightleftharpoons H_2S,(g)]\) is \(1.08 \times 10^7\) at 700°C. What is the value of the equilibrium constant for the following related reactions

a. \((H_2,(g)+12\,S_2,(g) \rightleftharpoons H_2S,(g))\)

b. \((4\,H_2,(g)+2\,S_2,(g) \rightleftharpoons 4\,H_2S,(g))\)

c. \((H_2S,(g) \rightleftharpoons H_2,(g)+12\,S_2,(g))\)

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**Numerical Answers**

1. In the given equilibrium reaction where \(K = 0.892\approx1\) has a concentration of the reactants that is approximately equal to the concentration of the products so neither formation of the reactants or products is favored. In the given equilibrium reaction where \(K = 3.25 \times 10^{-8}>1\) has a concentration of the products that is relatively small compared to the concentration of the reactants so the formation of the products is favored. In the given equilibrium reaction where \(K = 5.26 \times 10^{-11}<1\) has a concentration of products that is relatively large compared to that of the concentration of the reactants so the formation of the reactants is favored.

2. a. \(\dfrac{[NO_2]^2}{[N_2O_4]}\)

b. \(\dfrac{[NO_2]}{[N_2O_4]^\dfrac{1}{2}}\)

Although the equilibrium constant expressions have a 2:1 ratio of concentration for the products to the concentration of the reactants for the same species involved to get the \(K\) value for a. We would need to square it to get the \(K\) value
for b.

3.

a. \(K' = \dfrac{[\text{NH}_3]}{[\text{N}_2]^{\frac{1}{2}}[\text{H}_2]^{\frac{3}{2}}}\)

b. \(K'' = \dfrac{[\text{NH}_3]^{\frac{2}{3}}}{[\text{N}_2]^{\frac{1}{2}}[\text{H}_2]}\)

\(K = \dfrac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}\)

\(K' = K^{\frac{1}{2}}\)

\(K'' = K^{\frac{1}{3}}\)

4.

a. \(K = \dfrac{[\text{H}_2]^2[\text{CO}_2]}{[\text{H}_2\text{O}]^2}\)

b. \(K = \dfrac{[\text{SbCl}_5]}{[\text{SbCl}_3][\text{Cl}_2]}\)

c. \(K = \dfrac{[\text{O}_2]^3}{[\text{O}_3]^2}\)

5.

a. \(K = \dfrac{[\text{NO}_2]^2}{[\text{NO}]^2[\text{O}_2]}\)

b. \(K = \dfrac{[\text{HI}]}{[\text{H}_2]^{\frac{1}{2}}[\text{I}_2]^{\frac{1}{2}}}\)

c. \(K = \dfrac{[\text{Ca}^{2+}][\text{OCl}^−]^2[\text{CO}_2]}{[\text{HOCl}]^2}\)

6.

a. \(K = \dfrac{[\text{NO}]^2[\text{Br}]}{[\text{NOBr}]^2} = \dfrac{[1.29\,\text{M}]^2[10.52\,\text{M}]}{[0.423\,\text{M}]^2} = 97.8\)

\(K_p = K(RT)^{\Delta n} = (97.8)((0.08206\frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}})((727 + 273.15)\text{K}))^{3-2} = 8.03 \times 10^4\)

b. \(K_p = K(RT)^{\Delta n} = K(RT)^{2-1} = K(RT) \rightarrow K = \dfrac{K_p}{RT} = \dfrac{63.1}{(0.08206\frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}})(1,200\,\text{K})} = 6.41\)

\(K = \dfrac{[\text{P}_2(\text{CO})]^2}{[\text{P}_2(\text{CO}_2)]} = \dfrac{[76.8, \text{atm}]^2}{93.5, \text{atm}} = 63.1\)

7.a.

\(K = \dfrac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = \dfrac{[0.001368\,\text{M}]}{[0.149316\,\text{M}]} = 1.25 \times 10^{-5}\)

\([\text{NO}_2] = (2)(0.150\,\text{M})(0.00456) = 0.001368\,\text{M}\)
\( ([\text{N}_2\text{O}_4]) = (0.150, M)(1 - 0.00456) = 0.149316, M \)

\( (K_p = K(RT)^{(\Delta n)} = (1.25 \times 10^{-5})((0.08206 \text{L \cdot atm/mol \cdot K})(-40 + 273.15 K))^{(2-1)} = 2.39 \times 10^{-4}) \)

b.

\( (K = \frac{[\text{CH}_3\text{OH}]}{[\text{CO}] [\text{H}_2]^2} = \frac{[14.5, M]}{[1.05, M][1.21, M]^2} = 9.47) \)

\( ([\text{CH}_3\text{OH}] = 7.193, \, g/\text{CH}_3\text{OH} \times \frac{1, \text{mol/CH}_3\text{OH}}{32.04, \, g/\text{CH}_3\text{OH}} \times \frac{1}{15.5, \text{L}} = 14.5, M) \)

\( ([\text{CO}] = 457.7, \, g/\text{CO} \times \frac{1, \text{mol/CO}}{28.01, \, g/\text{CO}} \times \frac{1}{15.5, \text{L}} = 1.05, M) \)

\( ([\text{H}_2] = 37.8, \, g/\text{H}_2 \times \frac{1, \text{mol/H}_2}{2.02, \, g/\text{H}_2} \times \frac{1}{15.5, \text{L}} = 1.21, M) \)

\( (K_p = K(RT)^{(\Delta n)} = (9.47)((0.08206 \text{L \cdot atm/mol \cdot K})(227 + 273.15 K))^{(1-3)} = 5.62 \times 10^{-4}) \)

8.

a.

\( (K = \frac{[\text{S}_2]}{[\text{H}_2]^2 [\text{S}]^2} = \frac{[1.00 \times 10^{-3}, M]^2[1.20 \times 10^{-3}, M]}{[3.32 \times 10^{-3}, M]^2} = 1.09 \times 10^{-4}) \)

\( (K_p = K(RT)^{(\Delta n)} = (1.09 \times 10^{-4})((0.08206 \text{L \cdot atm/mol \cdot K})(1065 + 273.15 K))^{(3-2)} = 1.20 \times 10^{-2}) \)

b.

\( (K = [\text{OH}^{-}]^2 [\text{Ba}^{2+}] = [0.2136, M]^2[0.1068, M] = 4.87 \times 10^{-3}) \)

\( ([\text{OH}^{-}] = 0.0534, \, \text{mol/} \text{OH}^{-} \times \frac{1, \text{mol/} \text{OH}^{-}}{0.25, \text{L}} = 0.2136, M) \)

\( ([\text{Ba}^{2+}] = 0.0267, \, \text{mol/} \text{Ba}^{2+} \times \frac{1, \text{mol/} \text{Ba}^{2+}}{0.25, \text{L}} = 0.1068, M) \)

\( (K_p = K(RT)^{(\Delta n)} = (4.87 \times 10^{-3})((0.08206 \text{L \cdot atm/mol \cdot K})(25 + 273.15 K))^{(3-1)} = 2.92) \)

9.

a.

\( (K = \frac{[\text{Cl}][\text{Cl}^-]^2}{[\text{NOCl}]^2} = 4.59 \times 10^{-4}) \)

\( (K_p = K(RT)^{(\Delta n)} = (4.59 \times 10^{-4})((0.08206 \text{L \cdot atm/mol \cdot K})(500 K))^{(3-2)} = 1.88 \times 10^{-2}) \)

b.

\( (K = \frac{[\text{Cl}_2][\text{Cl}]}{[\text{Cl}_2]^2}[\text{Cl}^-] = \frac{[9.80 \times 10^{-2}, M]}{[4.77 \times 10^{-1}, M][7.28 \times 10^{-4}, M]} \)

10
\(10^{-3}\,\text{M}\) = 28.2

\(\left[\text{PCl}_5\right] = 10.2\,\text{g}\,\text{PCl}_5 \times \frac{1\,\text{mol}\,\text{PCl}_5}{208.2388\,\text{g}\,\text{PCl}_5} \times \frac{1}{0.5\,\text{L}} = 9.80 \times 10^{-2}\,\text{M}\)

\(\left[\text{Cl}_2\right] = 16.9\,\text{g}\,\text{Cl}_2 \times \frac{1\,\text{mol}\,\text{Cl}_2}{70.9\,\text{g}\,\text{Cl}_2} \times \frac{1}{0.5\,\text{L}} = 4.77 \times 10^{-1}\,\text{M}\)

\(\left[\text{PCl}_3\right] = 0.500\,\text{g}\,\text{PCl}_3 \times \frac{1\,\text{mol}\,\text{PCl}_3}{137.33\,\text{g}\,\text{PCl}_3} \times \frac{1}{0.5\,\text{L}} = 7.28 \times 10^{-3}\,\text{M}\)

\(K_p = K(RT)^\Delta n = (28.2)((0.08206\,\text{L} \cdot \text{atm}/\text{mol} \cdot \text{K})(250+273.15)\text{K})^{1-2} = 6.57 \times 10^{-1}\)

10. \(2\,\text{SO}_2\,(g) + \text{O}_2\,(g) + 2\,\text{Na}_2\text{CO}_3\,(s) \rightleftharpoons 2\,\text{CO}_2\,(g) + 2\,\text{Na}_2\text{SO}_4\,(s)\)]

11. \(\text{NH}_3\,(g) + \frac{5}{4}\,\text{O}_2\,(g) \rightleftharpoons \text{NO}\,(g) + \frac{3}{2}\,\text{H}_2\text{O}\,(g)\)]

12. If the reaction rate of the forward reaction is doubled the magnitude of the equilibrium constant is doubled. If the reaction rate of the reverse reaction for the overall reaction is described by a factor of 3 the magnitude of the equilibrium constant is increased by a factor of 3.

13. \(K' = \dfrac{[\text{H}_2\text{S}]^2}{[\text{H}_2][\text{S}_2]^\frac{1}{2}} = 1.08 \times 10^7\)
   a. \(K = \dfrac{[\text{H}_2\text{S}]^4}{[\text{H}_2]^4[\text{S}_2]^2} = (1.08 \times 10^7)^4[\text{H}_2]^4[\text{S}_2]^2 = 3.29 \times 10^{13}\)  
   b. \(K = \dfrac{[\text{H}_2\text{S}]^4}{[\text{H}_2]^4[\text{S}_2]^2} = (1.08 \times 10^7)^4[\text{H}_2]^4[\text{S}_2]^2 = 1.17 \times 10^{14}\)  
   c. \(K = \dfrac{[\text{H}_2\text{S}]^4}{[\text{H}_2]^4[\text{S}_2]^2} = (1.08 \times 10^7)^4[\text{H}_2]^4[\text{S}_2]^2 = 3.04 \times 10^{14}\)

15.3: Interpreting & Working with Equilibrium Constants

Conceptual Problems

1. Describe how to determine the magnitude of the equilibrium constant for a reaction when not all concentrations of the substances are known.

2. Calculations involving systems with very small or very large equilibrium constants can be dramatically simplified by making certain assumptions about the concentrations of products and reactants. What are these assumptions when \(K\) is (a) very large and (b) very small? Illustrate this technique using the system \(\text{A} + 2\text{B} \rightleftharpoons \text{C}\) for which you are to calculate the concentration of the product at equilibrium starting with only \text{A} and \text{B}. Under what circumstances should simplifying assumptions not be used?

Conceptual Answers

1. The magnitude of the equilibrium constant for a reaction depends on the form in which the chemical reaction is written. For example, writing a chemical reaction in different but chemically equivalent forms causes the magnitude of the equilibrium constant to be different but can be related by comparing their respective magnitudes.

2. a. When \(K\) is very large the reactants are converted almost entirely to products, so we can assume that the reaction proceeds 100% to completion.
\( K = \frac{[C]}{[A][B]^2} = \frac{[C]}{\text{very small}} = \frac{1}{0} = \infty \rightarrow [C] = \infty \)

b. When \( K \) is very small the reactants do not tend to form products readily, and the equilibrium lies to the left as written, favoring the formation of the reactants.

\( K = \frac{[C]}{[A][B]^2} = \frac{\text{very small} \times [C]}{[A][B]^2} = \frac{0}{1} = 0 \rightarrow [C] = 0 \)

Simplifying assumptions should not be used if the equilibrium constant is not known to be very large or very small.

**Numerical Problems**

*Please be sure you are familiar with the quadratic formula before proceeding to the Numerical Problems.*

1. In the equilibrium reaction \( A + B \rightleftharpoons C \), what happens to \( K \) if the concentrations of the reactants are doubled? tripled? Can the same be said about the equilibrium reaction \( 2A \rightleftharpoons B + C \)?

2. The following table shows the reported values of the equilibrium \( P_{O_2} \) at three temperatures for the reaction \( Ag_2O(s) \rightleftharpoons 2Ag(s) + \frac{1}{2}O_2(g) \), for which \( \Delta H^\circ = 31 \text{ kJ/mol} \). Are these data consistent with what you would expect to occur? Why or why not?

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>( P_{O_2} ) (mmHg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>182</td>
</tr>
<tr>
<td>184</td>
<td>143</td>
</tr>
<tr>
<td>191</td>
<td>126</td>
</tr>
</tbody>
</table>

3. Given the equilibrium system \( N_2O_4(g) \rightleftharpoons 2NO_2(g) \), what happens to \( K_p \) if the initial pressure of \( N_2O_4 \) is doubled? If \( K_p \) is \( 1.7 \times 10^{-4} \) at 2300°C, and the system initially contains 100% \( N_2O_4 \) at a pressure of \( 2.6 \times 10^2 \) atm, what is the equilibrium pressure of each component?

4. At 430°C, 4.20 mol of \( HI \) in a 9.60 L reaction vessel reaches equilibrium according to the following equation:

\( H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \)

At equilibrium, \([H_2] = 0.047 \text{ M}\) and \([HI] = 0.345 \text{ M}\). What are \( K \) and \( K_p \) for this reaction?

5. Methanol, a liquid used as an automobile fuel additive, is commercially produced from carbon monoxide and hydrogen at 300°C according to the following reaction:

\( CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g) \)

with \( K_p = 1 \times 10^{-4} \times 300°C \). If 56.0 g of \( CO \) is mixed with excess hydrogen in a 250 mL flask at this temperature, and the hydrogen pressure is continuously maintained at 100 atm, what would be the maximum percent yield of methanol? What pressure of hydrogen would be required to obtain a minimum yield of methanol of 95% under these conditions?

6. Starting with pure \( A \), if the total equilibrium pressure is 0.969 atm for the reaction \( A(s) \rightleftharpoons 2B(g) + C(g) \), what is \( K_p \)?

7. The decomposition of ammonium carbamate to \( NH_3 \) and \( CO_2 \) at 40°C is written as

\( NH_4CO_2 \rightleftharpoons NH_3(g) + CO_2(g) \)

If the partial pressure of \( NH_3 \) at equilibrium is 0.242 atm, what is the equilibrium partial pressure of \( CO_2 \)? What is the total gas pressure of the system? What is \( K_p \)?

8. At 375 \( K \), \( K_p \) for the reaction \( SO_2Cl_2 \rightleftharpoons SO_2(g) + Cl_2(g) \) is 2.4, with pressures expressed in atmospheres. At 303 \( K \), \( K_p \) is \( 2.9 \times 10^{-2} \).
a. What is $K$ for the reaction at each temperature?

b. If a sample at 375 K has 0.100 M $\text{Cl}_2$ and 0.200 M $\text{SO}_2$ at equilibrium, what is the concentration of $\text{SO}_2\text{Cl}_2$?

c. If the sample given in part b is cooled to 303 K, what is the pressure inside the bulb?

9. For the gas-phase reaction $a\,\text{A} \rightleftharpoons b\,\text{B}$, show that $K_p = K(RT)^{\Delta n}$ assuming ideal gas behavior.

10. For the gas-phase reaction $\text{I}_2 \rightleftharpoons 2\,\text{I}$, show that the total pressure is related to the equilibrium pressure by the following equation: $P_T = \sqrt{K_p P_{\text{I}_2} + P_{\text{I}_2}}$.

11. Experimental data on the system $\text{Br}_2(\text{l}) \rightleftharpoons \text{Br}_2(\text{aq})$ are given in the following table. Graph $\text{Br}_2(\text{aq})$ versus moles of $\text{Br}_2(\text{l})$ present; then write the equilibrium constant expression and determine $K$.

<table>
<thead>
<tr>
<th>Grams $\text{Br}_2$ in 100 mL Water</th>
<th>$[\text{Br}_2]$ (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>0.0626</td>
</tr>
<tr>
<td>2.5</td>
<td>0.156</td>
</tr>
<tr>
<td>3.0</td>
<td>0.188</td>
</tr>
<tr>
<td>4.0</td>
<td>0.219</td>
</tr>
<tr>
<td>4.5</td>
<td>0.219</td>
</tr>
</tbody>
</table>

12. Data accumulated for the reaction $\text{n-butane(g)} \rightleftharpoons \text{isobutane(g)}$ at equilibrium are shown in the following table. What is the equilibrium constant for this conversion? If 1 mol of n-butane is allowed to equilibrate under the same reaction conditions, what is the final number of moles of n-butane and isobutane?

<table>
<thead>
<tr>
<th>Moles n-butane</th>
<th>Moles Isobutane</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>1.25</td>
</tr>
<tr>
<td>1.0</td>
<td>2.5</td>
</tr>
<tr>
<td>1.50</td>
<td>3.75</td>
</tr>
</tbody>
</table>

13. Solid ammonium carbamate ($NH_4CO_2NH_2\,(s)$) dissociates completely to ammonia and carbon dioxide when it vaporizes: $\text{NH}_4\text{CO}_2\text{NH}_2\,(s) \rightleftharpoons 2\,\text{NH}_3\,(g)+\text{CO}_2\,(g)$ At 25°C, the total pressure of the gases in equilibrium with the solid is 0.116 atm. What is the equilibrium partial pressure of each gas? What is $\langle K \rangle_p$? If the concentration of $\text{CO}_2\,(g)$ is doubled and then equilibrates to its initial equilibrium partial pressure +x atm, what change in the $\langle \text{NH}_3\,(g) \rangle$ concentration is necessary for the system to restore equilibrium?

14. The equilibrium constant for the reaction $\text{COCl}_2\,(g) \rightleftharpoons \text{CO}\,(g)+\text{Cl}_2\,(g)$ is $K = 2.2 \times 10^{-10}$ at 100°C. If the initial concentration of $\text{COCl}_2\,(g)$ is $3.05 \times 10^{-4}$ M, what is the partial pressure of each gas at equilibrium at 100°C? What assumption can be made to simplify your calculations?

15. Aqueous dilution of $\text{IO}_4^−\,(aq)$ results in the following reaction: $\text{IO}_4^−\,(aq)+2\,\text{H}_2\,(aq)\rightleftharpoons \text{H}_4\text{IO}_6\,(aq)$, with $K = 3.5 \times 10^{-2}$. If you begin with 50 mL of a 0.896 M solution
of \((IO_4^-)\) that is diluted to 250 mL with water, how many moles of \((H_4IO_6^-)\) are formed at equilibrium?

16. Iodine and bromine react to form \((IBr)\), which then sublimes. At 184.4°C, the overall reaction proceeds according to the following equation: \(2I_2(g) + Br_2(g) \rightarrow 2IBr(g)\) with \(K_p = 1.2 \times 10^2\). If you begin the reaction with 7.4 g of \((I_2)\) vapor and 6.3 g of \((Br_2)\) vapor in a 1.00 L container, what is the concentration of \((IBr(g))\) at equilibrium? What is the partial pressure of each gas at equilibrium? What is the total pressure of the system?

17. For the reaction \(2C(s) + N_2(g) + 5H_2 \rightarrow 2CH_3NH_2(g)\) with \(K = 1.8 \times 10^{-6}\). If you begin the reaction with 1.0 mol of \((N_2)\), 2.0 mol of \((H_2)\), and sufficient \((C(s))\) in a 2.00 L container, what are the concentrations of \((N_2)\) and \((CH_3NH_2)\) at equilibrium? What happens to \((K)\) if the concentration of \((H_2)\) is doubled?

**Numerical Answers**

1. In both cases, the equilibrium constant will remain the same as it does not depend on the concentrations.

2. No, the data is not consistent with what I would expect to occur because enthalpy is positive indicating that the reaction is endothermic thus heat is on the left side of the reaction. As the temperature is raised \((P(O_2))\) would be expected to increase to counteract the constraint.

3. If the initial pressure of \((N_2O_4)\) was doubled then \((K_p)\) is one half of the original value.

\[
\frac{2.6 \times 10^2}{2.6 \times 10^2 - x} = 2.6 \times 10^{-1} = \frac{(2x)^2}{2.6 \times 10^2 - x} \rightarrow 2x = 44.2 - 0.17x \rightarrow x \approx 3.303 \text{ atm}
\]

\[P_{N_2O_4} = 2.6 \times 10^2 - 3.303 = 2.6 \times 10^2 \text{ atm}\]

\[P_{NO_2} = 2(3.303) = 6.6 \text{ atm}\]

4.

\[
K = \frac{[HI]^2}{[H_2][I_2]} = \frac{0.345}{(0.047)(0.047)} = 157
\]

\[
K_p = (RT)^{\Delta n} = (157)(0.08206 \times \text{molar concentration of } K)(430 + 273.15) = 157
\]

5.

\[
\text{Maximum Percent Yield} = \frac{\text{Actual}}{\text{Theoretical}} \times 100\% = \frac{212.593}{376.127} \times 100\% = 56.52\%
\]
\[ PV = nRT \rightarrow P = \frac{1.999 \text{ mol}}{28.01 \text{ g CO}} \times 376.127 \text{ atm} \]
\[(\text{CO}) = 56.0 \text{ g CO} \times \frac{1 \text{ mol CO}}{28.01 \text{ g CO}} = 1.999 \text{ mol CO} \]
\[ K_p = \frac{P_{CH_3OH}}{(P_{CO})(P_{H_2})^2} \rightarrow 1.3 \times 10^{-4} = \frac{x}{(376.02 - x)(100^2)} \]
\[ 1.3 = \frac{x}{376.07 - x} \rightarrow 488.965 - 1.3x = x \rightarrow 488.965 = 2.3x \rightarrow x = 212.593 \text{ atm} \]

\[ K_p = \frac{(P_{CH_3OH})}{(P_{CO})(P_{H_2})^2} \rightarrow 1.3 \times 10^{-4} = \frac{357.320}{(376.127 - 357.320)(P_{H_2})^2} \rightarrow 0.002444(P_{H_2})^2 = 357.320 \rightarrow (P_{H_2}) = 382.300 \approx 3.8 \times 10^2 \text{ atm} \]

\[ \text{Minimum Percent Yield} = \frac{\text{Actual}}{\text{Theoretical}} \times 100\% \rightarrow 95\% = \frac{x}{376.127} \times 100\% \rightarrow x = 357.320 \text{ atm} \]

<table>
<thead>
<tr>
<th>(CO)</th>
<th>(2H₂, H₃O⁺)</th>
<th>(CH₃OH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>376.127</td>
<td>100</td>
</tr>
<tr>
<td>C</td>
<td>-x</td>
<td>-2x</td>
</tr>
<tr>
<td>E</td>
<td>376.127-x</td>
<td>100 (maintained)</td>
</tr>
</tbody>
</table>

6. \[ K_p = \frac{(P_B)^2(P_C)}{P_A} = \frac{[2x]^2[x]}{[0.969-x]} = \frac{4x^3}{0.969-x} \]

<table>
<thead>
<tr>
<th>(A)</th>
<th>(2B)</th>
<th>(C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0.969</td>
<td>0</td>
</tr>
<tr>
<td>C</td>
<td>-x</td>
<td>+2x</td>
</tr>
<tr>
<td>E</td>
<td>0.969-x</td>
<td>2x</td>
</tr>
</tbody>
</table>

7.
\[ P_{(CO)_2} = P_{(tot)} - P_{(NH_3)} = P_{(tot)} - 0.242, \text{ atm} \]
\[ P_{(tot)} = P_{(NH_3)} + P_{(CO_2)} = 0.242, \text{ atm} + P_{(CO_2)} \]
\[ K_p = (P_{(NH_3)})^2(P_{(CO_2)}) = (0.242, \text{ atm})^2(P_{(CO_2)}) \]

8. a.
At $375\,K$: $K_p = (RT)^{Δn}$ → $K = \frac{K_p}{(RT)^{Δn}} = \frac{2.9 \times 10^{-2}}{(0.08206 \frac{L \cdot atm}{mol \cdot K})(375\,K)^{2-1}} = 7.80 \times 10^{-2}$

At $303\,K$: $K_p = (RT)^{Δn}$ → $K = \frac{K_p}{(RT)^{Δn}} = \frac{2.9 \times 10^{-2}}{(0.08206 \frac{L \cdot atm}{mol \cdot K})(303\,K)^{2-1}} = 1.17 \times 10^{-3}$

b. $K = \frac{[SO_2][Cl_2]}{[SO_2Cl_2]} → [SO_2Cl_2] = \frac{[0.200\,M][0.100\,M]}{7.80 \times 10^{-2}} = 2.56 \times 10^{-1}\,M$

c. If the sample given in part b is cooled to $303\,(K)$, the pressure inside the bulb would decrease.

9. $P_T = P_I + P_{I_2} = \sqrt{K_pP_{I_2}} + P_{I_2}$

10. $P_T = P_I + P_{I_2} = \sqrt{K_pP_{I_2}} + P_{I_2}$

11. The graph should be a positive linear correlation.
12. \( K = \frac{[\text{isobutane}]}{[\text{n-butane}]} = \frac{x}{1-x} \)

\[
\begin{array}{c|c|c}
\text{(n-butane)} & \text{(isobutane)} \\
\hline
I & 1 & 0 \\
C & -x & +x \\
E & 1-x & x \\
\end{array}
\]

13.
\( P_{\text{NH}_3} = 2x = 2(0.0387) = 7.73 \times 10^{-2}\, \text{atm} \)
\( P_{\text{CO}_2} = x = 3.87 \times 10^{-2}\, \text{atm} \)
\( K_p = (P_{\text{NH}_3})^2(P_{\text{CO}_2}) = (2x)^2(x) = 4x^3 = 4(0.0387)^3 = 2.32 \times 10^{-4} \)
\( P_{\text{tot}} = P_{\text{NH}_3} + P_{\text{CO}_2} \rightarrow 0.116 = 2x + x \rightarrow 0.116 = 3x \rightarrow x = 0.0387 \)

If the concentration of \( P_{\text{CO}_2} \) is doubled and then equilibrates to its initial equilibrium partial pressure +x atm, the concentration of \( P_{\text{NH}_3} \) should also be doubled for the system to restore equilibrium.

\[
\begin{array}{c|c|c}
\text{(NH}_3\text{)(3))} & \text{(CO}_2\text{)(2))} \\
\hline
I & 0 & 0 \\
C & 2x & x \\
E & 2x & x \\
\end{array}
\]

14.
\( P_{\text{COCl}_2} = 9.34 \times 10^{-2} - x = 9.34 \times 10^{-2} - 9.34 \times 10^{-22} = 9.34 \times 10^{-2}\, \text{atm} \)
\( P_{\text{CO}} = x = 9.34 \times 10^{-22}\, \text{atm} \)
\( P_{\text{Cl}_2} = x = 9.34 \times 10^{-22}\, \text{atm} \)

Assume that the equilibrium mainly lies on the reactants side because the \( K_p \) value is less than 1.

\( K_p = \frac{(P_{\text{CO}})(P_{\text{Cl}_2})}{(P_{\text{COCl}_2})} \rightarrow 2.2 \times 10^{-10} = \frac{x^2}{9.34 \times 10^{-2} - x} \rightarrow 2.0548 \times 10^{-11} - 2.2 \times 10^{-10}x = x^2 \rightarrow x^2 + 2.2 \times 10^{-10}x - 2.0548 \times 10^{-11} = 0 \rightarrow x = 9.34 \times 10^{-22} \)

\( PV = nRT \rightarrow P = \frac{\text{V}}{\text{mol}} \times 3.05 \times 10^{-3} \times 0.08206 \times \text{L/atom} \times \text{mol} \times \text{mol}^{-1} \)
\[
\frac{(COCl_2)}{(CO)} = 9.34 \times 10^{-2}
\]

<table>
<thead>
<tr>
<th></th>
<th>(\text{(COCl}_2\text{)})</th>
<th>(\text{(CO)})</th>
<th>(\text{(Cl}_2\text{)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>(9.34 \times 10^{-2})</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C</td>
<td>(-x)</td>
<td>(+x)</td>
<td>(+x)</td>
</tr>
<tr>
<td>E</td>
<td>(9.34 \times 10^{-2} - x)</td>
<td>(x)</td>
<td>(x)</td>
</tr>
</tbody>
</table>

15. \([\text{H}_4\text{IO}_6^-]=x=1.6 \times 10^{-3}\text{\,mol}\) \(K\) \(\frac{[\text{H}_4\text{IO}_6^-]}{[\text{IO}_4^-]} \rightarrow 3.5 \times 10^{-2} = \frac{x}{(0.0448-x)} \rightarrow x=1.568 \times 10^{-3}\)

\([\text{IO}_4^-]: 50\text{\,mL} \times \frac{1\text{\,L} \text{IO}_4^-}{1,000\text{\,mL} \text{IO}_4^-} \times \frac{0.896\text{\,mol} \text{IO}_4^-}{1\text{\,L} \text{IO}_4^-} = 0.0448\text{\,mol}\)

16. \(PV=nRT \rightarrow \frac{P}{RT} = \frac{n}{V} \rightarrow 3.5 \times 10^{-1} \text{\,M}\) \(P = \frac{nRT}{V} = (2.92 \times 10^{-2}\text{\,M})(0.08206\frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}})(184.4+273.15)\text{\,K} = 1.096\text{\,atm}\)

\([\text{H}_2\text{I}_2\text{Br}_2]=x=1.2 \times 10^{-2}\) \(K_p= \frac{(P_{\text{I}_2})(P_{\text{Br}_2})}{(P_{\text{H}_2\text{I}_2\text{Br}_2})^2} \rightarrow 1.2 \times 10^{-2} = \frac{2x}{(1.096-x)(1.479-x)} = \frac{2x}{x^2-2.575x+1.62098} \rightarrow 0.012x^2-0.0309x+0.0194518=2x \rightarrow 0.012x^2-2.0309+0.0194518=0 \rightarrow x=12.9468\)

\([\text{I}_2\text{Br}_2]=7.4\text{\,g} \times \frac{1\text{\,mol} \text{I}_2\text{Br}_2}{253\text{\,g} \text{I}_2\text{Br}_2} \times \frac{1}{1.00\text{\,L}} = 2.92 \times 10^{-2}\text{\,M}\)

\([PV=nRT \rightarrow \text{P}=\frac{nRT}{V} = (3.94 \times 10^{-2}\text{\,M})(0.08206\frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}})(184.4+273.15)\text{\,K} = 1.479\text{\,atm}\)
\([\text{Br}_2] = 6.3 \text{ g} \text{Br}_2 \times \frac{1 \text{ mol} \text{Br}_2}{159.808 \text{ g} \text{Br}_2} = 3.94 \times 10^{-2} \text{ M}\)

17.

\([\text{N}_2] = 0.5 - 12x = 0.5 - 12(0.000471330) = 0.494 \text{ M}\)

\([\text{CH}_3\text{NH}_2] = 2x = 2(0.000471330) = 9.43 \times 10^{-4} \text{ M}\)

If the concentration of H\(_2\) is doubled, then \(K = \frac{[\text{CH}_3\text{NH}_2]^2}{[\text{N}_2][\text{H}_2]^5} = \frac{(9.43 \times 10^{-4})^2}{(0.494)(1.998)^5} = 5.65 \times 10^{-8}\)

\(2 \times [\text{H}_2] = 2(1.0 - 2.5x) = 2(1.0 - 2.5(0.000471330)) = 1.998 \text{ M}\)

\(K = \frac{[\text{CH}_3\text{NH}_2]^2}{[\text{N}_2][\text{H}_2]^5} \rightarrow 1.8 \times 10^{-6} = \frac{(2x)^2}{(0.5-x)(1.0-5x)^5} \rightarrow x = 0.000471330 \text{ M}\)

\(\begin{array}{cccc}
\text{(Cl)} & \text{(N}_2\text{)} & \text{(H}_2\text{)} & \text{(CH}_3\text{NH}_2\text{)} \\
\text{I} & - & 0.5 & 1.0 & 0 \text{ } \text{ } \text{ } \\
\text{C} & - & -x & -5x & 2x \text{ } \text{ } \text{ } \\
\text{E} & - & 0.5-x & 1.0-5x & 2x \text{ } \text{ } \text{ } \\
\end{array}\)

\([\text{N}_2] = 1.00 \text{ mol} \text{N}_2 \times \frac{1}{2.00 \text{ L}} = 0.5 \text{ M}\)

\([\text{H}_2] = 2.00 \text{ mol} \text{H}_2 \times \frac{1}{2.00 \text{ L}} = 1.0 \text{ M}\)

15.4: Heterogeneous Equilibria

15.5: Calculating Equilibrium Constants

15.6: Applications of Equilibrium Constants

Conceptual Problems

1. During a set of experiments, graphs were drawn of [reactants] versus [products] at equilibrium. Using Figure 15.8 and Figure 15.9 as your guides, sketch the shape of each graph using appropriate labels.

   a. \(\text{(H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{O}(g))\)

   b. \(\text{(2\text{MgO(s)} \rightleftharpoons \text{Mg}(s)+\text{O}_2(g))}\)
2. Write an equilibrium constant expression for each reaction system. Given the indicated changes, how must the concentration of the species in bold change if the system is to maintain equilibrium?

a. \(2\,\text{NaHCO}_3\,(s) \rightleftharpoons Na_2\text{CO}_3\,(s) + CO_2\,(g)+ H_2O\,(g)\): \([CO_2]\) is doubled.

b. \(N_2F_4\,(g) \rightleftharpoons 2\,NF_2\,(g)\): \([NF_2]\) is decreased by a factor of 2.

c. \(H_2\,(g) + I_2\,(g) \rightleftharpoons 2\,HI\,(g)\): \([I_2]\) is doubled.

3. Write an equilibrium constant expression for each reaction system. Given the indicated changes, how must the concentration of the species in bold change if the system is to maintain equilibrium?

a. \(CS_2\,(g) + 4\,H_2\,(g) \rightleftharpoons CH_4\,(g) + 2\,H_2S\,(g)\): \([CS_2]\) is doubled.

b. \(PCl_5\,(g) \rightleftharpoons PCl_3\,(g) + Cl_2\,(g)\): \([Cl_2]\) is decreased by a factor of 2.

c. \(4\,NH_3\,(g) + 5\,O_2\,(g) \rightleftharpoons 4\,NO\,(g) + 6\,H_2O\,(g)\): \([NO]\) is doubled.

**Conceptual Answer**

1. 

a. According to Figure 15.8, we could obtain a graph with the x-axis labeled \([H_2O]\,(l)\,(M)\) and y-axis labeled \([H_2O]\,(g)\,(M)\). The graph should have a positive linear correlation. For any equilibrium concentration of \([H_2O]\,(g)\), there is only one equilibrium \([H_2O]\,(l)\). Because the magnitudes of the two concentrations are directly proportional, a large \([H_2O]\,(g)\) at equilibrium requires a large \([H_2O]\,(l)\) and vice versa. In this case, the slope of the line is equal to \(1/(K)\).

b. According to Figure 15.9, we could obtain a graph with the x-axis labeled \([O2]\,(M)\) and y-axis labeled \([MgO]\,(M)\). Because \([O_2]\,(g)\) is the only one in gaseous form, the graph would depend on the concentration of \([O_2]\).

c. According to Figure 15.8, we could obtain a graph with the x-axis labeled \([O_3]\,(M)\) and y-axis labeled \([O2]\,(M)\). The graph should have a positive linear correlation. For every \([3\,O_2]\,(g)\) there is \([2\,O_3]\,(g)\). Because the magnitudes of the two concentrations are directly proportional, a large \([O_3]\,(g)\) at equilibrium requires a large \([O_2]\,(g)\) and vice versa. In this case, the slope of the line is equal to \(1/(K)\).

d. According to figure 15.8, we could obtain a graph with the x-axis labeled \([O2]\,(M)\) and y-axis labeled \([SO2]\,(M)\). The graph should have a positive linear correlation. For every \([3\,O_2]\,(g)\) there is \([2\,SO_2]\,(g)\). Because the magnitudes of the two concentrations are directly proportional, a large \([O_2]\,(g)\) at equilibrium requires a large \([SO_2]\,(g)\) and vice versa. In this case, the slope of the line is equal to \(1/(K)\).

2. 

a.
If \([CO_2]\) is doubled, \([H_2O]\) should be halved if the system is to maintain equilibrium.

b.

\[
K = \frac{[NF_2]^2}{[N_2F_4]}
\]

If \([NF_2]\) is decreased by a factor of 2, then \([N_2F_4]\) must also be decreased by a factor of 2 if the system is to maintain equilibrium.

c.

\[
K = \frac{[HI]^2}{[H_2][I_2]}
\]

If \([HI]\) is doubled then \([H_2][I_2]\) must also be doubled if the system is to maintain equilibrium.

3.

a.

\[
K = \frac{[CH_4][H_2S]^2}{[CS_2][H_2]^4}
\]

If \([CS_2]\) is doubled then \([H_2]\) must be decreased by a factor of \(2\sqrt{4} \approx 1.189\) if the system is to maintain equilibrium.

b.

\[
K = \frac{[PCl_3]}{[Cl_2][PCl_5]}
\]

If \([Cl_2]\) is halved then \([PCl_5]\) must also be halved if the system is to maintain equilibrium.

c.

\[
K = \frac{[NO]^4[H_2O]^6}{[NH_3][O_2]^5}
\]

If \([NO]\) is doubled then \([H_2O]\) must also be multiplied by \(22/3 \approx 1.587\) if the system is to maintain equilibrium.

---

**Numerical Problems**

1. The data in the following table were collected at 450°C for the reaction \(N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)\):

<table>
<thead>
<tr>
<th>P (atm)</th>
<th>(NH_3)</th>
<th>(N_2)</th>
<th>(H_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 (equilibrium)</td>
<td>1.740</td>
<td>6.588</td>
<td>21.58</td>
</tr>
<tr>
<td>P (atm)</td>
<td>(\langle \text{NH}_3 \rangle)</td>
<td>(\langle \text{N}_2 \rangle)</td>
<td>(\langle \text{H}_2 \rangle)</td>
</tr>
<tr>
<td>---------</td>
<td>----------------</td>
<td>----------------</td>
<td>----------------</td>
</tr>
<tr>
<td>100</td>
<td>15.20</td>
<td>19.17</td>
<td>65.13</td>
</tr>
<tr>
<td>600</td>
<td>321.6</td>
<td>56.74</td>
<td>220.8</td>
</tr>
</tbody>
</table>

The reaction equilibrates at a pressure of 30 atm. The pressure on the system is first increased to 100 atm and then to 600 atm. Is the system at equilibrium at each of these higher pressures? If not, in which direction will the reaction proceed to reach equilibrium?

2. For the reaction \(\text{A} \rightleftharpoons \text{B} + \text{C}\), \(K\) at 200°C is 2.0. A 6.00 L flask was used to carry out the reaction at this temperature. Given the experimental data in the following table, all at 200°C, when the data for each experiment were collected, was the reaction at equilibrium? If it was not at equilibrium, in which direction will the reaction proceed?

<table>
<thead>
<tr>
<th>Experiment</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.50 M</td>
<td>2.50 M</td>
<td>2.50 M</td>
</tr>
<tr>
<td>2</td>
<td>1.30 atm</td>
<td>1.75 atm</td>
<td>14.15 atm</td>
</tr>
<tr>
<td>3</td>
<td>12.61 mol</td>
<td>18.72 mol</td>
<td>6.51 mol</td>
</tr>
</tbody>
</table>

3. The following two reactions are carried out at 823 K:

\[\text{CoO(s)} + \text{H}_2(g) \rightleftharpoons \text{Co(s)} + \text{H}_2\text{O(g)} \text{ with } K = 67\]

\[\text{CoO(s)} + \text{CO(g)} \rightleftharpoons \text{Co(s)} + \text{CO}_2(g) \text{ with } K = 490\]

a. Write the equilibrium expression for each reaction.
b. Calculate the partial pressure of both gaseous components at equilibrium in each reaction if a 1.00 L reaction vessel initially contains 0.316 mol of \(\langle \text{H}_2 \rangle\) or \(\langle \text{CO} \rangle\) plus 0.500 mol \(\langle \text{CoO} \rangle\).
c. Using the information provided, calculate Kp for the following reaction: \(\text{H}_2(g) + \text{CO}_2(g) \rightleftharpoons \text{CO(g)} + \text{H}_2\text{O(g)}\)
d. Describe the shape of the graphs of [reactants] versus [products] as the amount of \(\langle \text{CoO} \rangle\) changes.

4. Hydrogen iodide (HI) is synthesized via \(\text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2\text{HI(g)}\), for which \(K_p = 54.5\) at 425°C. Given a 2.0 L vessel containing \(1.12 \times 10^{-2}\) mol of \(\langle \text{H}_2 \rangle\) and \(1.8 \times 10^{-3}\) mol of \(\langle \text{I}_2 \rangle\) at equilibrium, what is the concentration of \(\langle \text{HI} \rangle\)? Excess hydrogen is added to the vessel so that the vessel now contains \(3.64 \times 10^{-1}\) mol of \(\langle \text{H}_2 \rangle\). Calculate \(\langle \text{Q} \rangle\) and then predict the direction in which the reaction will proceed. What are the new equilibrium concentrations?

**Answers**

1. The system is not at equilibrium at each of these higher pressures. To reach equilibrium, the reaction will proceed to the right to decrease the pressure because the equilibrium partial pressure is less than the total pressure.
2.

1. \( K = \frac{[B][C]}{[A]} = \frac{[2.50][2.50]}{[2.50]} = 2.50 \)

2. \( K_p = K(RT)^{\Delta n} \rightarrow K = \frac{K_p}{(RT)^{\Delta n}} = \frac{19.0}{((0.08206 \frac{L \cdot atm}{mol \cdot K})(200+273.15)K)^{2-1}} = 0.49 \)

3. \( K = \frac{[B][C]}{[A]^2} = \frac{(18.72)(6.51)}{12.61} = 9.7 \)

Experiment 1 is about the same as the given \( K \) value and thus considered to be about equilibrium. The second experiment has a \( K \) value that is about 1 so neither the formation of the reactants or products is favored. The third experiment has a \( K \) value that is larger than 1 so the formation of the products is favored.

3.

a. \( K = \frac{[H_2O]}{[H_2]} \)

\( K = \frac{[CO_2]}{[C]} \)

b. \([H_2] = [CO] = 0.316 \text{ mol} \times \frac{1}{1.00 \text{ L}} = 0.316 \text{ M} \)

\([CO_2] = 0.5 \text{ mol} \times \frac{1}{1.00 \text{ L}} = 0.5 \text{ M} \)

Reaction 1:

\( PV = nRT \rightarrow P = \frac{nRT}{V} = (4.65 \times 10^{-3})(0.08206 \frac{L \cdot atm}{mol \cdot K})(823 \text{ K}) = 0.314 \)

\( ((H_2)[2]) = 0.316 - x = 0.316 - 0.311 = 4.65 \times 10^{-3} \)

\( PV = nRT \rightarrow P = \frac{nRT}{V} = (0.311)(0.08206 \frac{L \cdot atm}{mol \cdot K})(823 \text{ K}) = 21.0 \)

\( ([H_2O] = x = 0.311) \)

I 0.316 0

C -x +x
\( K = \frac{[\text{H}_2\text{O}]}{[\text{H}_2]} \rightarrow 67 = \frac{x}{0.316 - x} \rightarrow x = 0.311 \)

Reaction 2:
\[
P_V = nRT \rightarrow P = \frac{nRT}{V} = \frac{(0.001)(0.08206 \text{L} \cdot \text{atm}/\text{mol} \cdot \text{K})(823 \text{K})}{21.3 \text{atm}} = 6.75 \times 10^{-2} \text{atm}
\]
\[
[\text{CO}] = 0.316 - x = 0.316 - 0.315 = 0.001 \text{M}
\]
\[
P_V = nRT \rightarrow P = \frac{nRT}{V} = \frac{(0.315)(0.08206 \text{L} \cdot \text{atm}/\text{mol} \cdot \text{K})(823 \text{K})}{21.3 \text{atm}} = 21.3 \text{atm}
\]
\[
[\text{CO}_2] = x = 0.315 \text{M}
\]
\[
K = \frac{[\text{CO}_2]}{[\text{CO}]} \rightarrow 490 = \frac{x}{0.316 - x} \rightarrow x = 0.315
\]

c. \( \text{H}_2(g) + \text{CO}_2(g) \rightleftharpoons \text{CO}(g) + \text{H}_2\text{O}(g) \)
\[
K_p = \frac{(P_{\text{CO}})(P_{\text{H}_2\text{O}})}{(P_{\text{H}_2})(P_{\text{CO}_2})} = \frac{(6.75 \times 10^{-2})(21)}{(0.314)(21.3)} = 0.21
\]

d. The shape of the graphs [reactants] versus [products] does not change as the amount of \( \text{CO}_2 \) changes because it is a solid.

4.
\[
P_V = nRT \rightarrow \frac{n}{V} = \frac{P}{RT} \rightarrow \frac{n}{V} = \frac{0.101798}{(0.08206 \text{L} \cdot \text{atm}/\text{mol} \cdot \text{K})((425 + 273.15) \text{K})} = 1.5 \times 10^{-4} \text{M} \cdot \text{HI}
\]
\[
[\text{HI}] = 2x = 2(0.050899) = 0.101798 \text{atm}
\]
\[
K_p = \frac{(P_{\text{HI}})^2}{(P_{\text{H}_2})(P_{\text{I}_2})} \rightarrow 54.5 = \frac{(2x)^2}{(3.2 \times 10^{-1} - x)(5.16 \times 10^{-2} - x)} \rightarrow x = 0.050899 \text{atm}
\]
\(\begin{array}{ccc}
\text{C} & \text{E} \\
\text{(H$_2$)} & \text{(I$_2$)} & \text{(HI)} \\
-x & -x & +2x \\
\end{array}\)

\[(3.2 \times 10^{-1})-x \quad (5.16 \times 10^{-2})-x \quad 2x\]

\[
\begin{align*}
(PV=nRT) \rightarrow P &= \frac{nRT}{V} = \frac{(5.6 \times 10^{-3})(0.08206)}{(425+273.15)(K)} = 3.2 \times 10^{-1}(atm) \\
\text{\([H$_2$]=1.12 \times 10^{-2}\) mol, } H$_2 \text{ times frac{1}{2.0}\text{L}=5.6 \times 10^{-3}(M)} \\
\text{\([I$_2$]=1.8 \times 10^{-3}\) mol, } I$_2 \text{ times frac{1}{2.0}\text{L}=9.0 \times 10^{-4}(M)}
\end{align*}\]

For excess hydrogen:

\[
\begin{align*}
Q &= \frac{\text{[HI]}}{\text{[H$_2$][I$_2$]}} = \frac{1.8 \times 10^{-3}}{(594.410)(1.09 \times 10^{-3})} = 2.8 \times 10^{-3} \\
\text{The reaction will proceed to the right to reach equilibrium.}
\end{align*}\]

\[
\begin{align*}
(PV=nRT) \rightarrow \frac{n}{V} &= \frac{P}{RT} \rightarrow \frac{0.103162}{(0.08206)(425+273.15)\text{K}} = 1.8 \times 10^{-3}(M) \\
\text{\([HI]=2x=2(0.051581)=0.103162\text{atm)} \\
\text{\([H$_2$]=10.427-x=10.427-0.051581=10.375\text{atm)} \\
\text{\([I$_2$]=5.16 \times 10^{-2}-x=5.16 \times 10^{-2}-0.051581=1.9 \times 10^{-5}\text{atm}\)}
\end{align*}\]

\[
\begin{align*}
K_p &= \frac{(P_{HI})^2}{(P_{H$_2$})(P_{I$_2$})} \rightarrow 54.5 = \frac{(2x)^2}{(10.427-x)(5.16 \times 10^{-2}-x)} \\
\text{\(x=0.051581\text{atm)}
\end{align*}\]

\[
\begin{align*}
\text{\([H$_2$]} & 10.427 \text{ \(\times 10^{-2}\times-x=10.427-0.051581=10.375\text{atm}\)} \\
\text{\([I$_2$]} & 5.16 \times 10^{-2}`x=5.16 \times 10^{-2}-0.051581=1.9 \times 10^{-5}\text{atm}\}
\end{align*}\]

\[
\begin{align*}
K_p &= \frac{(P_{HI})^2}{(P_{H$_2$})(P_{I$_2$})} \rightarrow 54.5 = \frac{(2x)^2}{(10.427-x)(5.16 \times 10^{-2}-x)} \\
\text{\(x=0.051581\text{atm)}
\end{align*}\]

\[
\begin{align*}
\text{\([H$_2$]} & 10.427 \text{ \(\times 10^{-2}\times-x=10.427-0.051581=10.375\text{atm}\)} \\
\text{\([I$_2$]} & 5.16 \times 10^{-2}`x=5.16 \times 10^{-2}-0.051581=1.9 \times 10^{-5}\text{atm}\}
\end{align*}\]

\[
\begin{align*}
\text{\([K_p]=\frac{(P_{HI})^2}{(P_{H$_2$})(P_{I$_2$})} \rightarrow 54.5 = \frac{(2x)^2}{(10.427-x)(5.16 \times 10^{-2}-x)} \\
\text{\(x=0.051581\text{atm)}
\end{align*}\]
\[ PV = nRT \quad \rightarrow \quad P = \frac{nRT}{V} = (0.182\text{ M})(0.08206\frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}})((425+273.15)\text{K}) = 10.427\text{ atm} \]

\[ [H_2] = 3.64 \times 10^{-1} \text{ mol H}_2 \times \frac{1}{2.0\text{ L}} = 0.182\text{ M} \]

15.7: Le Chatelier's Principle