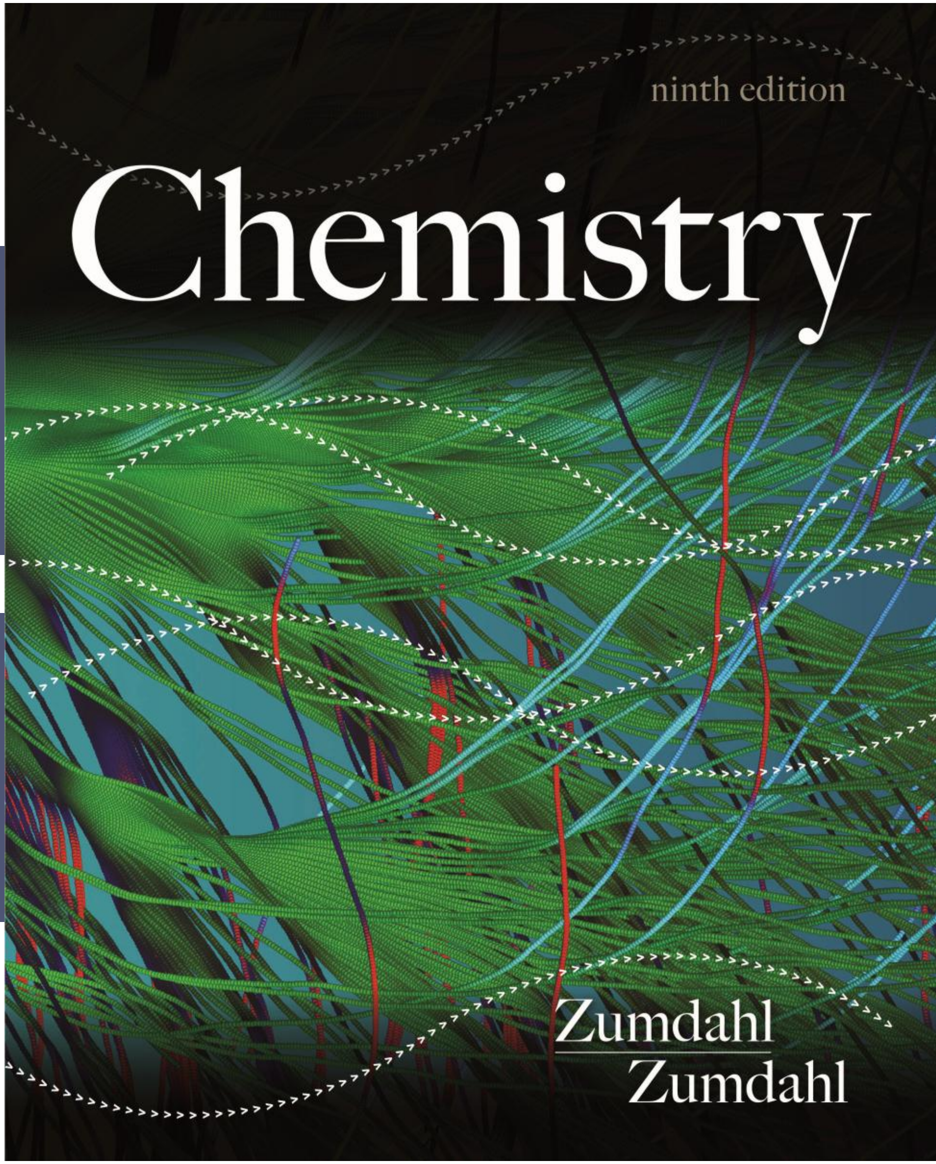

Chapter 13

Chemical Equilibrium

Chapter 13
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Chemical Equilibrium

- State where the concentrations of all reactants and products remain constant with time
  - Attained by reactions that take place in a closed environment
- May favor either products or reactants
  - If products are favored, the equilibrium position of the reaction lies far to the right

Chemical Equilibrium (Continued)

  - If reactants are favored, the equilibrium position of the reaction lies far to the left
- Visible changes cannot be detected in reactions that have achieved chemical equilibrium
  - Frantic activity takes place on a molecular level
  - Equilibrium is not static but is a highly dynamic situation

Figure 13.2 - Changes in Concentrations with Time for the Reaction between Water and Carbon Monoxide

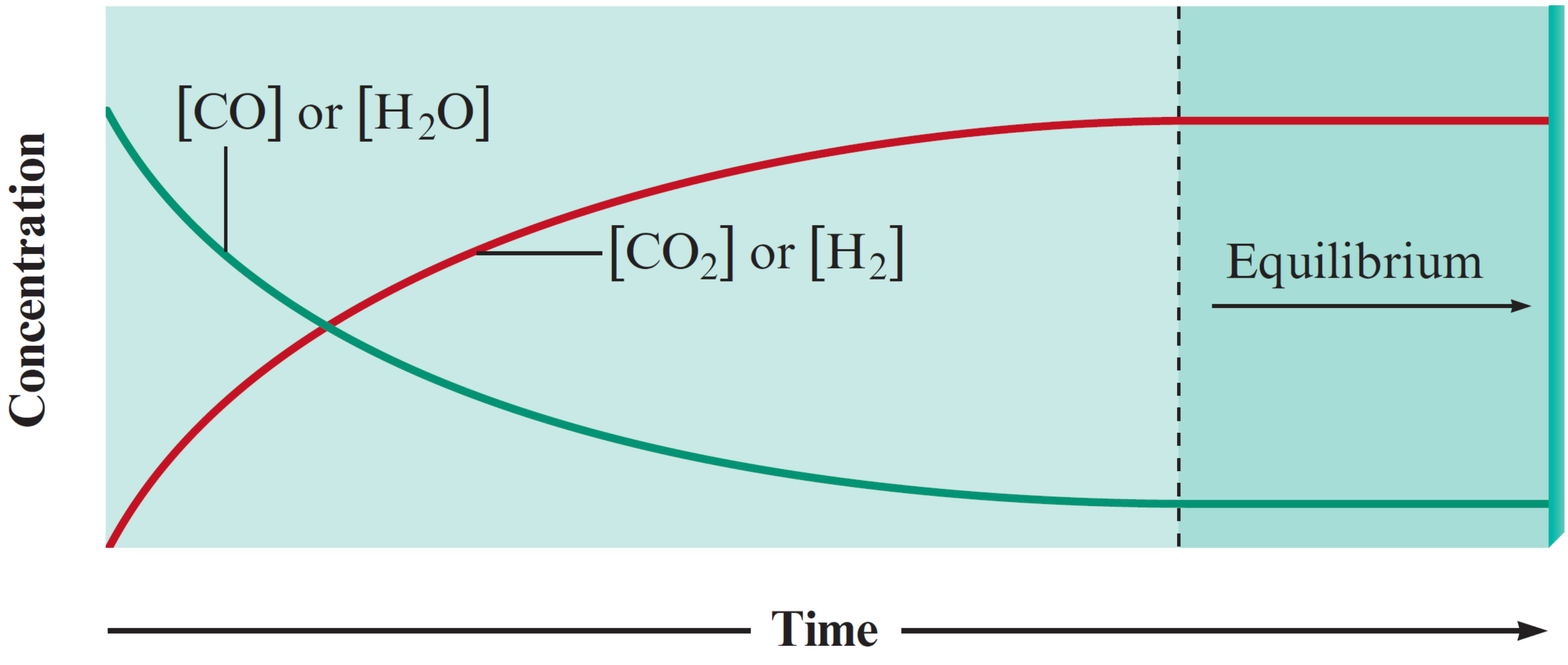


Figure 13.3 - Molecular Representation of the Reaction between Water and Carbon Monoxide

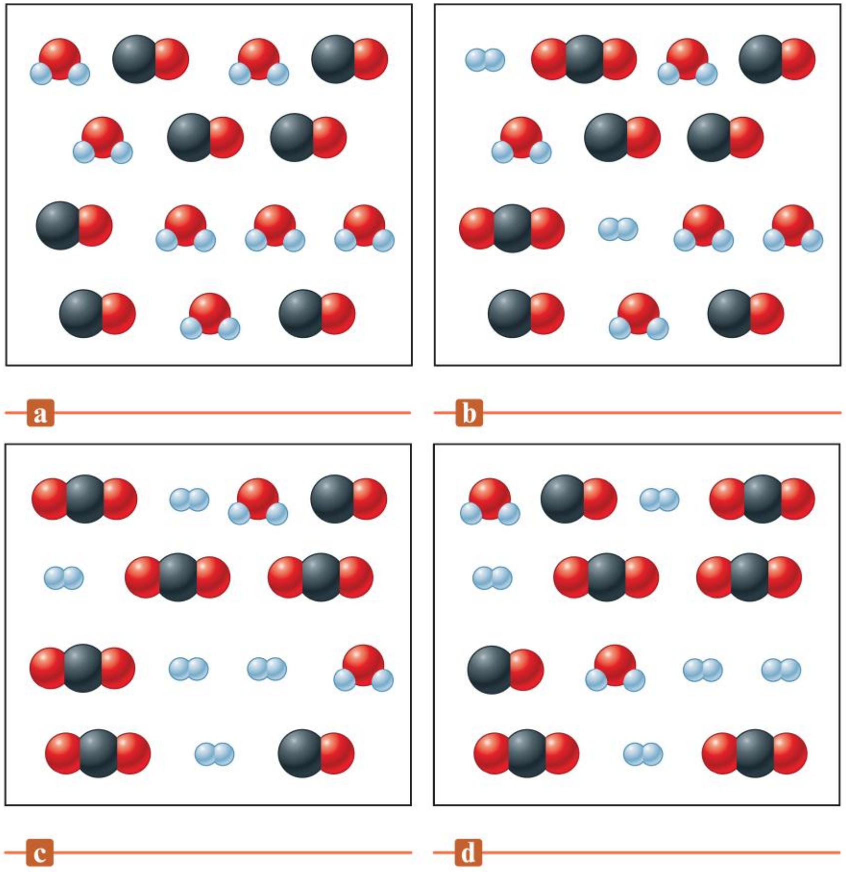
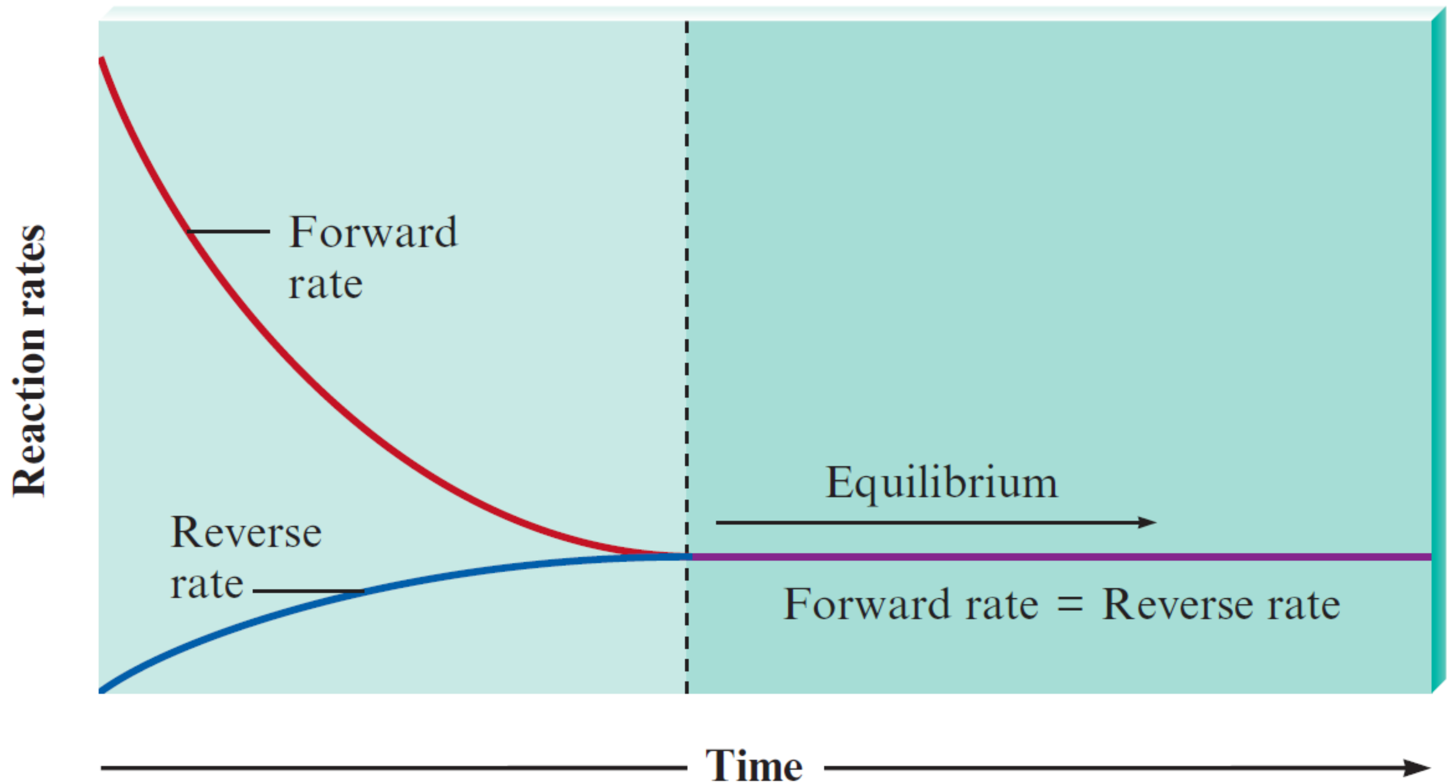


Figure 13.4 - Changes in the Rates of Forward and Reverse Reactions Involving Water and Carbon Monoxide



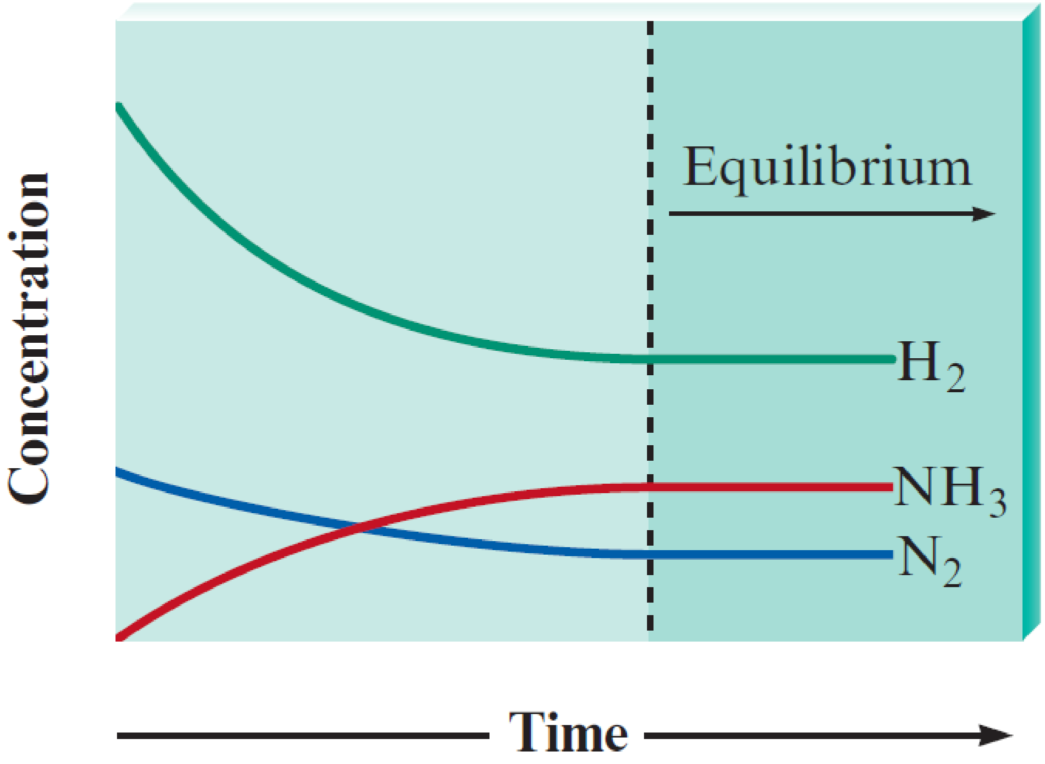
Factors Determining Equilibrium Position of a Reaction

- Initial concentrations
- Relative energies of reactants and products
- Relative degree of organization of reactants and products

Characteristics of Chemical Equilibrium

- Concentrations of the reactants and products in a given chemical equation remain unchanged because:
  - System is at chemical equilibrium
  - Forward and reverse reactions are too slow
    - System moves to equilibrium at a rate that cannot be detected
      - Applicable to nitrogen, hydrogen, and ammonia mixture at 25° C

Figure 13.5 - A Concentration Profile for the Formation of Ammonia



Law of Mass Action

- Consider the following reaction :

$$j\mathrm{A} + k\mathrm{B} \rightleftharpoons l\mathrm{C} + m\mathrm{D}$$

  - A, B, C, and D are chemical species, and *j*, *k*, *l*, and *m* are the respective coefficients
  - The law of mass action is represented by the following **equilibrium expression**

$$K = \frac{[\mathrm{C}]^l[\mathrm{D}]^m}{[\mathrm{A}]^j[\mathrm{B}]^k}$$

Law of Mass Action (Continued)

- Square brackets indicate the concentrations of the chemical species at equilibrium
- *K* is the **equilibrium constant**

Interactive Example 13.1 - Writing Equilibrium Expressions

- Write the equilibrium expression for the following reaction:

$$4NH_3(g) + 7O_2(g) \rightleftharpoons 4NO_2(g) + 6H_2O(g)$$

Interactive Example 13.1 - Solution

- Applying the law of mass action gives

Coefficient of NO_2

Coefficient of H_2O

$$K = \frac{[NO_2]^4[H_2O]^6}{[NH_3]^4[O_2]^7}$$

Coefficient of O_2

Coefficient of NH_3

Interactive Example 13.2 - Calculating the Values of *K*

- The following equilibrium concentrations were observed for the Haber process for synthesis of ammonia at 127° C:

$$[NH_3] = 3.1 \times 10^{-2} \text{ mol/L}$$

$$[N_2] = 8.5 \times 10^{-1} \text{ mol/L}$$

$$[H_2] = 3.1 \times 10^{-3} \text{ mol/L}$$

Interactive Example 13.2 - Calculating the Values of *K*

(Continued)

a) Calculate the value of *K* at 127°C for this reaction

b) Calculate the value of the equilibrium constant at 127°C for the following reaction:

$$2HN_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$$

c) Calculate the value of the equilibrium constant at 127°C given by the following equation:

$$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightleftharpoons NH_3(g)$$

Interactive Example 13.2 - Solution (a)

- The balanced equation for the Haber process is

$$N_2(g) + 3H_2(g) \rightleftharpoons 2HN_3(g)$$

  - Thus,

$$K = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(3.1 \times 10^{-2})^2}{(8.5 \times 10^{-1})(3.1 \times 10^{-3})^3} = 3.8 \times 10^4$$

  - Note that *K* is written without units

Interactive Example 13.2 - Solution (b)

- To determine the equilibrium expression for the dissociation of ammonia, the reaction is written in the reverse order
  - This leads to the following expression:

$$K' = \frac{[N_2][H_2]^3}{[NH_3]^2} = \frac{1}{K} = \frac{1}{3.8 \times 10^4} = 2.6 \times 10^{-5}$$

Interactive Example 13.2 - Solution (c)

- Determine the equilibrium constant using the law of mass action

$$K'' = \frac{[NH_3]}{[N_2]^{1/2}[H_2]^{3/2}}$$

  - Compare the above expression to the one obtained in solution (a)

Interactive Example 13.2 - Solution (c) (Continued)

$$\frac{[NH_3]}{[N_2]^{1/2}[H_2]^{3/2}} = \left(\frac{[NH_3]^2}{[N_2][H_2]^3}\right)^{1/2}$$

$$K'' = K^{1/2}$$

- Thus,

$$K'' = K^{1/2} = (3.8 \times 10^4)^{1/2} = 1.9 \times 10^2$$

Equilibrium Expression - Conclusions

- Consider the following reaction:

$$j\mathrm{A} + k\mathrm{B} \rightleftharpoons l\mathrm{C} + m\mathrm{D}$$

  - The equilibrium expression is

$$K = \frac{[\mathrm{C}]^l [\mathrm{D}]^m}{[\mathrm{A}]^j [\mathrm{B}]^k}$$

  - Reversing the original reaction results in a new expression

$$K' = \frac{[\mathrm{A}]^j [\mathrm{B}]^k}{[\mathrm{C}]^l [\mathrm{D}]^m} = \frac{1}{K}$$

Equilibrium Expression - Conclusions (Continued)

- Multiplying the original reaction by the factor *n* gives

$$njA + nkB \rightleftharpoons nlC + nmD$$

- The equilibrium expression becomes

$$K'' = \frac{[C]^{nl}[D]^{nm}}{[A]^{nj}[B]^{nk}} = K^{n}$$

Table 13.1 - Synthesis of Ammonia at Different Concentrations of Nitrogen and Hydrogen

Experiment	Initial Concentrations	Equilibrium Concentrations	$K = \frac{[NH_3]^2}{[N_2][H_2]^3}$
I	$[N_2]_0 = 1.000\ M$ $[H_2]_0 = 1.000\ M$ $[NH_3]_0 = 0$	$[N_2] = 0.921\ M$ $[H_2] = 0.763\ M$ $[NH_3] = 0.157\ M$	$K = 6.02 \times 10^{-2}$
II	$[N_2]_0 = 0$ $[H_2]_0 = 0$ $[NH_3]_0 = 1.000\ M$	$[N_2] = 0.399\ M$ $[H_2] = 1.197\ M$ $[NH_3] = 0.203\ M$	$K = 6.02 \times 10^{-2}$
III	$[N_2]_0 = 2.00\ M$ $[H_2]_0 = 1.00\ M$ $[NH_3]_0 = 3.00\ M$	$[N_2] = 2.59\ M$ $[H_2] = 2.77\ M$ $[NH_3] = 1.82\ M$	$K = 6.02 \times 10^{-2}$

Equilibrium Position versus Equilibrium Constant

Equilibrium position	Equilibrium constant
• Refers to each set of equilibrium concentrations • There can be infinite number of positions for a reaction • Depends on initial concentrations	• One constant for a particular system at a particular temperature • Remains unchanged • Depends on the ratio of concentrations

Example 13.3 - Equilibrium Positions

- The following results were collected for two experiments involving the reaction at 600° C between gaseous SO_2 and O_2 to form gaseous sulfur trioxide:

Experiment 1		Experiment 2	
Initial	**Equilibrium**	**Initial**	**Equilibrium**
$[SO_2]_0 = 2.00\ M$	$[SO_2] = 1.50\ M$	$[SO_2]_0 = 0.500\ M$	$[SO_2] = 0.590\ M$
$[O_2]_0 = 1.50\ M$	$[O_2] = 1.25\ M$	$[O_2]_0 = 0$	$[O_2] = 0.0450\ M$
$[SO_3]_0 = 3.00\ M$	$[SO_3] = 3.50\ M$	$[SO_3]_0 = 0.350\ M$	$[SO_3] = 0.260\ M$

  - Show that the equilibrium constant is the same in both cases

Example 13.3 - Solution

- The balanced equation for the reaction is

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

  - From the law of mass action,

$$K = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$$

Example 13.3 - Solution (Continued)

- For experiment 1

$$K_1 = \frac{(3.50)^2}{(1.50)^2(1.25)} = 4.36$$

- For experiment 2,

$$K_2 = \frac{(0.260)^2}{(0.590)^2(0.0450)} = 4.32$$

  - The value of *K* is constant, within experimental error

Relationship between the Pressure and the Concentration of a Gas

- Consider the ideal gas equation

$$PV = nRT \quad \text{(or)} \quad P = \left(\frac{n}{V}\right)RT = CRT$$

  - *C* represents the molar concentration of a gas
    - *C* = *n*/*V* or *C* equlas the number of moles *n* of gas per unit volume *V*

Equilibrium Expression for the Ammonia Synthesis Reaction

- In terms of concentration:

$$K = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{C_{NH_3}{}^2}{(C_{N_2})(C_{H_2}{}^3)} = K_C$$

- In terms of equilibrium partial pressures of gases:

$$K_p = \frac{P_{NH_3}{}^2}{(P_{N_2})(P_{H_2}{}^3)}$$

Equilibrium Expression for the Ammonia Synthesis Reaction (Continued)

- In these equations:
  - K and K_C are commonly used symbols for an equilibrium constant in terms of concentrations
  - K_p is the equilibrium constant in terms of partial pressures

Interactive Example 13.4 - Calculating the Values of K_p

- Consider the reaction for the formation of nitrosyl chloride at 25° C

$$2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g)$$

  - The pressures at equilibrium were found to be

$$P_{NOCl} = 1.2 \text{ atm}$$

$$P_{NO} = 5.0 \times 10^{-2} \text{ atm}$$

$$P_{Cl_2} = 3.0 \times 10^{-1} \text{ atm}$$

  - Calculate the value of K_p for this reaction at 25° C

Interactive Example 13.4 - Solution

- For this reaction,

$$K_p = \frac{P_{NOCl}{}^2}{(P_{NO_2})^2(P_{Cl_2})} = \frac{(1.2)^2}{(5.0 \times 10^{-2})^2(3.0 \times 10^{-1})}$$

$$K_p = 1.9 \times 10^3$$

Relationship between K and K_p

- Consider the following general reaction:

$$j\mathrm{A} + k\mathrm{B} \rightleftharpoons l\mathrm{C} + m\mathrm{D}$$

  - The relationship between K and K_p is

$$K_{\mathrm{p}} = K(RT)^{\Delta n}$$

    - Δn - Sum of the coefficients of the gaseous products minus the sum of the coefficients of the gaseous reactants

Deriving the Relationship between K and K_p

- For a general reaction,

$$K_p = \frac{(P_C^{\,l})(P_D^{\,m})}{(P_A^{\,j})(P_B^{\,k})} = \frac{(C_C \times RT)^l (C_D \times \mathrm{RT})^m}{(C_A \times \mathrm{RT})^j (C_B \times RT)^k}$$

$$= \frac{(C_C^{\,l})(C_D^{\,m})}{(C_A^{\,j})(C_B^{\,k})} \times \frac{(RT)^{l+m}}{(RT)^{j+k}} = K(RT)^{(l+m)-(j+k)}$$

$$= K(RT)^{\Delta n}$$

  - $\Delta n = (l + m) - (j + k)$
    - Difference in the sums of the coefficients for the gaseous products and reactants

Critical Thinking

- The text gives an example reaction for which $K = K_p$
  - The text states this is true "because the sum of the coefficients on either side of the balanced equation is identical. . . ."
  - What if you are told that for a reaction, $K = K_p$, and the sum of the coefficients on either side of the balanced equation is not equal?
    - How is this possible?

Interactive Example 13.5 - Calculating K from K_p

- Using the value of K_p obtained in example 13.4, calculate the value of K at 25° C for the following reaction:

$$2\text{NO}(g) + \text{Cl}_2(g) \rightleftharpoons 2\text{NOCl}(g)$$

Interactive Example 13.5 - Solution

- The value of K_p can be used to calculate K using the formula $K_p = K(RT)^{\Delta n}$
  - $T = 25 + 273 = 298$ K
  - $\Delta n = \underbrace{2}_{\text{Sum of product coefficients}} - \underbrace{(2+1)}_{\text{Sum of reactant coefficients}} = -1$
- Thus,

$$K_p = K(RT)^{\overset{\Delta n}{-1}} = \frac{K}{RT}$$

Interactive Example 13.5 - Solution (Continued)

- Therefore,

$$\begin{aligned} K &= K_{\mathrm{p}}(RT) \\ &= (1.9 \times 10^{3})(0.08206)(298) \\ &= 4.6 \times 10^{4} \end{aligned}$$

Homogeneous and Heterogeneous Equilibria

- **Homogeneous equilibria**: Involve reactants and products that are in one phase
- **Heterogeneous equilibria**: Involve reactants and products that exist in more than one phase

Heterogeneous Equilibria

- Consider the thermal decomposition of calcium carbonate

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

- Applying the law of mass action gives the equilibrium expression

$$K' = \frac{[CO_2][CaO]}{[CaCO_3]}$$

Heterogeneous Equilibria (Continued 1)

- Position of the equilibrium does not depend on the amounts of pure solids or liquids present
- Thus ,

$$K' = \frac{[CO_2]C_1}{C_2}$$

  - C_1 and C_2 - Constants that represent the concentrations of the solids CaO and $CaCO_3$, respectively
- Rearranging the expression gives

$$\frac{C_2K'}{C_1} = K = [CO_2]$$

Heterogeneous Equilibria (Continued 2)

- Summary of results
  - If pure solids or pure liquids are involved in a chemical reaction, their concentrations are not included in the equilibrium expression for the reaction
    - Does not apply to solutions or gases

Interactive Example 13.6 - Equilibrium Expressions for Heterogeneous Equilibria

- Write the expressions for K and K_p for the following processes:
  a. Solid phosphorus pentachloride decomposes to liquid phosphorus trichloride and chlorine gas
  b. Deep blue solid copper(II) sulfate pentahydrate is heated to drive off water vapor to form white solid copper(II) sulfate

Interactive Example 13.6 - Solution (a)

- The balanced equation for the reaction is

$$PCl_5(s) \rightleftharpoons PCl_3(l) + Cl_2(g)$$

  - The equilibrium expressions are

$$K = [Cl_2] \text{ and } K_p = P_{Cl_2}$$

  - In this case neither the pure solid PCl_5 nor the pure liquid PCl_3 is included in the equilibrium expressions

Interactive Example 13.6 - Solution (b)

- The balanced equation for the reaction is

$$\mathrm{CuSO_4 \cdot 5H_2O}(s) \rightleftharpoons \mathrm{CuSO_4}(s) + \mathrm{5H_2O}(g)$$

  - The equilibrium expressions are

$$K = [\mathrm{H_2O}]^5 \text{ and } K_\mathrm{p} = (P_{\mathrm{H_2O}})^5$$

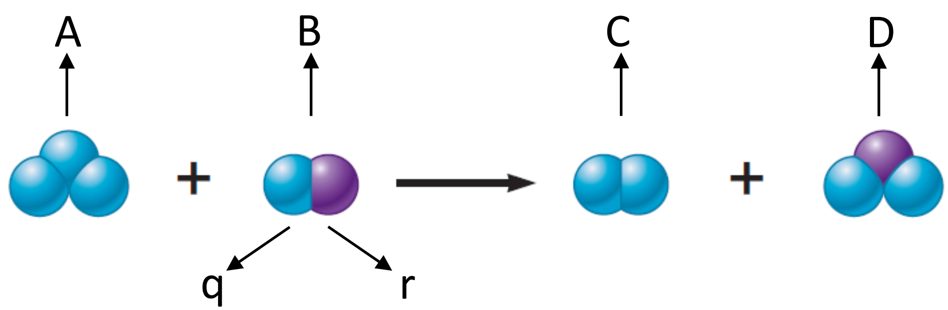
  - The solids are not included

Uses of the Equilibrium Constant

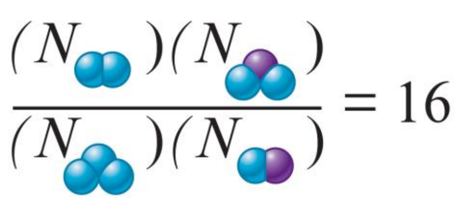
- Helps in predicting features of reactions, such as determining:
  - Tendency (not speed) of a reaction to occur
  - Whether a given set of concentrations represent an equilibrium condition
  - Equilibrium position that will be achieved from a given set of initial concentrations

Uses of the Equilibrium Constant - Example

- Consider the following reaction:

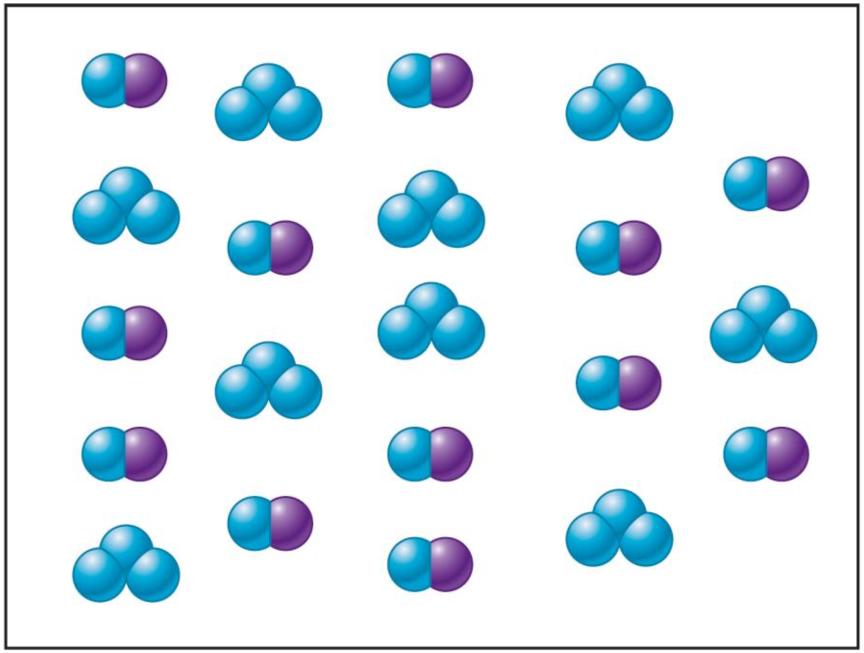


  - q and r represent two different types of atoms
  - Assume that the equilibrium constant is 16



Uses of the Equilibrium Constant - Example (Continued 1)

- The following figure depicts the proportions of reactants A and B in the reaction:



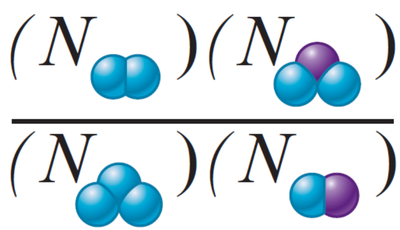
Uses of the Equilibrium Constant - Example (Continued 2)

- Assume that five molecules of A disappear so that the system can reach equilibrium
  - To maintain equilibrium, 5 molecules of B will also disappear, forming 5 C and 5 D molecules

Initial Conditions			***New Conditions***		
9		molecules	$9 - 5 = 4$		molecules
12		molecules	$12 - 5 = 7$		molecules
0		molecules	$0 + 5 = 5$		molecules
0		molecules	$0 + 5 = 5$		molecules

Uses of the Equilibrium Constant - Example (Continued 3)

- The new conditions do not match the equilibrium position

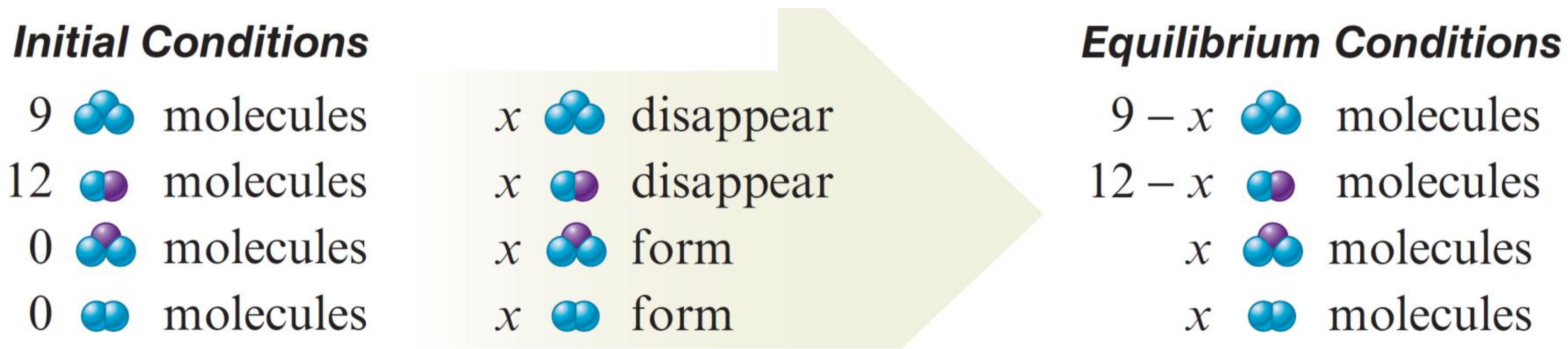


$$= \frac{(5)(5)}{(4)(7)} = 0.9$$

  - Equilibrium can be achieved by increasing the numerator and decreasing the denominator
    - System moves to the right - More than 5 original reactant molecules disappear

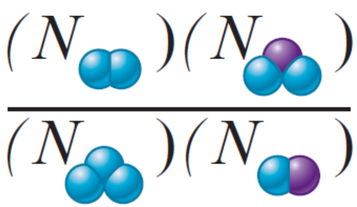
Uses of the Equilibrium Constant - Example (Continued 4)

- Let *x* be the number of molecules that need to disappear so that the system can reach equilibrium



Uses of the Equilibrium Constant - Example (Continued 5)

- The following ratio must be satisfied for the system to reach equilibrium:



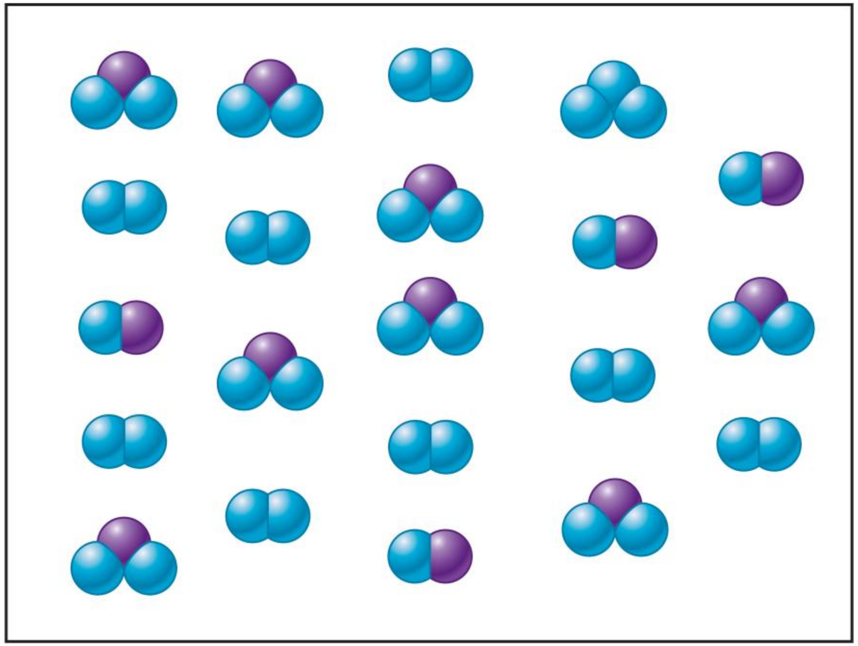
$$= 16 = \frac{(x)(x)}{(9-x)(12-x)}$$

  - It is known that *x* is greater than 5 and lesser than 9
    - Using trial and error, *x* is determined to be 8

$$\frac{(x)(x)}{(9-x)(12-x)} = \frac{(8)(8)}{(9-8)(12-8)} = \frac{64}{4} = 16$$

Uses of the Equilibrium Constant - Example (Continued 6)

- The following figure depicts the equilibrium mixture:



- 8 C molecules
- 8 D molecules
- 1 A molecule
- 4 B molecules

The Extent of a Reaction

- Tendency for a reaction to occur is given by the magnitude of K
- When the value of K is much larger than 1:
  - At equilibrium, the reaction system will consist of mostly products
  - Equilibrium lies to the right
  - Reaction goes essentially to completion

The Extent of a Reaction (Continued)

- When the value of *K* is very small:
  - The system at equilibrium will consist mostly of reactants
  - Equilibrium position lies far to the left
  - Reaction does not occur to any significant extent

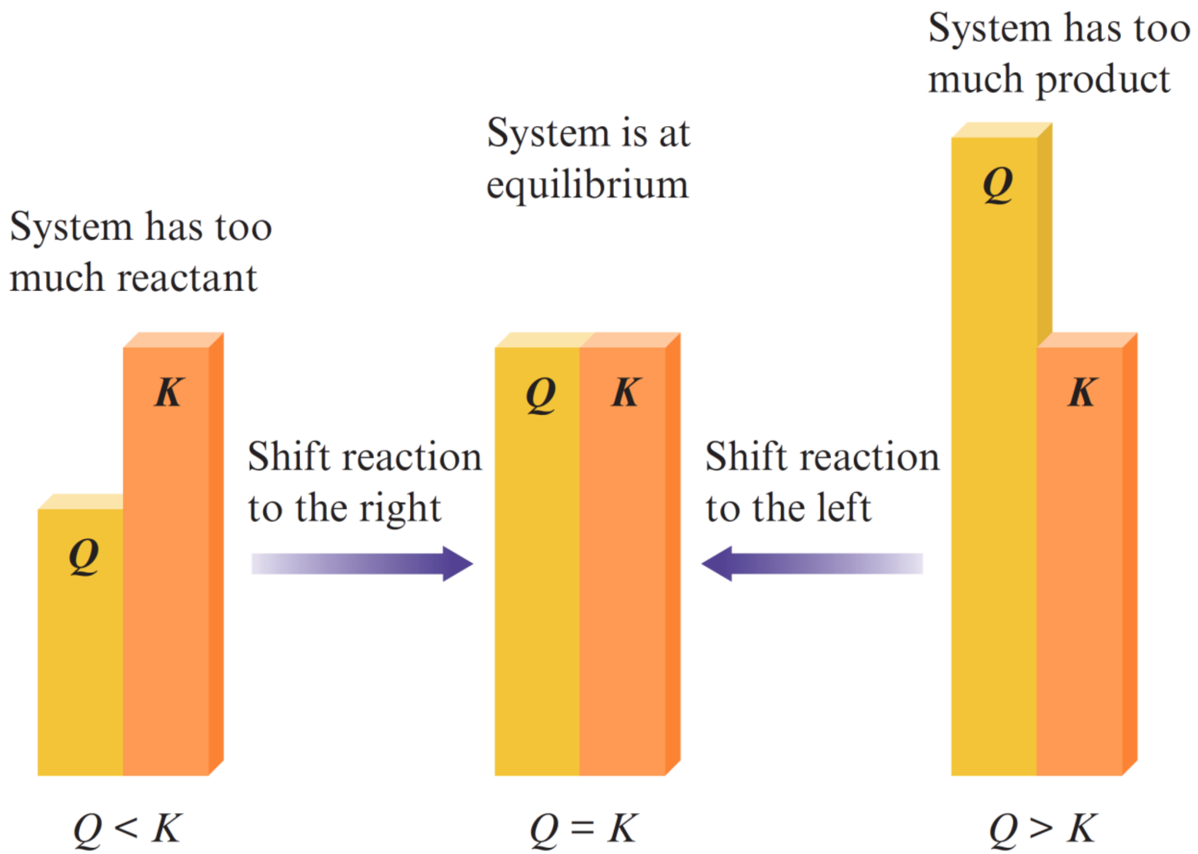
Size of *K* and Time Required to Reach Equilibrium

- Not directly related
  - Time required depends on the rate of the reaction
    - Determined by the size of the activation energy
  - Size of *K* is determined by thermodynamic factors
    - Example - Energy difference between products and reactants

Reaction Quotient, *Q*

- Used to determine the direction of movement toward equilibrium when all of the initial concentrations are nonzero
- Obtained by applying the law of mass action
  - Use initial concentrations instead of equilibrium concentrations

Figure 13.8 -The Relationship between Reaction Quotient *Q* and Equilibrium Constant *K*



Interactive Example 13.7 - Using the Reaction Quotient

- For the synthesis of ammonia at 500° C, the equilibrium constant is 6.0×10^{-2}
  - Predict the direction in which the system will shift to reach equilibrium in the following case:
    - $[NH_3]_0 = 1.0 \times 10^{-3}$ *M*
    - $[N_2]_0 = 1.0 \times 10^{-5}$ *M*
    - $[H_2]_0 = 2.0 \times 10^{-3}$ *M*

Interactive Example 13.7 - Solution

- Calculate the value of *Q*

$$Q = \frac{[NH_3]_0^2}{[N_2]_0[H_2]_0^3} = \frac{(1.0 \times 10^{-3})^2}{(1.0 \times 10^{-5})(2.0 \times 10^{-3})^3}$$

$$= 1.3 \times 10^7$$

  - Since $K = 6.0 \times 10^{-2}$, Q is much greater than K

Interactive Example 13.7 - Solution (Continued)

- To attain equilibrium:
  - The concentrations of the products must be decreased
  - The concentrations of the reactants must be increased
    - Therefore, the system will shift to the left

$$N_2(g) + 3H_2(g) \longleftarrow 2NH_3(g)$$

Calculating Equilibrium Pressures and Concentrations

- Typical equilibrium problem
  - Determine equilibrium concentrations of reactants and products
    - Value of equilibrium constant and initial concentrations are provided
- Mathematically complicated problem
  - Develop strategies to solve the problem using information provided

Interactive Example 13.8 - Calculating Equilibrium Pressures I

- Dinitrogen tetroxide in its liquid state was used as one of the fuels on the lunar lander for the NASA Apollo missions
  - In the gas phase, it decomposes to gaseous nitrogen dioxide:

$$\mathrm{N_2O_4}(g) \rightleftharpoons 2\mathrm{NO_2}(g)$$

Interactive Example 13.8 - Calculating Equilibrium Pressures I (Continued)

- Consider an experiment in which gaseous N_2O_4 was placed in a flask and allowed to reach equilibrium at a temperature where $K_p = 0.133$
  - At equilibrium, the pressure of N_2O_4 was found to be 2.71 atm
  - Calculate the equilibrium pressure of $NO_2(g)$

Interactive Example 13.8 - Solution

- The equilibrium pressures of the gases NO_2 and N_2O_4 must satisfy the following relationship:

$$K_p = \frac{{P_{NO_2}}^2}{P_{N_2O_4}} = 0.133$$

- Solve for the equilibrium pressure of NO_2

$${P_{NO_2}}^2 = K_p(P_{N_2O_4}) = (0.133)(2.71) = 0.360$$

Interactive Example 13.8 - Solution (Continued)

- Therefore,

$$P_{NO_2} = \sqrt{0.360} = 0.600$$

Interactive Example 13.9 - Calculating Equilibrium Pressures II

- At a certain temperature, a 1.00 L flask initially contained 0.298 mole of $PCl_3(g)$ and 8.70×10^{-3} mole of $PCl_5\ (g)$
  - After the system had reached equilibrium 2.00×10^{-3} mole of $Cl_2\ (g)$ was found in the flask
  - Gaseous PCl_5 decomposes according to the reaction

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

    - Calculate the equilibrium concentrations of all species and the value of *K*

Interactive Example 13.9 - Solution

- The equilibrium expression for this reaction is

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

  - To find the value of *K*:
    - Calculate the equilibrium concentrations of all species
    - Substitute the derived quantities into the equilibrium expression

Interactive Example 13.9 - Solution (Continued 1)

- Determine the initial concentrations

$$[Cl_2]_0 = 0$$

$$[PCl_3]_0 = \frac{0.298 \text{ mol}}{1.00 \text{ L}} = 0.298\ M$$

$$[PCl_5]_0 = \frac{8.70 \times 10^{-3} \text{ mol}}{1.00 \text{ L}} = 8.70 \times 10^{-3}\ M$$

Interactive Example 13.9 - Solution (Continued 2)

- Determine the change required to reach equilibrium

$$PCl_5(g) \longrightarrow PCl_3(g) + Cl_2(g)$$

$$\underbrace{2.00 \times 10^{-3}\ \text{mol}}_{\text{Net amount of } PCl_5 \text{ decomposed}} \longrightarrow \underbrace{2.00 \times 10^{-3}\ \text{mol} + 2.00 \times 10^{-3}\ \text{mol}}_{\text{Net amounts of products formed}}$$

  - Apply these values to the initial concentrations

Interactive Example 13.9 - Solution (Continued 3)

- Determine the equilibrium concentrations

$$[Cl_2] = \underset{[Cl_2]_0}{\underset{\uparrow}{0}} + \frac{2.00 \times 10^{-3}\ \text{mol}}{1.00\ \text{L}} = 2.00 \times 10^{-3}\ M$$

$$[PCl_3] = \underset{[PCl_3]_0}{\underset{\uparrow}{0.298\ M}} + \frac{2.00 \times 10^{-3}\ \text{mol}}{1.00\ \text{L}} = 0.300\ M$$

$$[PCl_5] = \underset{[PCl_5]_0}{8.70 \times 10^{-3}\ M} - \frac{2.00 \times 10^{-3}\ \text{mol}}{1.00\ \text{L}} = 6.70 \times 10^{-3}\ M$$

Interactive Example 13.9 - Solution (Continued 4)

- Determine the value of *K*
  - Substitute the equilibrium concentrations into the equilibrium expression

$$K = \frac{[Cl_2][PCl_3]}{[PCl_5]} = \frac{(2.00 \times 10^{-3})(0.300)}{6.70 \times 10^{-3}}$$

$$= 8.96 \times 10^{-2}$$

Interactive Example 13.11 - Calculating Equilibrium Concentrations II

- Assume that the reaction for the formation of gaseous hydrogen fluoride from hydrogen and fluorine has an equilibrium constant of 1.15×10^2 at a certain temperature
  - In a particular experiment, 3.000 moles of each component were added to a 1.500 L flask
  - Calculate the equilibrium concentrations of all species

Interactive Example 13.11 - Solution

- The balanced equation for this reaction is

$$H_2(g) + F_2(g) \rightleftharpoons 2HF(g)$$

- The equilibrium expression is

$$K = 1.15 \times 10^2 = \frac{[HF]^2}{[H_2][F_2]}$$

- The initial concentrations are

$$[HF]_0 = [H_2]_0 = [F_2]_0 = \frac{3.000 \text{ mol}}{1.500 \text{ L}} = 2.000\ M$$

Interactive Example 13.11 - Solution (Continued 1)

- The value of *Q* is

$$Q = \frac{[HF]_0^2}{[H_2]_0[F_2]_0} = \frac{(2.000)^2}{(2.000)(2.000)} = 1.000$$

  - Since *Q* is much less than *K*, the system must shift to the right to reach equilibrium
- To determine what change in concentration is necessary, define the change needed in terms of *x*

Interactive Example 13.11 - Solution (Continued 2)

- Let x be the number of moles per liter of H_2 consumed to reach equilibrium
- The stoichiometry of the reaction shows that x mol/L F_2 also will be consumed and $2x$ mol/L HF will be formed

$$H_2(g) \quad + F_2(g) \quad \longrightarrow 2HF(g)$$

$$x \text{ mol/L} + x \text{ mol/L} \longrightarrow 2x \text{ mol/L}$$

Interactive Example 13.11 - Solution (Continued 3)

- Determine the equilibrium concentrations in terms of *x*

Initial Concentration (mol/L)	Change (mol/L)	Equilibrium Concentration (mol/L)
$[H_2]_0 = 2.000$	$-x$	$[H_2] = 2.000 - x$
$[F_2]_0 = 2.000$	$-x$	$[F_2] = 2.000 - x$
$[HF]_0 = 2.000$	$+2x$	$[HF] = 2.000 + 2x$

Interactive Example 13.11 - Solution (Continued 4)

- The concentrations can be expressed in a shorthand table as follows:

	$H_2(g)$	$+$	$F_2(g)$	$\rightleftharpoons$	$2HF(g)$
Initial	2.000		2.000		2.000
Change	$-x$		$-x$		$+2x$
Equilibrium	$2.000 - x$		$2.000 - x$		$2.000 + 2x$

  - To solve for the value of *x*, substitute the equilibrium concentrations into the equilibrium expression

Interactive Example 13.11 - Solution (Continued 5)

$$K = 1.15 \times 10^2 = \frac{[HF]^2}{[H_2][F_2]} = \frac{(2.000 + 2x)^2}{(2.000 - x)^2}$$

- The right side of this equation is a perfect square, so taking the square root of both sides gives

$$\sqrt{1.15 \times 10^2} = \frac{2.000 + 2x}{2.000 - x}$$

Therefore, $x = 1.528$

Interactive Example 13.11 - Solution (Continued 6)

- The equilibrium concentrations are

$$[H_2] = [F_2] = 2.000\ M - x = 0.472\ M$$

$$[HF] = 2.000\ M + 2x = 5.056\ M$$

- Reality check
  - Checking the values by substituting them into the equilibrium expression gives the same value of *K*

Problem-Solving Strategy - Solving Equilibrium Problems

1. Write the balanced equation for the reaction
2. Write the equilibrium expression using the law of mass action
3. List the initial concentrations
4. Calculate *Q*, and determine the direction of the shift to equilibrium

Problem-Solving Strategy - Solving Equilibrium Problems (Continued)

5. Define the change needed to reach equilibrium
   - Define the equilibrium concentrations by applying the change to the initial concentrations
6. Substitute the equilibrium concentrations into the equilibrium expression
   - Solve for the unknown
7. Check the calculated equilibrium concentrations by making sure they give the correct value of K

Interactive Example 13.12 - Calculating Equilibrium Pressures

- Assume that gaseous hydrogen iodide is synthesized from hydrogen gas and iodine vapor at a temperature where the equilibrium constant is 1.00×10^{2}
  - Suppose HI at 5.000×10^{-1} atm, H_2 at 1.000×10^{-2} atm, and I_2 at 5.000×10^{-3} atm are mixed in a 5.000 L flask
    - Calculate the equilibrium pressures of all species

Interactive Example 13.12 - Solution

- The balanced equation for this process is

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

- The equilibrium expression in terms of pressure is

$$K_p = \frac{P_{HI^2}}{\left(P_{H_2}\right)\left(P_{I_2}\right)} = 1.00 \times 10^2$$

Interactive Example 13.12 - Solution (Continued 1)

- The initial pressures provided are
  - ${P_{HI}}^0 = 5.000 \times 10^{-1}$ atm
  - ${P_{H_2}}^0 = 1.000 \times 10^{-2}$ atm
  - ${P_{I_2}}^0 = 5.000 \times 10^{-3}$ atm
- The value of Q for this system is

$$Q = \frac{\left({P_{HI}}^0\right)^2}{\left({P_{H_2}}^0\right)\left({P_{I_2}}^0\right)} = \frac{\left(5.000 \times 10^{-1} \text{ atm}\right)^2}{\left(1.000 \times 10^{-2} \text{ atm}\right)\left(5.000 \times 10^{-3} \text{ atm}\right)} = 5.000 \times 10^3$$

Interactive Example 13.12 - Solution (Continued 2)

- Since *Q* is greater than *K*, the system will shift to the left to reach equilibrium

- Use pressures for a gas-phase system at constant temperature and volume
  - Pressure is directly proportional to the number of moles

$$P = n\left(\frac{RT}{V}\right) \longleftarrow \text{Constant if constant } T \text{ and } V$$

Interactive Example 13.12 - Solution (Continued 3)

- Let *x* be the change in pressure (in atm) of H_2 as the system shifts left toward equilibrium
  - This leads to the following equilibrium pressures:

	$H_2(g)$	+	$I_2(g)$	$\rightleftharpoons$	$2HI(g)$
Initial	1.000×10^{-2}		5.000×10^{-3}		5.000×10^{-1}
Change	$+x$		$+x$		$-2x$
Equilibrium	$1.000 \times 10^{-2} + x$		$5.000 \times 10^{-3} + x$		$5.000 \times 10^{-1} - 2x$

Interactive Example 13.12 - Solution (Continued 4)

- Determine the value of K_p

$$K_p = \frac{(P_{HI})^2}{(P_{H_2})(P_{I_2})} = \frac{(5.000 \times 10^{-1} - 2x)^2}{(1.000 \times 10^{-2} + x)(5.000 \times 10^{-3} + x)}$$

  - Multiply and collect terms that yield the quadratic equation where $a = 9.60 \times 10^1$, $b = 3.5$, and $c = -2.45 \times 10^{-1}$

$$(9.60 \times 10^1)x^2 + 3.5x - (2.45 \times 10^{-1}) = 0$$

Interactive Example 13.12 - Solution (Continued 5)

- From the quadratic formula, the correct value for *x* is 3.55×10^{-2} atm

- The equilibrium pressures can now be calculated from the expressions involving *x*

$$P_{HI} = 5.000 \times 10^{-1}\text{atm} - 2\left(3.55 \times 10^{-2}\right)\text{atm} = 4.29 \times 10^{-1}\text{atm}$$

$$P_{H_2} = 1.000 \times 10^{-2}\text{atm} + 3.55 \times 10^{-2}\text{atm} = 4.55 \times 10^{-2}\text{atm}$$

$$P_{I_2} = 5.000 \times 10^{-3}\text{atm} + 3.55 \times 10^{-2}\text{atm} = 4.05 \times 10^{-2}\text{atm}$$

Interactive Example 13.12 - Solution (Continued 6)

- Reality check

$$\frac{{P_{\mathrm{HI}}}^2}{P_{\mathrm{H_2}} \cdot P_{\mathrm{I_2}}} = \frac{(4.29 \times 10^{-1})^2}{(4.55 \times 10^{-2})(4.05 \times 10^{-2})} = 99.9$$

  - This agrees with the given value of K (1.00×10^2)
    - Thus, the calculated equilibrium concentrations are correct

Treating Systems That Have Small Equilibrium Constants

- Consider the decomposition of gaseous NOCl at 35° C with an equilibrium constant of 1.6×10^{-5}
  - The following steps determine the equilibrium concentrations of NOCl, NO, and Cl_2 when one mole of NOCl is placed in a 2.0 L flask:
  - The balanced equation is

$$2\mathrm{NOCl}(g) \rightleftharpoons 2\mathrm{NO}(g) + \mathrm{Cl}_2(g)$$

Treating Systems that have Small Equilibrium Constants
(Continued 1)

- The equilibrium expression is

$$K = \frac{[NO]^2[Cl_2]}{[NOCl]^2} = 1.6 \times 10^{-5}$$

- The initial concentrations are

$$[NOCl]_0 = \frac{1.0 \text{ mol}}{2.0 \text{ L}} = 0.50\ M$$

$$[NO]_0 = 0$$

$$[Cl_2]_0 = 0$$

Treating Systems that have Small Equilibrium Constants
(Continued 2)

- Since there are no products initially, the system will move to the right to reach equilibrium
  - Let *x* be the change in concentration of Cl_2 needed to reach equilibrium
    - The changes in the concentrations can be obtained from the following balanced equitation:

$$\begin{array}{ccccc} 2\mathrm{NOCl}(g) & \longrightarrow & 2\mathrm{NO}(g) & + & \mathrm{Cl}_2(g) \\ 2x & \longrightarrow & 2x & + & x \end{array}$$

Treating Systems that have Small Equilibrium Constants
(Continued 3)

- The concentrations can be summarized as follows:

	$2NOCl(g)$	$\rightleftharpoons$	$2NO(g)$	$+$	$Cl_2(g)$
Initial	0.50		0		0
Change	$-2x$		$+2x$		$+x$
Equilibrium	$0.50 - 2x$		$2x$		x

  - The equilibrium concentrations must satisfy the following equilibrium expression

$$K = 1.6 \times 10^{-5} = \frac{[NO]^2[Cl_2]}{[NOCl]^2} = \frac{(2x)^2(x)}{(0.50 - 2x)^2}$$

Treating Systems that have Small Equilibrium Constants
(Continued 4)

- In this situation, *K* is so small that the system will not proceed far to the right to reach equilibrium
- *x* represents a relatively small number, so when *x* is small

$$0.50 - 2x \approx 0.50$$

  - Simplify the equilibrium expression using this approximation

$$1.6 \times 10^{-5} = \frac{(2x)^2(x)}{(0.50 - 2x)^2} \approx \frac{(2x)^2(x)}{(0.50)^2} = \frac{4x^3}{(0.50)^2}$$

Treating Systems that have Small Equilibrium Constants
(Continued 5)

- Solving for x^3 gives

$$x^3 = \frac{(1.6 \times 10^{-5})(0.50)^2}{4} = 1.0 \times 10^{-6}$$

$$x = 1.0 \times 10^{-2}$$

- Test the validity of the approximation
  - If $x = 1.0 \times 10^{-2}$, then

$$0.50 - 2x = 0.50 - 2(1.0 \times 10^{-2}) = 0.48$$

Treating Systems that have Small Equilibrium Constants
(Continued 6)

- The difference between 0.50 and 0.48 is 0.02
  - This discrepancy will have little effect on the outcome
    - Since 2*x* is very small compared with 0.50, the value of *x* obtained should be very close to the exact value
  - Use the approximate value of *x* to calculate equilibrium concentrations

$$[\text{NOCl}] = 0.50 - 2x \approx 0.50\ M$$

$$[\text{NO}] = 2x = 2(1.0 \times 10^{-2}\ M) = 2.0 \times 10^{-2}\ M$$

$$[\text{Cl}_2] = x = 1.0 \times 10^{-2}\ M$$

Treating Systems that have Small Equilibrium Constants
(Continued 7)

- Reality check

$$\frac{[NO]^2[Cl_2]}{[NOCl]^2} = \frac{(2.0 \times 10^{-2})^2(1.0 \times 10^{-2})}{(0.50)^2} = 1.6 \times 10^{-5}$$

  - Since the given value of *K* is the same, these calculations are correct
    - The small value of *K* and the resulting small shift to the right to reach equilibrium allowed simplification

Critical Thinking

- You have learned how to treat systems that have small equilibrium constants by making approximations to simplify the math
  - What if the system has a very large equilibrium constant? What can you do to simplify the math for this case?
    - Use the example from the text, change the value of the equilibrium constant to 1.6×10^5, and rework the problem
      - Why can you not use approximations for the case in which $K = 1.6$?

Le Châtelier's Principle

- If a change is imposed on a system at equilibrium, the position of the equilibrium will shift in a direction that tends to reduce that change
- Helps in the qualitative prediction of the effects of changes in concentration, pressure, and temperature on a system at equilibrium

The Effect of a Change in Concentration

- Consider the synthesis of ammonia
  - Suppose there is an equilibrium position described by the following concentrations:
    - $[N_2] = 0.399\ M$
    - $[H_2] = 1.197\ M$
    - $[NH_3] = 0.202\ M$
  - Assume that 1.000 mol/L N_2 is injected into the system
    - Predicting the result involves calculating the value of Q

The Effect of a Change in Concentration (Continued 1)

- The concentrations before the system adjusts are

$$[N_2]_0 = 0.399\ M + \underbrace{1.000\ M}_{\text{Added } N_2} = 1.399\ M$$

$$[H_2]_0 = 1.197\ M$$

$$[NH_3]_0 = 0.202\ M$$

  - These are labeled as initial concentrations as the system is no longer at equilibrium

The Effect of a Change in Concentration (Continued 2)

- Determine the value of *Q*

$$Q = \frac{[NH_3]_0^{\ 2}}{[N_2]_0[H_2]_0^{\ 3}} = \frac{(0.202)^2}{(1.399)(1.197)^3} = 1.70 \times 10^{-2}$$

  - The value of *K* must be calculated from the first set of equilibrium concentrations

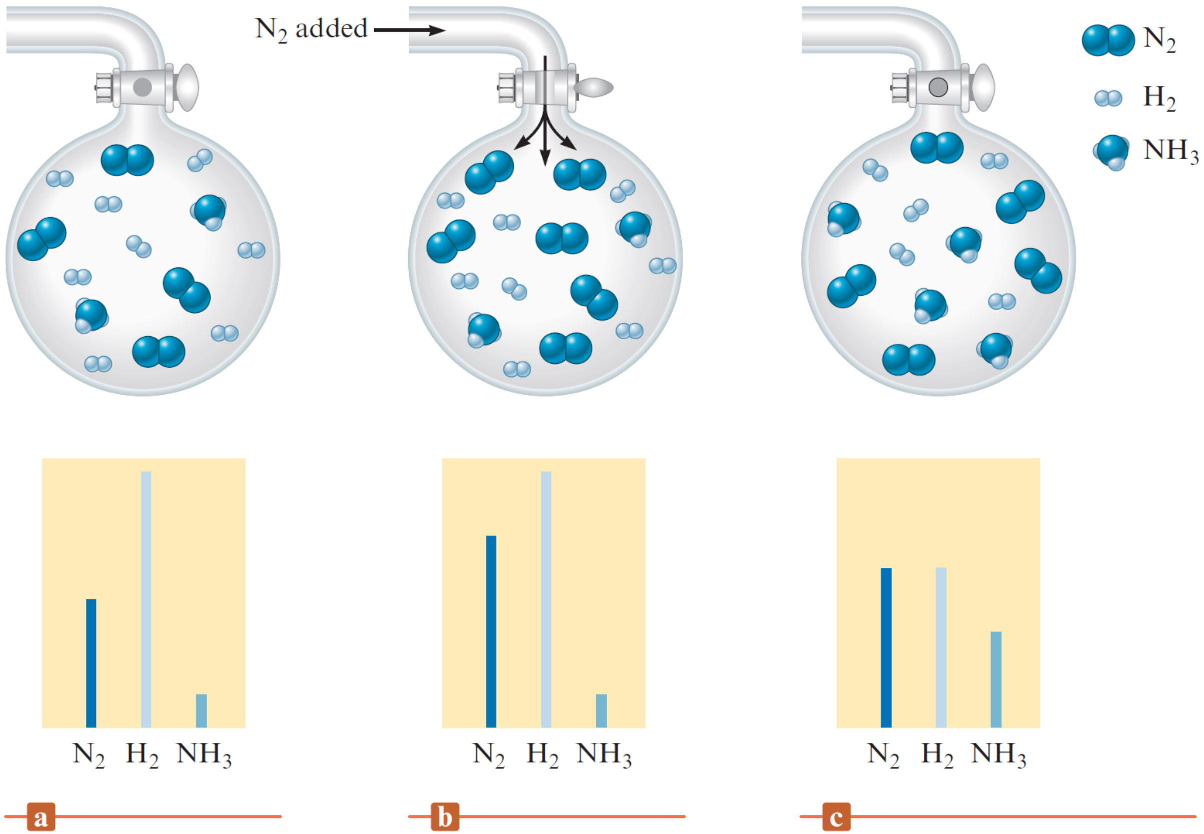
$$K = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(0.202)^2}{(0.399)(1.197)^3} = 5.96 \times 10^{-2}$$

The Effect of a Change in Concentration (Continued 3)

- $Q < K$ because the concentration of N_2 was increased
  - The system will shift to the right to come to the new equilibrium position

Equilibrium Position I		Equilibrium Position II
$[N_2] = 0.399\ M$		$[N_2] = 1.348\ M$
$[H_2] = 1.197\ M$	$\xrightarrow[\text{of } N_2 \text{ added}]{1.000 \text{ mol/L}}$	$[H_2] = 1.044\ M$
$[NH_3] = 0.202\ M$		$[NH_3] = 0.304\ M$

Figure 13.9 - Predicting Equilibrium Shift for Ammonia Synthesis Reaction Using Le Châtelier's Principle



Alternate Definition for Le Châtelier's principle

- If a component is added to a reaction system at equilibrium, the equilibrium position will shift in the direction that lowers the concentration of that component
  - If a component is removed, the opposite effect occurs
    - System at equilibrium exists at constant T and P or constant T and V

Interactive Example 13.13 - Using Le Châtelier's Principle I

- Arsenic can be extracted from its ores by first reacting the ore with oxygen (called roasting) to form solid As_4O_6, which is then reduced using carbon

$$\mathrm{As_4O_6}(s) + 6\mathrm{C}(s) \rightleftharpoons \mathrm{As_4}(g) + 6\mathrm{CO}(g)$$

Interactive Example 13.13 - Using Le Châtelier's Principle I (Continued)

- Predict the direction of the shift of the equilibrium position in response to each of the following changes in conditions:
  a. Addition of carbon monoxide
  b. Addition or removal of carbon or tetraarsenic hexoxide (As_4O_6)
  c. Removal of gaseous arsenic (As_4)

Interactive Example 13.13 - Solution

a. Le Châtelier's principle predicts that the shift will be away from the substance whose concentration is increased
   - Equilibrium position will shift to the left when carbon monoxide is added

b. The amount of a pure solid has no effect on the equilibrium position

Interactive Example 13.13 - Solution (Continued)

- Changing the amount of carbon or tetraarsenic hexoxide will have no effect

c. If gaseous arsenic is removed, the equilibrium position will shift to the right to form more products

- In industrial processes, the desired product is often continuously removed from the reaction system to increase the yield

The Effect of a Change in Pressure

- Methods used to change the pressure of a reaction system with gaseous components:
  - Add or remove a gaseous reactant or product
  - Add an inert gas (not the one involved in the reaction)
  - Change the volume of the container

The Effect of a Change in Pressure - Key Points

- Addition of an inert gas increases the total pressure
  - Does not affect the concentrations or partial pressures of the reactants or products
- When the volume of the container holding a gaseous system is reduced, the system responds by reducing its own volume
  - Total number of gaseous molecules is reduced

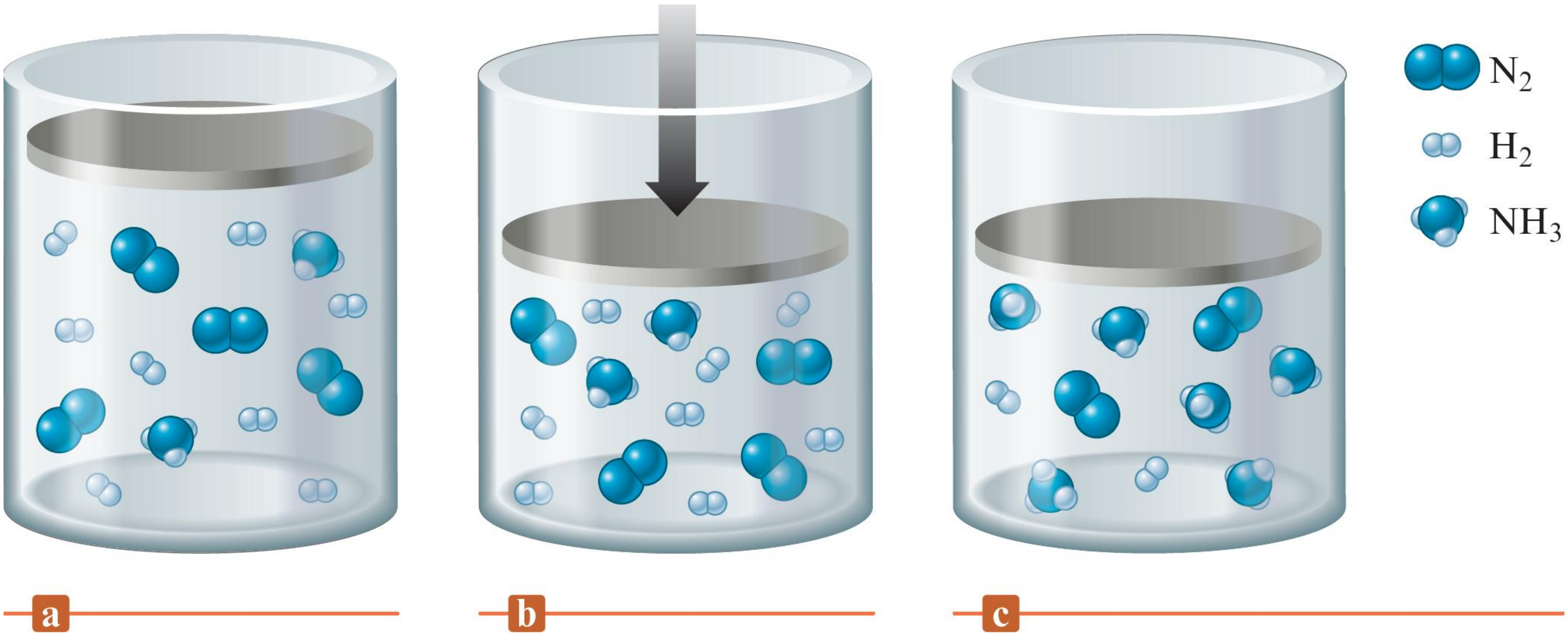
The Effect of a Change in Pressure - Key Points (Continued)

- Rearranging the ideal gas law gives

$$V = \left(\frac{RT}{P}\right)n$$

- At constant temperature (T) and pressure (P), $V \propto n$
  - Equilibrium position shifts toward the side of the reaction that involves smaller number of gaseous molecules in the balanced equation

Figure 13.11 - Effect of Volume on Equilibrium Position



Critical Thinking

- You and a friend are studying for a chemistry exam
  - What if your friend says, "Adding an inert gas to a system of gaseous components at equilibrium never changes the equilibrium position"?
    - How do you explain to your friend that this holds true for a system at constant volume but is not necessarily true for a system at constant pressure? When would it hold true for a system at constant pressure?

Interactive Example 13.14 - Using Le Châtelier's Principle II

- Predict the shift in equilibrium position that will occur during the preparation of liquid phosphorus trichloride

$$P_4(s) + 6Cl_2(g) \rightleftharpoons 4PCl_3(l)$$

  - Assume that the volume is reduced

Interactive Example 13.14 - Solution

- Since P_4 and PCl_3 are a pure solid and a pure liquid, respectively, we need to consider only the effect of the change in volume on Cl_2
  - Volume is decreased, so the position of the equilibrium will shift to the right
    - Reactant side contains six gaseous molecules, and the product side has none

The Effect of a Change in Temperature

- Value of *K* changes with the temperature
- Consider the synthesis of ammonia, an exothermic reaction

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + 92\ \text{kJ}$$

  - According to Le Châtelier’s principle, the shift will be in the direction that consumes energy
    - Concentration of NH_3 decreases and that of N_2 and H_2 increases, thus decreasing the value of *K*

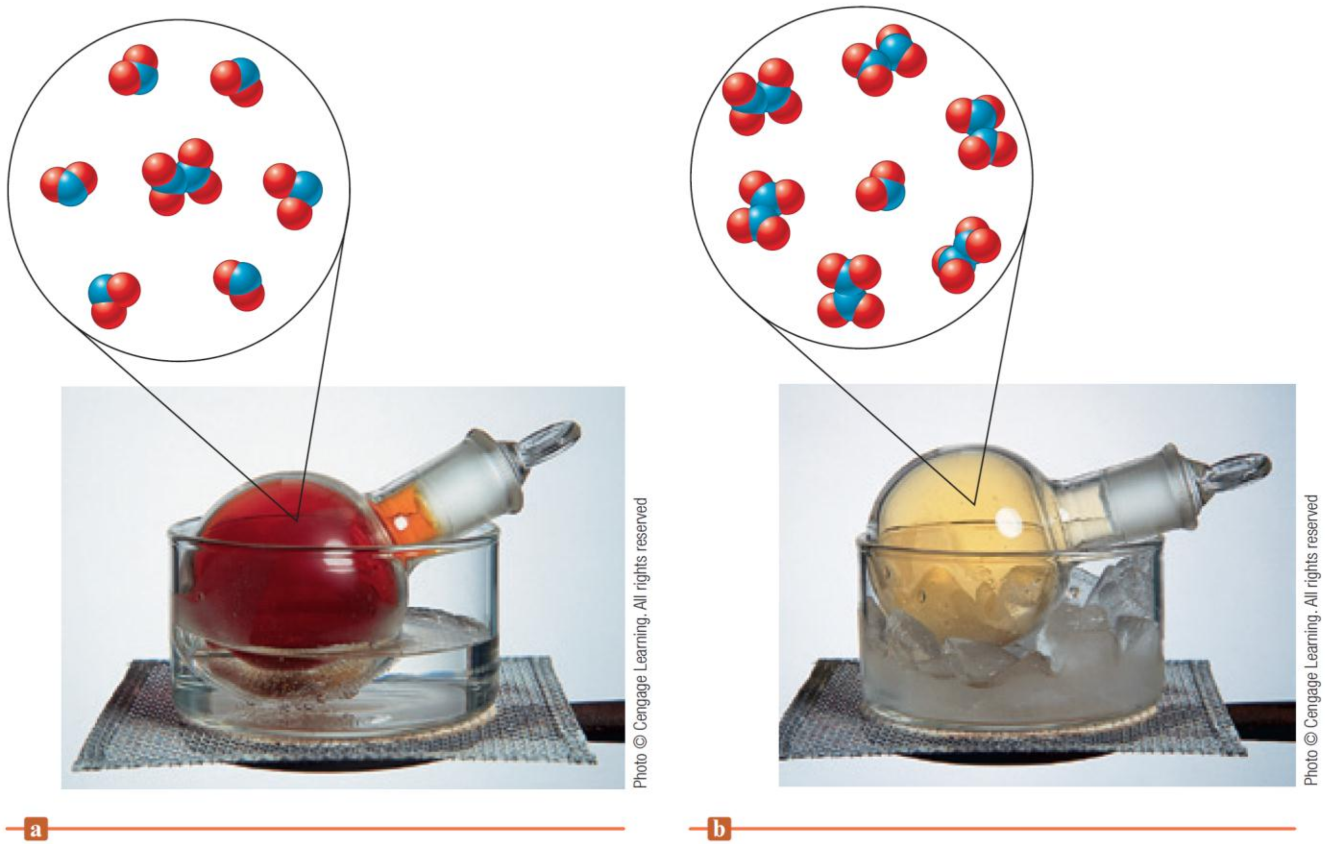
The Effect of a Change in Temperature (Continued)

- Consider the decomposition of calcium carbonate, an endothermic reaction

$$556\ \text{kJ} + \text{CaCO}_3(s) \rightleftharpoons \text{CaO}(s) + \text{CO}_2(g)$$

  - Increase in temperature causes the equilibrium to shift to the right
    - Value of *K* increases

Influence of Temperature on Equilibrium



Using Le Châtelier's Principle - A Summary

- Treat energy as a reactant (endothermic process) or as a product (exothermic process)
- Predict the direction of shift in the same way as when an actual reactant or product is added or removed

Interactive Example 13.15 - Using Le Châtelier's Principle III

- For the following reaction, predict how the value of *K* changes as the temperature is increased:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad \Delta H^{\circ} = -198 \text{ kJ}$$

Interactive Example 13.15 - Solution

- This is an exothermic reaction
  - Energy can be regarded as a product
- As the temperature is increased, the value of K decreases
  - The equilibrium shifts to the left

Table 13.4 - Shifts in the Equilibrium Position for the Formation of Nitrogen Dioxide

Change	Shift
Addition of $N_2O_4(g)$	Right
Addition of $NO_2(g)$	Left
Removal of $N_2O_4(g)$	Left
Removal of $NO_2(g)$	Right
Addition of $He(g)$	None
Decrease container volume	Left
Increase container volume	Right
Increase temperature	Right
Decrease temperature	Left