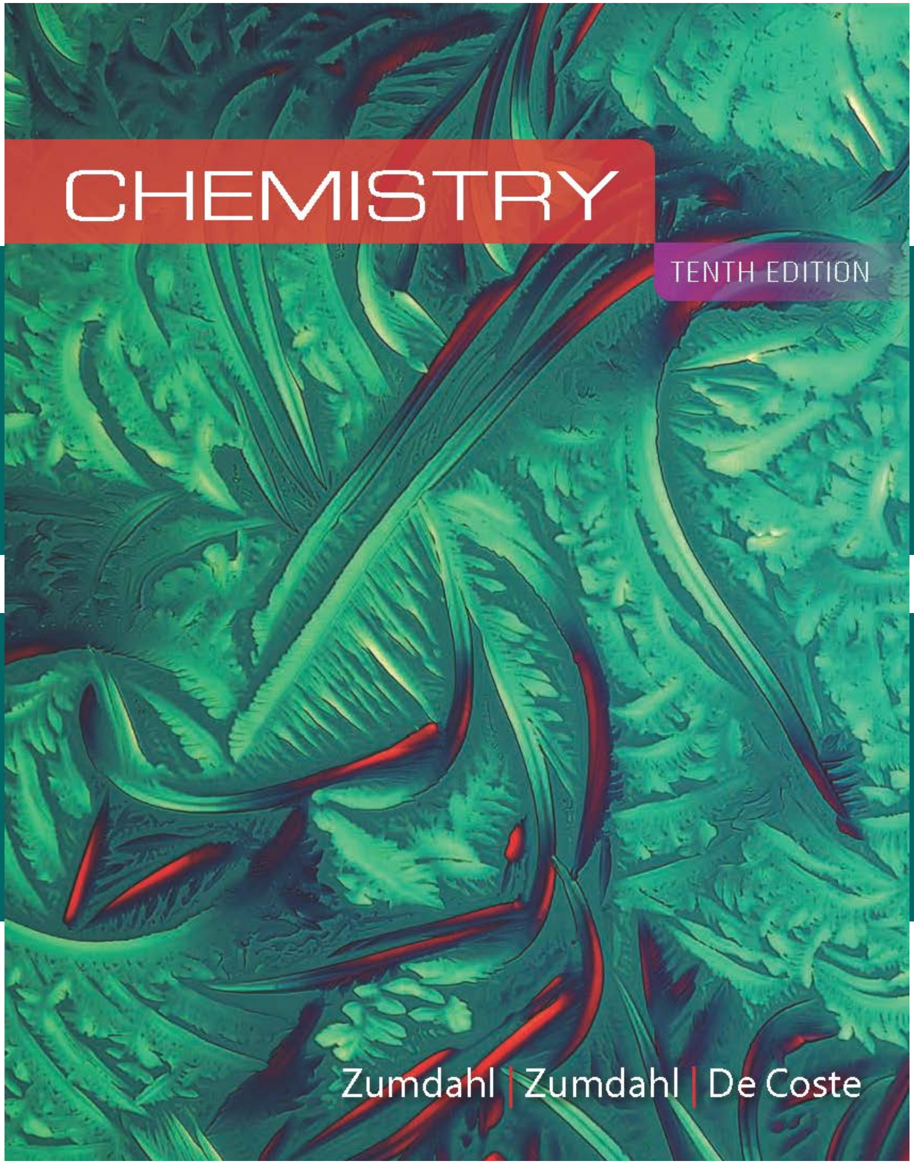

Chapter 13

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

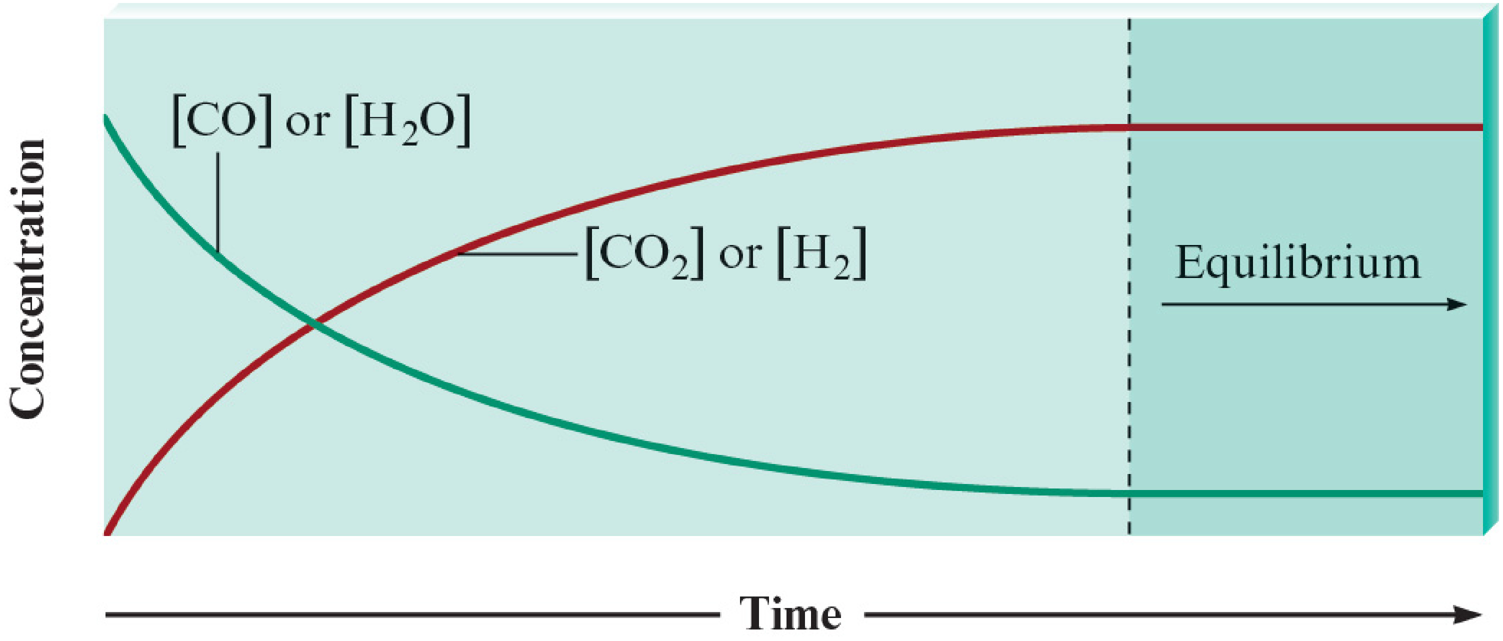
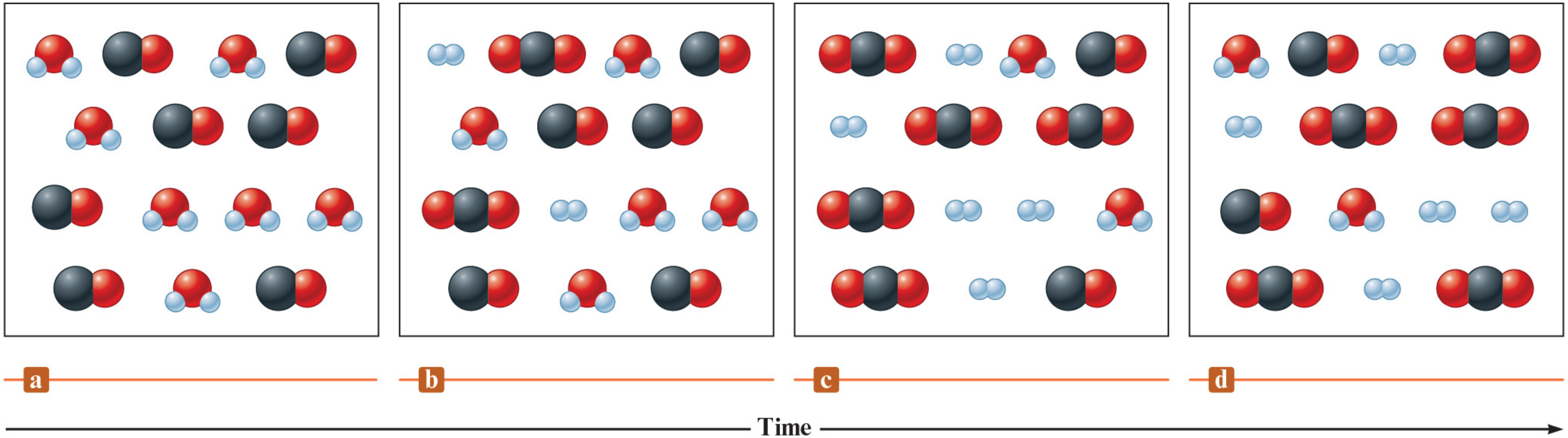


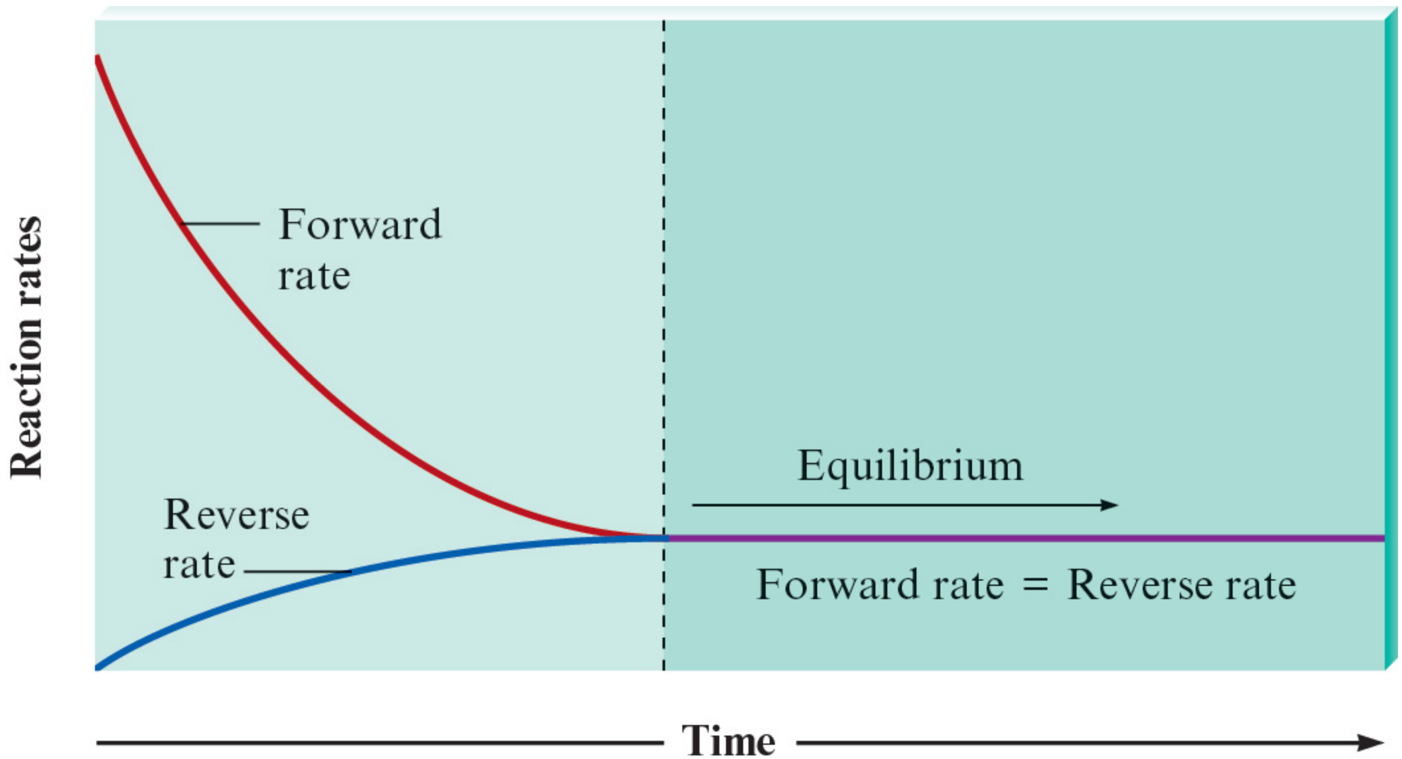
Figure 13.3 - Molecular Representation of the Reaction between Water and Carbon Monoxide



(a) H_2O and CO are mixed in equal numbers and begin to react (b) to form CO_2 and H_2

After time has passed, equilibrium is reached (c) and the numbers of reactant and product molecules then remain constant over time (d)

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



Rates do not change in the same way with time because the forward reaction has a much larger rate constant than the reverse reaction

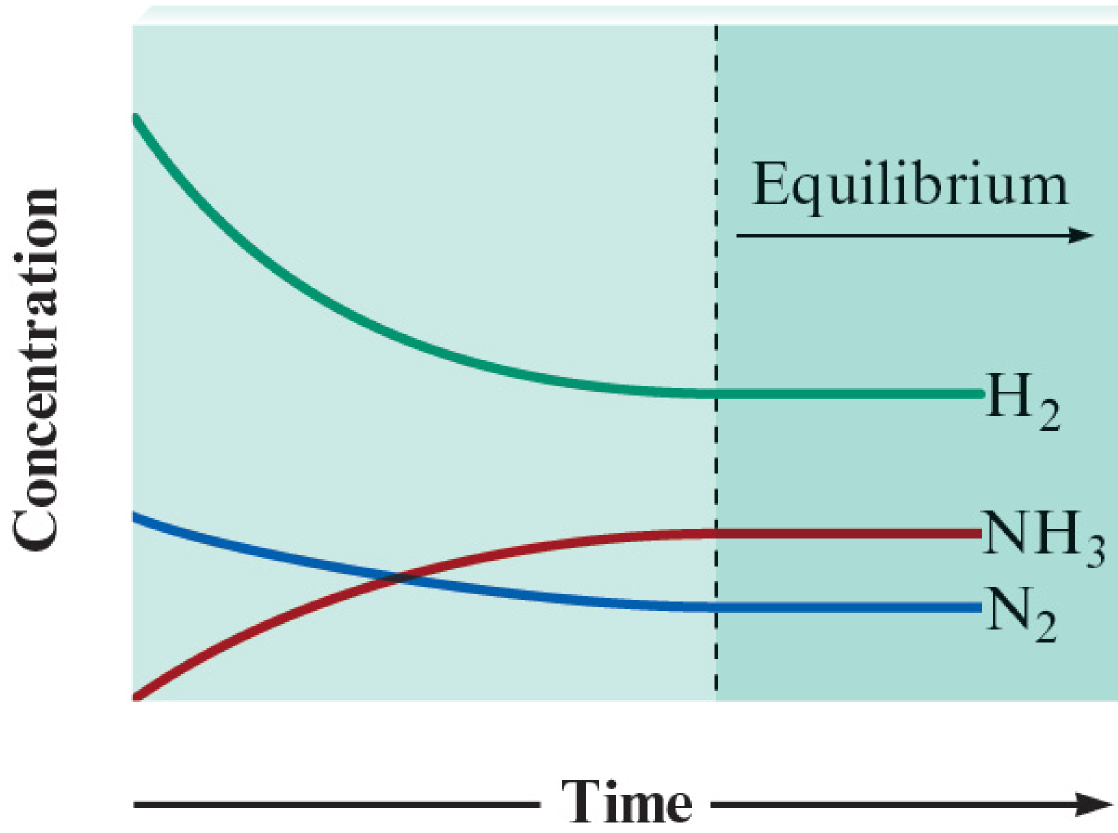
Factors Determining Equilibrium Position of a Reaction

- 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 very 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 - Concentration Profile for the Formation of Ammonia



Join In (1)

- Consider the following equation:

$$CO(g) + H_2O(g) \Leftrightarrow CO_2(g) + H_2(g)$$

  - Which of the following must be true at equilibrium?

Join In (1) (continued)

a. $[CO_2] = [H_2]$ because they are in a 1:1 mole ratio in the balanced equation
b. The total concentration of the reactants is equal to the total concentration of the products
c. The total concentration of the reactants is greater than the total concentration of the products
d. The total concentration of the products is greater than the total concentration of the reactants
e. None of these is true

Join In (2)

- Which of the following is true about chemical equilibrium?
    a. It is microscopically and macroscopically static
    b. It is microscopically and macroscopically dynamic
    c. It is microscopically static and macroscopically dynamic
    d. It is microscopically dynamic and macroscopically static

Law of Mass Action

- Consider the following reaction:

$$jA + kB \Leftrightarrow lC + mD$$

  - 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**

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

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:

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

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:

$$2\mathrm{NH_3}(g) \Leftrightarrow \mathrm{N_2}(g) + 3\mathrm{H_2}(g)$$

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

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

Interactive Example 13.2 - Solution (a)

- The balanced equation for the Haber process is

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

  - 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

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

  - 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:

$$\mathrm{jA + kB \Leftrightarrow lC + mD}$$

  - 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

$$\mathrm{njA} + \mathrm{nkB} \Leftrightarrow \mathrm{nlC} + n\mathrm{mD}$$

- The equilibrium expression becomes

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

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

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

  - 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* equals 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 the 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

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

  - The pressures at equilibrium were found to be

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

$$P_{\mathrm{NO}} = 5.0 \times 10^{?} \text{ atm}$$

$$P_{\mathrm{Cl}_2} = 3.0 \times 10^{?} \text{ atm}$$

  - 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:

$$\mathrm{jA + kB \Leftrightarrow lC + mD}$$

  - The relationship between K and K_p is

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

    - 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,

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

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

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

  - $\Delta n = (l + m) - (j + k)$
    - 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:

$$2\mathrm{NO}(g) + \mathrm{Cl_2}(g) \Leftrightarrow 2\mathrm{NOCl}(g)$$

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,

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

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

$$\mathrm{CaCO_3}(s) \Leftrightarrow \mathrm{CaO}(s) + \mathrm{CO_2}(g)$$

- Applying the law of mass action gives the equilibrium expression

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

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

$$PCl_5\,(s) \Leftrightarrow PCl_3(l) + Cl_2(g)$$

  - 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

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

  - The equilibrium expressions are

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

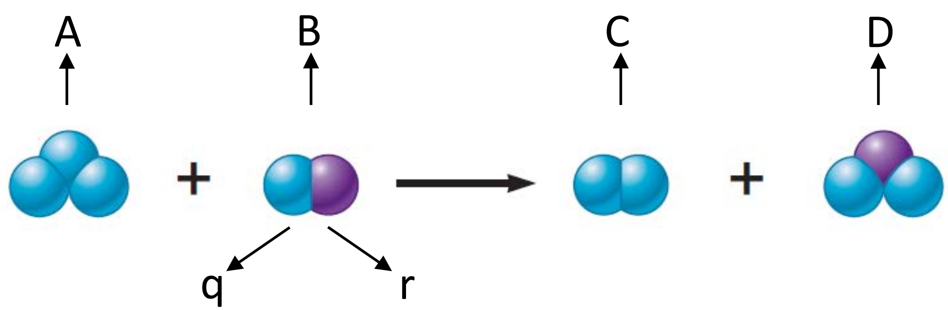
  - The solids are not included

Uses of the Equilibrium Constant

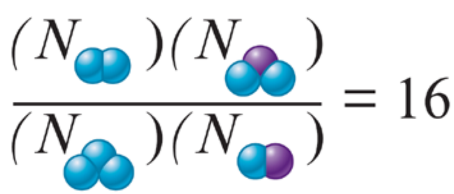
- Helps in predicting features of reactions, which includes determining:
  - Tendency (not speed) of a reaction to occur
  - Whether a given set of concentrations represents an equilibrium condition
  - Equilibrium position that will be achieved from a given set of initial concentrations

Uses of the Equilibrium Constant - Example

- Consider the following reaction:

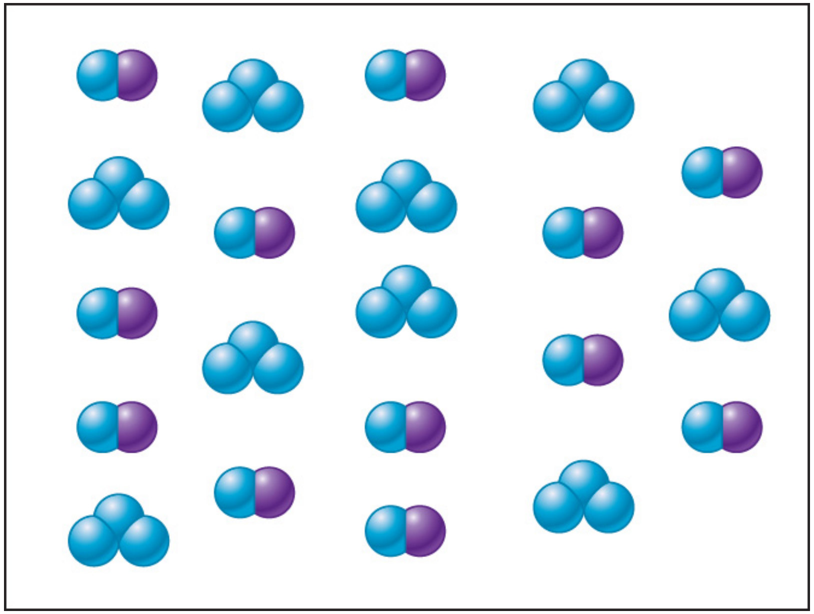


  - q and r represent two different types of atoms
  - Assume that the equilibrium constant is 16



Uses of the Equilibrium Constant - Example (continued 1)

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



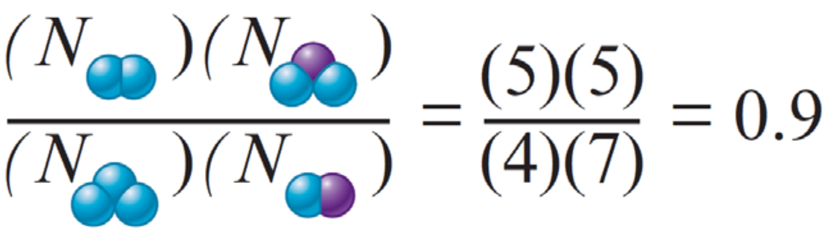
Uses of the Equilibrium Constant - Example (continued 2)

- 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)

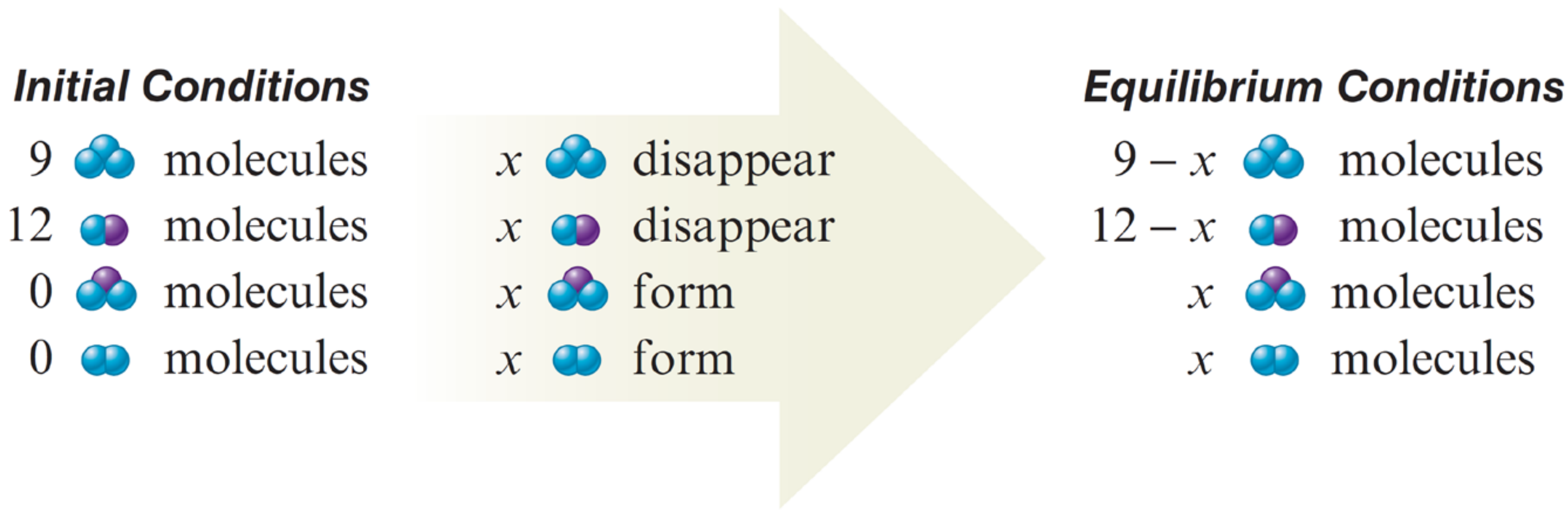
- The new conditions do not match the equilibrium position



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

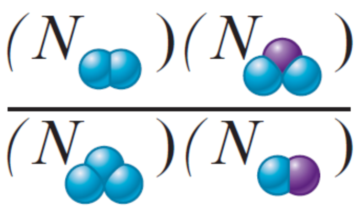
Uses of the Equilibrium Constant - Example (continued 4)

- 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:



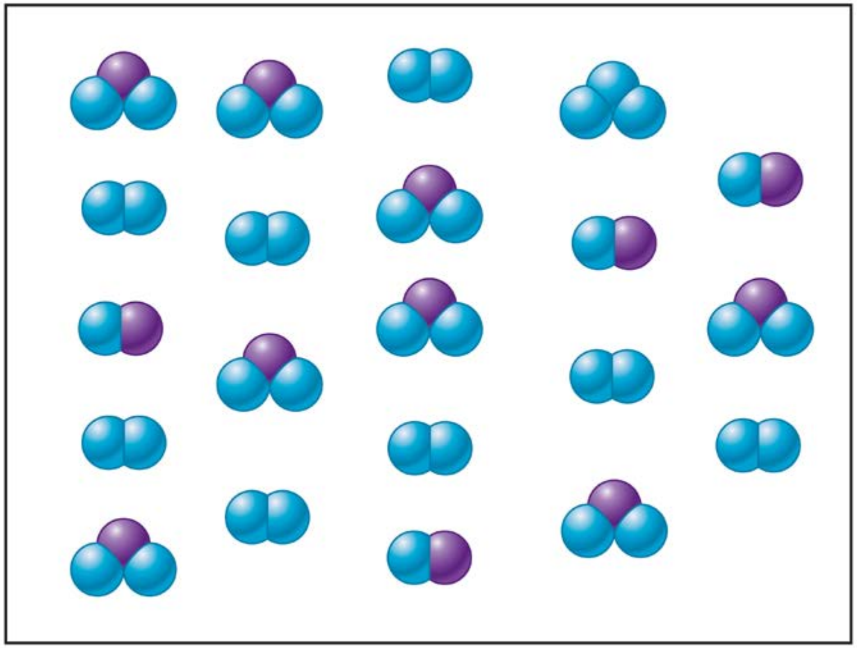
$$= 16 = \frac{(x)(x)}{(9-x)(12-x)}$$

  - 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

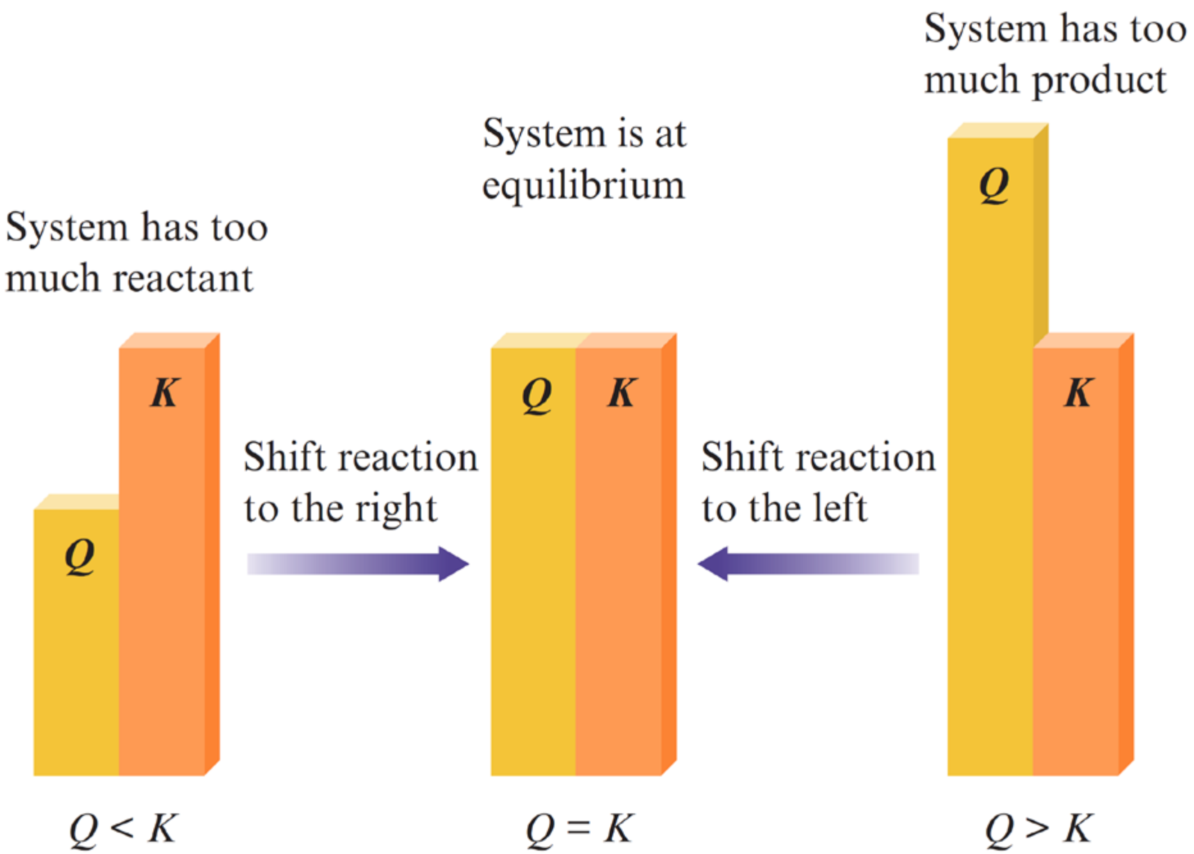
Size of *K* and Time Required to Reach Equilibrium

- 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*

$$Q = \frac{[NH_3]_0^2}{[N_2]_0[H_2]_0^3} = \frac{\left(1.0 \times 10^{-3}\right)^2}{\left(1.0 \times 10^{-5}\right)\left(2.0 \times 10^{-3}\right)^3}$$
$$= 1.3 \times 10^7$$

- 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 the 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:

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

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

$$\mathrm{PCl_5}(g) \Leftrightarrow \mathrm{PCl_3}(g) + \mathrm{Cl_2}(g)$$

    - 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

$$[\mathrm{Cl_2}]_0 = 0$$

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

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

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

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

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

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

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:

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

- 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:

$$Q = \frac{[\mathrm{HF}]_0^2}{[\mathrm{H}_2]_0[\mathrm{F}_2]_0} = \frac{(2.000)^2}{(2.000)(2.000)} = 1.000$$

  - 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

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

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

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*

Thank you