A general chemistry Libretexts Textmap organized around the textbook

**Chemistry: The Central Science**

by Brown, LeMay, Busten, Murphy, and Woodward

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These are homework exercises to accompany the Textmap created for "Chemistry: The Central Science" by Brown et al. Complementary General Chemistry question banks can be found for other Textmaps and can be accessed here. In addition to these publicly available questions, access to private problems bank for use in exams and homework is available to faculty only on an individual basis; please contact Delmar Larsen for an account with access permission.
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 concentrations or amounts 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 C(\(^{14}\)C) in a decomposing organism

Conceptual Answer

3. Both forward and reverse reactions occur but at the same rate. Na\(^+\) and Cl\(^-\) ions continuously leave the surface of an NaCl crystal to enter solution, while at the same time Na\(^+\) and Cl\(^-\) ions in solution precipitate on the surface of the crystal.

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. \(2HF_{(g)} \rightleftharpoons H_{2(g)}+F_{2(g)}\)
   b. \(C_{(s)} + 2H_{2(g)} \rightleftharpoons CH_{4(g)}\)
   c. \(\ce{H_2C=CH_{2(g)}} + H_{2(g)} \rightleftharpoons C_2H_{6(g)}\)
   d. \(2Hg_{(l)} + O_{2(g)} \rightleftharpoons 2HgO_{(s)}\)

3. Classify each equilibrium system as either homogeneous or heterogeneous.
   a. \(\text{NH}_4CO_2NH_{2(s)} \rightleftharpoons 2NH_{(g)}+CO_{2(g)}\)
   b. \(\text{C}_{(s)} + O_{2(g)} \rightleftharpoons CO_{2(g)}\)
   c. \(2\text{Mg}_{(s)} + O_{2(g)} \rightleftharpoons 2\text{MgO}_{(s)}\)
d. \(\text{AgCl}_{(s)} \rightleftharpoons \text{Ag}^{+}_{(aq)} + \text{Cl}^{-}_{(aq)}\)

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 \(\text{N}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{NO}_{(g)}\) is carried out at elevated temperatures to drive the reaction toward the formation of 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. \(\text{CO}_{(g)} + \text{H}_2\text{O}_{(g)} \rightleftharpoons \text{CO}_2(g) + \text{H}_2(g)\)
   b. \(\text{PCl}_3(g) + \text{Cl}_2(g) \rightleftharpoons \text{PCl}_5(g)\)
   c. \(\text{SO}_3(g) \rightleftharpoons 3\text{O}_2(g)\)

9. Write the equilibrium constant expressions for \(K\) and \(K_p\) as appropriate for each reaction.
   a. \(\text{2NO}_{(g)} + \text{O}_2(g) \rightleftharpoons 2\text{NO}_2(g)\)
   b. \(\frac{1}{2}\text{H}_2(g) + 12\text{I}_2(g) \rightleftharpoons \text{HI}_{(g)}\)
   c. \(\text{cis-stilbene}_{(soln)} \rightleftharpoons \text{trans-stilbene}_{(soln)}\)

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. \(\text{2S}_{(s)} + 3\text{O}_2(g) \rightleftharpoons 2\text{SO}_3(g)\)
    b. \(\text{C}_{(s)} + \text{CO}_2(g) \rightleftharpoons 2\text{CO}_{(g)}\)
    c. \(\text{2ZnS}_{(s)} + \text{3O}_2(g) \rightleftharpoons 2\text{ZnO}_{(s)} + 2\text{SO}_2(g)\)

12. Write the equilibrium constant expressions for \(K\) and \(K_p\) for each equilibrium reaction.
    a. \(\text{2HgO}_{(s)} \rightleftharpoons 2\text{Hg}_{(l)} + \text{O}_2(g)\)
    b. \(\text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2\text{HI}_{(g)}\)
    c. \(\text{NH}_4\text{CO}_2\text{NH}_2(s) \rightleftharpoons 2\text{NH}_3(g) + \text{CO}_2(g)\)

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

14. For a certain series of reactions, if \(\text{OH}^-\text{HCO}_3^-\text{CO}_3^-=\text{K}_1\) and \(\text{OH}^-\text{H}_2\text{CO}_3\text{CO}_3^-=\text{K}_2\), what is the equilibrium constant expression for the overall reaction? Write the overall equilibrium equation.

15. In the equation for an enzymatic reaction, \(\text{ES}\) represents the complex formed between the substrate \(\text{S}\) and the enzyme protein \(\text{E}\). In the final step of the following oxidation reaction, the product \(\text{P}\) dissociates from the \(\text{ES}_{(2)}\) complex, which regenerates the active enzyme:

    \[
    \text{E} + \text{S} \rightleftharpoons \text{ES} \quad (\text{K}_{1})
    \]
    \[
    \text{ES} + \text{O}_{2} \rightleftharpoons \text{ESO}_2 \quad (\text{K}_{2})
    \]
    \[
    \text{ESO}_2 \rightleftharpoons \text{E} + \text{P} \quad (\text{K}_{3})
    \]

    Give the overall reaction equation and show that \(\text{K} = \text{K}_1 \times \text{K}_2 \times \text{K}_3\).
Conceptual Answers

1. The equilibrium constant for the reaction written in reverse: \( K' = \dfrac{1}{K} \).

3. Each system is heterogeneous.

5. Rapid cooling “quenches” the reaction mixture and prevents the system from reverting to the low-temperature equilibrium composition that favors the reactants.

7. \( K = \dfrac{k_f}{k_r} \)
   \( K = \dfrac{[C]^c[D]^d}{[A]^a[B]^b} \)

9.
   a. \( K = \dfrac{[NO_2]^2}{[NO]^2[O_2]} \) \( K_p = \dfrac{(P_{N_2O})^2}{(P_{NO})^2(P_{O_2})} \)
   b. \( K = \dfrac{[HI]}{[H_2]^{1/2}[I_2]^{1/2}} \) \( K_p = \dfrac{P_{HI}}{(P_{H_2})^{1/2}(P_{I_2})} \)
   c. \( K = \dfrac{[\text{trans-stilbene}]}{[\text{cis-stilbene}]} \)

11.
   a. \( K = \dfrac{[SO_3]^2}{[O_2]^3} \) \( K_p = \dfrac{(P_{SO_3})^2}{(P_{O_2})^3} \)
   b. \( K = \dfrac{[CO]^2}{[CO_2]} \) \( K_p = \dfrac{(P_{CO})^2}{P_{CO_2}} \)
   c. \( K = \dfrac{[SO_2]^2}{[O_2]^3} \) \( K_p = \dfrac{(P_{SO_2})^2}{(P_{O_2})^3} \)

13. At equilibrium, \( [A] = \sqrt{B} \) and \( \Delta n = -1 \) so \( K_p = K(RT)^{\Delta n} = \dfrac{K}{RT} \) and the difference increases as \( T \) increases.

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. \( N_2O_{(g)} \rightleftharpoons 2NO_{(g)} \)
   b. \( \dfrac{1}{2}N_2O_{(g)} \rightleftharpoons NO_{(g)} \)

3. Write the equilibrium constant expression for each reaction.
   a. \( \dfrac{1}{2}N_2_{(g)} + \dfrac{3}{2}H_2_{(g)} \rightleftharpoons NH_{3(g)} \)
   b. \( \dfrac{1}{3}N_2_{(g)} + H_2_{(g)} \rightleftharpoons \dfrac{2}{3}NH_{3(g)} \)

   How are these two expressions mathematically related to the equilibrium constant expression for \( N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \)?

4. Write an equilibrium constant expression for each reaction.
   a. \( C_{(s)} + 2H_2O_{(g)} \rightleftharpoons CO_{2(g)} + 2H_{2(g)} \)
5. Give an equilibrium constant expression for each reaction.
   1. \(2\text{NO}_\text{(g)} + \text{O}_2\text{(g)} \rightleftharpoons 2\text{NO}_2\text{(g)}\)
   2. \([\text{H}_2\text{(g)}] + [\text{Cl}_2\text{(g)}] \rightleftharpoons [\text{HCl}\text{]}\) \[\text{(aq)}\]
   3. \(2\text{SO}_\text{(g)} + 3\text{Cl}_2\text{(g)} \rightleftharpoons 2\text{SO}_3\text{(g)} + 6\text{Cl}_2\text{(g)}\)

6. Calculate \(\langle K \rangle\) and \(\langle K_p \rangle\) 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 \(\text{NO}\) is 1.29 M, \(\text{Br}_2\) is 10.52 M, and \(\text{NOBr}\) is 0.423 M.
   b. \(\text{CO}_\text{(g)} + \text{CO}_2\text{(g)} \rightleftharpoons 2\text{CO}_\text{(g)}\): at 1200 K, a 2.00 L vessel at equilibrium has partial pressures of 93.5 atm \(\text{CO}_2\) and 76.8 atm \(\text{CO}\), and the vessel contains 3.55 g of carbon.

7. Calculate \(\langle K \rangle\) and \(\langle K_p \rangle\) (where applicable) 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°C, a 0.150 M sample of \(\text{N}_2\text{O}_4\) undergoes a decomposition of 0.456%.
   b. \(\text{CO}_2\text{(g)} + \text{OH}^-\text{(aq)} \rightleftharpoons \text{CO}_3\text{OH}^-\text{(aq)}\): at 227°C in a 15.5 L reaction vessel with a total pressure of \(6.71 \times 10^2\) atm \(\text{CO}_2\) and 76.8 atm \(\text{CO}\), and the vessel contains 3.55 g of carbon.

8. Determine \(\langle K \rangle\) and \(\langle K_p \rangle\) (where applicable) for each reaction.
   a. \(\text{H}_2\text{(g)} + \text{S}_2\text{(g)} \rightleftharpoons 2\text{H}_2\text{S}_\text{(g)}\): at 1065°C, an equilibrium mixture consists of \(1.00 \times 10^{-3}\) M \(\text{H}_2\), \(1.20 \times 10^{-3}\) M \(\text{S}_2\), and \(3.32 \times 10^{-3}\) M \(\text{H}_2\text{S}\).
   b. \(\text{Ba}^{2+}\text{(aq)} + \text{OH}^-\text{(aq)} \rightleftharpoons \text{Ba(OH)}^-\text{(aq)}\): 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 \(\langle K \rangle\) and \(\langle K_p \rangle\) (where applicable) for each reaction.
   a. \(\text{NO}_\text{(g)} + \text{Cl}_2\text{(g)} \rightleftharpoons 2\text{NOCl}\text{(g)}\): at 500 K, a 24.3 mM sample of \(\text{NOCl}\) has decomposed, leaving an equilibrium mixture that contains 72.7% of the original amount of \(\text{NOCl}\).
   b. \(\text{Cl}_2\text{(g)} + \text{PCl}_3\text{(g)} \rightleftharpoons \text{PCl}_5\text{(g)}\): at 250°C, a 500 mL reaction vessel contains 16.9 g of \(\text{Cl}_2\) gas, 0.500 g of \(\text{PCl}_3\), and 10.2 g of \(\text{PCl}_5\) at equilibrium.

10. The equilibrium constant expression for a reaction is \([\text{CO}_2]^{2/3}[\text{SO}_2]^{2/3}[\text{O}_2]\). What is the balanced chemical equation for the overall reaction if one of the reactants is \(\text{Na}_2\text{CO}_3\text{(s)}\)?

11. The equilibrium constant expression for a reaction is \(\langle\text{Na}^{2+}\rangle[\text{H}_2\text{O}]^{3/2}[\text{NH}_3][\text{O}_2]^{5/4}\). What is the balanced chemical equation for the overall reaction?

12. Given \(K = k_f/k_r\), 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 \(\text{H}_2\text{(g)} + \text{S}_2\text{(g)} \rightleftharpoons 2\text{H}_2\text{S}_\text{(g)}\) is \(1.08 \times 10^7\) at 700°C. What is the value of the equilibrium constant for the following related reactions?
   a. \(\text{H}_2\text{(g)} + 12\text{S}_2\text{(g)} \rightleftharpoons 2\text{H}_2\text{S}_\text{(g)}\)
   b. \(4\text{H}_2\text{(g)} + 2\text{S}_2\text{(g)} \rightleftharpoons 4\text{H}_2\text{S}_\text{(g)}\)
   c. \(2\text{H}_2\text{S}_\text{(g)} \rightleftharpoons \text{H}_2\text{(g)} + 12\text{S}_2\text{(g)}\)
Numerical Answers

1. \( K = 0.892 \): the concentrations of the products and the reactants are approximately equal at equilibrium so neither is favored; \( K = 3.25 \times 10^8 \): the ratio of the concentration of the products to the reactants at equilibrium is very large so the formation of products is favored; \( K = 5.26 \times 10^{-11} \): the ratio of the concentration of the products to the reactants at equilibrium is very small so the formation of products is not favored.

3.

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

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

5.

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

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

c. \( K = \dfrac{[\text{Ca}^{2+}][\text{Cl}^{-}]^2[\text{P}_{\text{CO}_2}]}{[\text{HOCl}]^2} \)

7.

a. \( K = 1.25 \times 10^{-5} \); \( K_p = 2.39 \times 10^{-4} \)

b. \( K = 9.43 \); \( K_p = 5.60 \times 10^{-3} \)

9.

a. \( K = \dfrac{[\text{Cl}_2][\text{NO}]^2}{[\text{NOCl}]^2} \); \( K_p = 4.59 \times 10^{-4} \); \( K_p = 1.88 \times 10^{-2} \)

b. \( K = \dfrac{[\text{PCl}_5][\text{Cl}_2]}{[\text{PCl}_3][\text{Cl}_2]} \); \( K_p = 0.658 \)

11.

\( \text{NH}_3 + \frac{5}{4} \text{O}_2 \rightarrow \text{NO} + \frac{3}{2} \text{H}_2 \text{O} \)\), which can also be written as follows: \( 4\text{NH}_3(g) + 5\text{O}_2(g) \rightarrow 4\text{NO}(g) + 6\text{H}_2\text{O}(g) \)

1. \( 3.29 \times 10^3 \)

2. \( 1.17 \times 10^{14} \)

3. \( 3.04 \times 10^{-4} \)

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 \( A + 2B \rightleftharpoons C \) for which you are to calculate the concentration of the product at equilibrium starting with only \( A \) and \( B \). Under what circumstances should simplifying assumptions not be used?

### 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 \( Ag_2O_{(s)} \rightleftharpoons 2Ag_{(s)} + 12O_{2(g)} \), for which \( \Delta H^\circ = 31 \) 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 \( 1.7 \times 10^{-1} \) 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, \( [HI] = 0.047\; \text{M} \) 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 \( K_p = 1.3 \times 10^{-4} \). 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 \( NH_4CO_2NH_2(s) \rightleftharpoons 2NH_3(g) + CO_2(g) \). 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 \( SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g) \) 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 \( Cl_2 \) and 0.200 M \( SO_2 \) at equilibrium, what is the concentration of
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 \(\text{aA \rightleftharpoons bB}\), 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: \(P_T = \sqrt{K_pP_{\text{I}_2} + P_{\text{I}_2}}\)

11. Experimental data on the system \(\text{Br}_2 \rightleftharpoons \text{Br}^{-}\) are given in the following table. Graph \(\text{[Br}_2\text{]}\) versus moles of \(\text{Br}_2\) 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\text{]}) (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 \(\text{n-butane(g) \rightleftharpoons isobutane(g)}\) at equilibrium are shown in the following table. What is the equilibrium constant for this conversion? If 1 mol of \(\text{n-butane}\) is allowed to equilibrate under the same reaction conditions, what is the final number of moles of \(\text{n-butane}\) and \(\text{isobutane}\)?

<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 \(\text{NH}_4\text{CO}_2\text{NH}_2\) 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 \(\text{K}_p\)? If the concentration of \(\text{CO}_2\) is doubled and then equilibrates to its initial equilibrium partial pressure \(+x\) atm, what change in the \(\text{NH}_3\) concentration is necessary for the system to restore equilibrium?

14. The equilibrium constant for the reaction \(\text{COCl}_2\rightarrow \text{CO}+\text{Cl}_2\) is \(K_p = 2.2 \times 10^{-10}\) at 100°C. If the initial concentration of \(\text{COCl}_2\) is \(3.05 \times 10^{-3}\;\text{M}\), 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 \(\text{IO}_4^-\) results in the following reaction: \(\text{IO}_4^-\rightarrow \text{IO}_3^-\text{IO}_2^-\text{H}_2\text{O}\) \(\text{H}_4\text{IO}_6\text{aq}\) with \(K = 3.5 \times 10^{-2}\). If you begin with 50 mL of a 0.896 M solution of \(\text{IO}_4^-\) that is diluted to 250 mL with water, how many moles of \(\text{H}_4\text{IO}_6\text{aq}\) are formed at equilibrium?

16. Iodine and bromine react to form \(\text{I}_2\), which then sublimes. At 184.4°C, the overall reaction proceeds according to the following equation: \(\text{I}_2(g)+\text{Br}_2(g) \rightleftharpoons 2\text{IBr}(g)\) with \(K_p = 1.2 \times 10^2\). If you begin the reaction with 7.4 g of \(\text{I}_2\) vapor and 6.3 g of \(\text{Br}_2\) vapor in a 1.00 L container, what is the concentration of
17. For the reaction \( \text{C}_{(s)} + 12\text{N}_{2(g)} + \frac{5}{2}\text{H}_{2(g)} \rightleftharpoons \text{CH}_3\text{NH}_2(g) \) with \( K = 1.8 \times 10^{-6} \). If you begin the reaction with 1.0 mol of \( \text{N}_2 \), 2.0 mol of \( \text{H}_2 \), and sufficient \( \text{C}_{(s)} \) in a 2.00 L container, what are the concentrations of \( \text{N}_2 \) and \( \text{CH}_3\text{NH}_2 \) at equilibrium? What happens to \( K \) if the concentration of \( \text{H}_2 \) is doubled?

15.4: Heterogeneous Equilibria

15.5: Calculating Equilibrium Constants

15.6: Applications of Equilibrium Constants

Conceptual Problems

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. \( 2\text{MgO}_{(s)} \rightleftharpoons 2\text{Mg}_{(s)} + \text{O}_2(g) \)
c. \( 2\text{O}_3(g) \rightleftharpoons 3\text{O}_2(g) \)
d. \( 2\text{PbS}_{(s)} + 3\text{O}_2(g) \rightleftharpoons 2\text{PbO}_{(s)} + 2\text{SO}_2(g) \)

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. \( 2\text{NaHCO}_3(s) \rightleftharpoons \text{Na}_2\text{CO}_3(s) + \text{CO}_2(g) + \text{H}_2\text{O}(g) \): \( [\text{CO}_2] \) is doubled.
b. \( \text{N}_2\text{F}_4(g) \rightleftharpoons 2\text{NF}_2(g) \): \( [\text{NF}] \) is decreased by a factor of 2.
c. \( \text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2\text{HI}(g) \): \( [\text{I}_2] \) is doubled.

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. \( \text{CS}_2(g) + 4\text{H}_2(2g) \rightleftharpoons \text{CH}_4(g) + 2\text{H}_2\text{S}(g) \): \( [\text{CS}_2] \) is doubled.
b. \( \text{PCl}_5(g) \rightleftharpoons \text{PCl}_3(g) + \text{Cl}_2(g) \): \( [\text{Cl}_2] \) is decreased by a factor of 2.
c. \( 4\text{NH}_3(g) + 5\text{O}_2(g) \rightleftharpoons 4\text{NO}_2(g) + 6\text{H}_2\text{O}(g) \): \( [\text{NO}_2] \) is doubled.

Conceptual Answer

3.
a. \(K=\frac{[CH_4][H_2S]^2}{[CS_2][H_2]^4}\); doubling \([CS_2]\) would require decreasing \([H_2]\) by a factor of \(2\sqrt{4} \approx 1.189\).

b. \(K=\frac{[PCl_3]}{[Cl_2][PCl_5]}\); if \([Cl_2]\) is halved, \([PCl_5]\) must also be halved.

c. \(K=\frac{[NO]^4[H_2O]^6}{[NH_3][O_2]^5}\); if \([NO]\) is doubled, \([H_2O]\) is multiplied by \(22/3 \approx 1.587\).

### 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>(\langle NH_3 \rangle)</th>
<th>(\langle N_2 \rangle)</th>
<th>(\langle H_2 \rangle)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 (equilibrium)</td>
<td>1.740</td>
<td>6.588</td>
<td>21.58</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 \(2A \rightleftharpoons B+3C\), \(K\) 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:

\(\text{[CoO(s)+H}_2(g) \rightleftharpoons Co}_2(g)+H_2O(g) \text{ with } K=671\)

\(\text{[Co}_2(g)+CO(g) \rightleftharpoons Co}_2(g)+CO_2(g) \text{ with } K=490\)

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 \(\langle H_2 \rangle\) or \(\langle CO \rangle\) plus 0.500 mol \(\langle CoO\rangle)\).
c. Using the information provided, calculate Kp for the following reaction: \[H_{2(g)}+CO_{2(g)} \rightleftharpoons CO_{(g)}+H_2O_{(g)}\]

d. Describe the shape of the graphs of [reactants] versus [products] as the amount of \(\text{CoO}\) 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 \(1.12 \times 10^{-2} \text{ mol}\) of \(\text{H}_2\) and \(1.8 \times 10^{-3} \text{ mol}\) of \(\text{I}_2\) at equilibrium, what is the concentration of \(\text{HI}\)? Excess hydrogen is added to the vessel so that the vessel now contains \(3.64 \times 10^{-1} \text{ mol}\) of \(\text{H}_2\). Calculate \(Q\) and then predict the direction in which the reaction will proceed. What are the new equilibrium concentrations?

Answers

1. Not at equilibrium; in both cases, the sum of the equilibrium partial pressures is less than the total pressure, so the reaction will proceed to the right to decrease the pressure.

3.

1. \(K=[\text{H}_2\text{O}][\text{H}_2] \); \(K=[\text{CO}_2][\text{CO}]\)
2. \(P_{\text{H}_2\text{O}} = 21.0 \text{ atm} \); \(P_{\text{H}_2} = 0.27 \text{ atm} \); \(P_{\text{CO}_2} = 21.3 \text{ atm} \); \(P_{\text{CO}} = 0.07 \text{ atm} \)
3. \(K_p = 0.14\)

The amount of \(\text{CoO}\) has no effect on the shape of a graph of products versus reactants as long as some solid \(\text{CoO}\) is present.

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15.7: Le Châtelier's Principle