GENERAL CHEMISTRY

Principles and Modern Applications

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Principles of Chemical Equilibrium

15

General Chemistry: Chapter 15

Principles of Chemical Equilibrium

CONTENTS

General Chemistry: Chapter 15

15-1 Dynamic Equilibrium

Equilibrium –opposing processes taking place at equal rates.

(a)   (b)

$I_2(H_2O) \rightleftharpoons I_2(CCl_4)$

$$H_2O(l) \rightleftharpoons H_2O(g)$$

$$NaCl(s) \overset{H_2O}{\rightleftharpoons} NaCl(aq)$$

$$CO(g) + 2\,H_2(g) \rightleftharpoons CH_3OH(g)$$
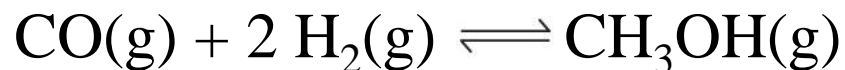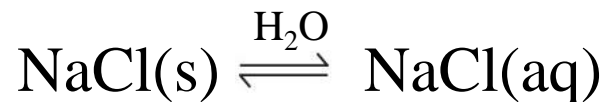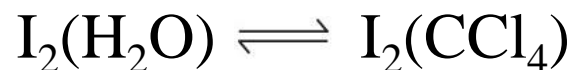
▲ FIGURE 15-1

Dynamic equilibrium in a physical process

General Chemistry: Chapter 15

15-2 The Equilibrium Constant Expression

The oxidation-reduction reaction of copper(II) and tin(II) in aqueous solution is reversible.

$$2\ Cu^{2+}(aq) + Sn^{2+}(aq) \xrightarrow{k_1} 2\ Cu^{+}(aq) + Sn^{4+}(aq)$$

$$2\ Cu^{+}(aq) + Sn^{4+}(aq) \xrightarrow{k_{-1}} 2\ Cu^{2+}(aq) + Sn^{2+}(aq)$$

$$2\ Cu^{2+}(aq) + Sn^{2+}(aq) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2\ Cu^{+}(aq) + Sn^{4+}(aq)$$
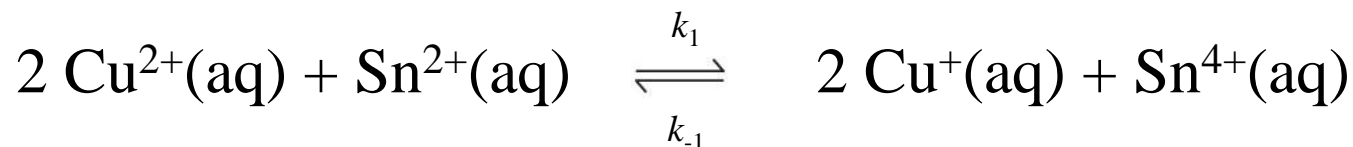
General Chemistry: Chapter 15

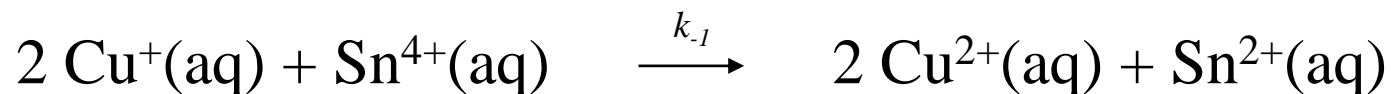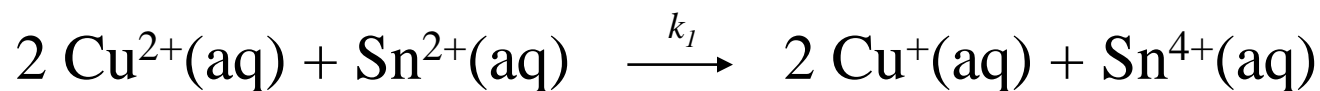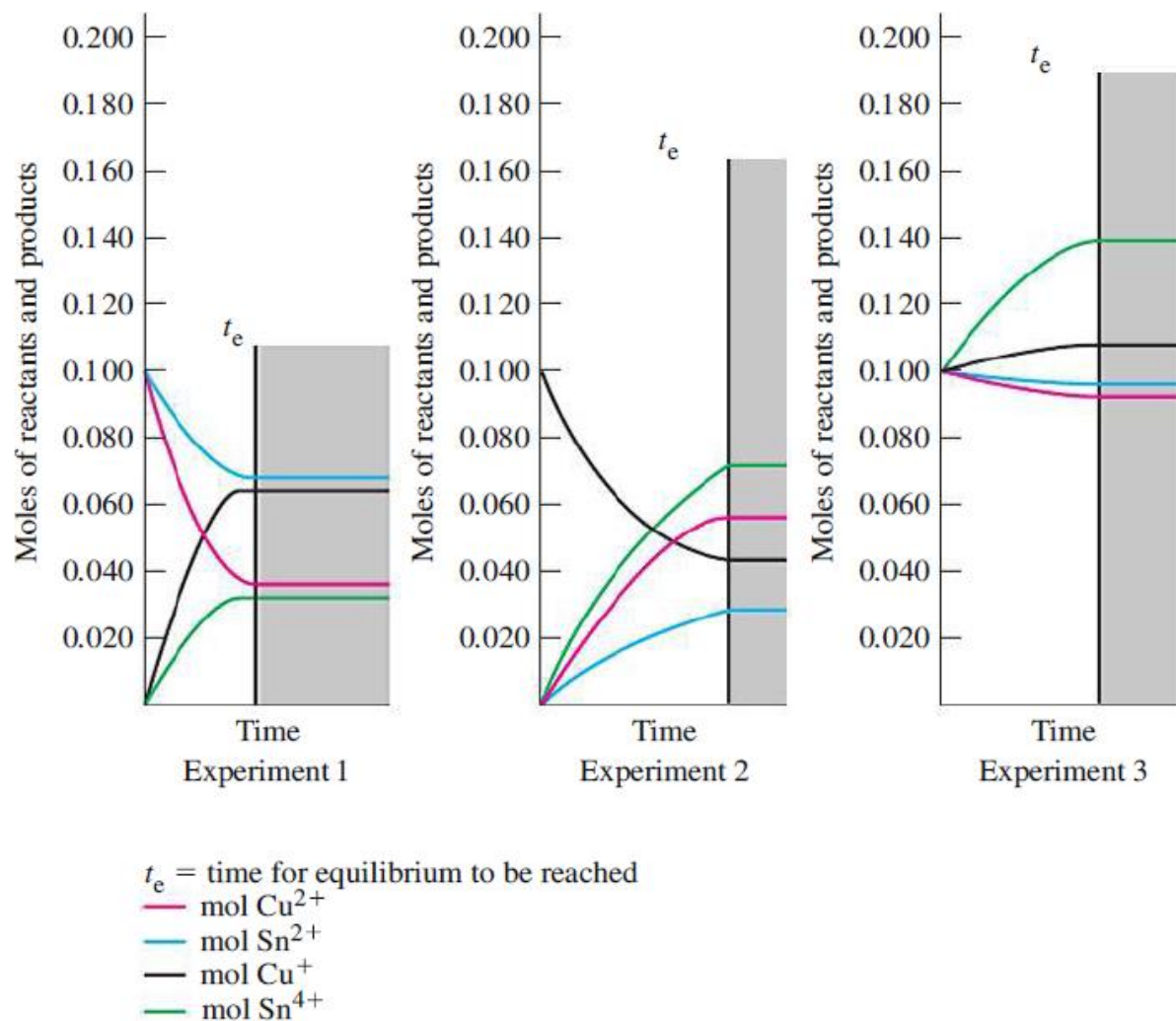## TABLE 15.1 Three Approaches to Equilibrium in the Reaction[a] $2\,Cu^{2+}(aq) + Sn^{2+}(aq) \rightleftharpoons 2\,Cu^{+}(aq) + Sn^{4+}(aq)$

	$Cu^{2+}(aq)$	$Sn^{2+}(aq)$	$Cu^{+}(aq)$	$Sn^{4+}(aq)$
Experiment 1				
Initial amounts, mol	0.100	0.100	0.000	0.000
Equilibrium amounts, mol	0.0360	0.0680	0.0640	0.0320
Equilibrium concentrations, mol/L	0.0360	0.0680	0.0640	0.0320
Experiment 2				
Initial amounts, mol	0.000	0.000	0.100	0.100
Equilibrium amounts, mol	0.0567	0.0283	0.0433	0.0717
Equilibrium concentrations, mol/L	0.0567	0.0283	0.0433	0.0717
Experiment 3				
Initial amounts, mol	0.100	0.100	0.100	0.100
Equilibrium amounts, mol	0.0922	0.0961	0.1078	0.1039
Equilibrium concentrations, mol/L	0.0922	0.0961	0.1078	0.1039

The concentrations printed in blue are used in the calculations in Table 15.2.
[a] Reaction carried out in 1.00 L of solution at 298 K.

General Chemistry: Chapter 15

▲ FIGURE 15-3

Three approaches to equilibrium in the reaction

$$2 Cu^{2+}(aq) + Sn^{2+}(aq) \rightleftharpoons 2 Cu^{+}(aq) + Sn^{4+}(aq)$$

The Equilibrium Constant and Activities

TABLE 15.2

Expt	Trial 1: $\dfrac{[Cu^+][Sn^{4+}]}{[Cu^{2+}][Sn^{2+}]}$	Trial 2: $\dfrac{(2 \times [Cu^+])[Sn^{4+}]}{(2 \times [Cu^{2+}])[Sn^{2+}]}$	Trial 3: $\dfrac{[Cu^+]^2[Sn^{4+}]}{[Cu^{2+}]^2[Sn^{2+}]}$
1	$\dfrac{0.0640 \times 0.0320}{0.0360 \times 0.0680} = 0.837$	$\dfrac{(2 \times 0.0640) \times 0.0320}{(2 \times 0.0360) \times 0.0680} = 0.837$	$\dfrac{0.0640^2 \times 0.0320}{0.0360^2 \times 0.0680} = 1.49$
2	$\dfrac{0.0433 \times 0.0717}{0.0567 \times 0.0283} = 1.93$	$\dfrac{(2 \times 0.0433) \times 0.0717}{(2 \times 0.0567) \times 0.0283} = 1.93$	$\dfrac{0.0433^2 \times 0.0717}{0.0567^2 \times 0.0283} = 1.48$
3	$\dfrac{0.1078 \times 0.1039}{0.0922 \times 0.0961} = 1.26$	$\dfrac{(2 \times 0.1078) \times 0.1039}{(2 \times 0.0922) \times 0.0961} = 1.26$	$\dfrac{0.1078^2 \times 0.1039}{0.0922^2 \times 0.0961} = 1.48$

Equilibrium concentration data are from Table 15.1. In Trial 1, the equilibrium concentration of Cu^+ and Sn^{2+} are placed in the numerator and the equilibrium concentration of Cu^{2+} and Sn^{4+}, in the denominator. In Trial 2, each concentration is multiplied by its stoichiometric coefficient. In Trial 3, each concentration is raised to a power equal to its stoichiometric coefficient. Trial 3 has essentially the same value for each experiment. This value is the equilibrium constant K.

*G. N. Lewis and M. Randall, *Thermodynamics*, McGraw Hill, New York, 1923.

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Activity

Thermodynamic concept introduced by Lewis.

Dimensionless ratio referred to a chosen reference state.

$$a_B = \frac{\gamma_B[B]}{c_B{}^0} = \gamma_B[B] \qquad c_B{}^0 \text{ is a standard reference state}$$

$$= 1 \text{ mol L}^{-1} \text{ (ideal conditions)}$$

- Accounts for non-ideal behaviour in solutions and gases.
- An *effective* concentration.

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Activity

A similar expression applies to gases

$$a_B = \frac{\gamma_B P_B}{P_B{}^0} = \gamma_B P_B$$

$P_B{}^0$ is a standard reference state

$= 1$ bar (ideal conditions)

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Reconsider the equilibrium between Cu^{2+} and Sn^{2+}
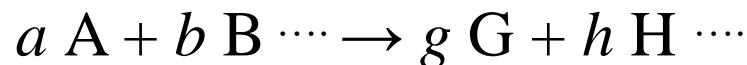
$$K = \frac{a_{Cu^+}^2 a_{Sn^{4+}}}{a_{Cu^{2+}}^2 a_{Sn^{2+}}} = 1.48 \qquad (15.5)$$

$$a_{Cu^+} = \frac{\gamma_{Cu^+}[Cu^+]}{c^\circ}; \qquad a_{Sn^{4+}} = \frac{\gamma_{Sn^{4+}}[Sn^{4+}]}{c^\circ}$$

$$a_{Cu^{2+}} = \frac{\gamma_{Cu^{2+}}[Cu^{2+}]}{c^\circ}; \qquad a_{Sn^{2+}} = \frac{\gamma_{Sn^{2+}}[Sn^{2+}]}{c^\circ}$$

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Reconsider the equilibrium between Cu²⁺ and Sn²⁺

$$K = \frac{\left(\dfrac{\gamma_{Cu^+}[Cu^+]_{eq}}{c^\circ}\right)^2 \dfrac{\gamma_{Sn^{4+}}[Sn^{4+}]_{eq}}{c^\circ}}{\left(\dfrac{\gamma_{Cu^{2+}}[Cu^{2+}]_{eq}}{c^\circ}\right)^2 \dfrac{\gamma_{Sn^{2+}}[Sn^{2+}]_{eq}}{c^\circ}} \approx \frac{[Cu^+]_{eq}^2[Sn^{4+}]_{eq}}{[Cu^{2+}]_{eq}^2[Sn^{2+}]_{eq}} = 1.48 \qquad \textbf{(15.6)}$$

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A general expression for K

$$a\,A + b\,B \cdots \longrightarrow g\,G + h\,H \cdots$$

Equilibrium constant $= K_c = \dfrac{[G]^g[H]^{h\,\cdots}}{[A]^a[B]^{b\,\cdots}}$

Thermodynamic Equilibrium constant

$$K_{eq} = \frac{(a_G)^g(a_H)^{h\,\cdots}}{(a_A)^a(a_B)^{b\,\cdots}} \approx \left(\frac{1}{c^\circ}\right)^{\Delta n}\left(\frac{[G]^g[H]^{h\,\cdots}}{[A]^m[B]^{n\,\cdots}}\right) = \left(\frac{1}{c^\circ}\right)^{\Delta n} K_{eq}$$

General Chemistry: Chapter 15

15-3 Relationships Involving the Equilibrium Constant

## Relationship of K to the Balanced Chemical Equation

Reversing an equation causes inversion of *K*.

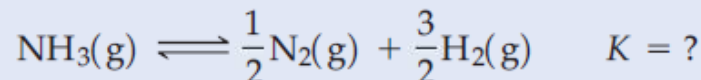Multiplying by coefficients by a common factor raises the equilibrium constant to the corresponding power.

Dividing the coefficients by a common factor causes the equilibrium constant to be taken to that root.

EXAMPLE 15-2   Relating K to the Balanced Chemical Equation

The following K value is given at 298 K for the synthesis of $NH_3(g)$ from its elements.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad K = 5.8 \times 10^5$$
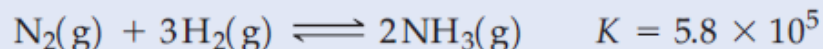
What is the value of K at 298 K for the following reaction?

$$NH_3(g) \rightleftharpoons \frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \qquad K = ?$$
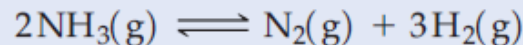
Analyze

The solution to this problem lies in recognizing that the reaction is the reverse and one-half of the given reaction. In this example we apply two of the rules given above that relate K to balanced chemical reactions.

Solve

First, reverse the given equation. This puts $NH_3(g)$ on the left side of the equation, where we need it.

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

The equilibrium constant K' becomes

$$K' = 1/(5.8 \times 10^5) = 1.7 \times 10^{-6}$$

Then, to base the equation on 1 mol $NH_3(g)$, divide all coefficients by 2.

$$NH_3(g) \rightleftharpoons \frac{1}{2}N_2(g) + \frac{3}{2}H_2(g)$$
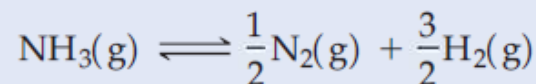
This requires the square root of K'.

$$K = \sqrt{1.7 \times 10^{-6}} = 1.3 \times 10^{-3}$$

Combining Equilibrium Constant Expressions

$$N_2O(g) + \tfrac{1}{2}O_2 \rightleftharpoons 2\,NO(g) \quad K_c = ?$$

$$N_2(g) + \tfrac{1}{2}O_2 \rightleftharpoons N_2O(g) \qquad K_{c(2)} = 2.7 \times 10^{+18} = \frac{[N_2O]}{[N_2][O_2]^{\frac{1}{2}}}$$

$$N_2(g) + O_2 \rightleftharpoons 2\,NO(g) \qquad K_{c(3)} = 4.7 \times 10^{-31} = \frac{[NO]^2}{[N_2][O_2]}$$
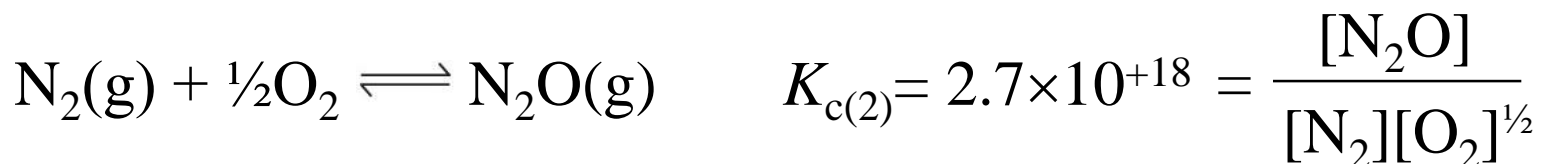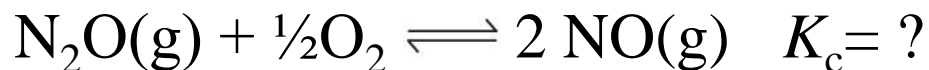
$$K_c = \frac{[NO]^2}{[N_2O][O_2]^{\frac{1}{2}}} = \frac{[NO]^2}{[N_2][O_2]}\frac{[N_2][O_2]^{\frac{1}{2}}}{[N_2O]} = K_{c(3)}\frac{1}{K_{c(2)}} = 1.7 \times 10^{-13}$$

General Chemistry: Chapter 15

Gases: The Equilibrium Constant, K_P

Mixtures of gases are solutions just as liquids are.

Use K_P, based upon *activities* of gases.

$$2\ SO_2(g) + O_2(g) \rightleftharpoons 2\ SO_3(g) \qquad K_P = \frac{(a_{SO_3})^2}{(a_{SO_2})^2(a_{O_2})}$$
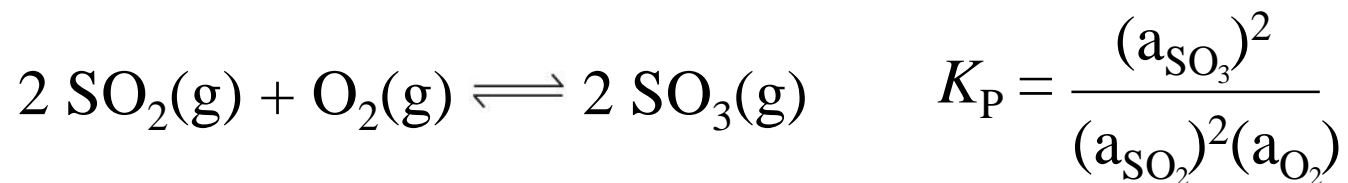
$$a_{SO_3} = \frac{P_{SO3}}{P^{\circ}} \qquad a_{SO_2} = \frac{P_{SO2}}{P^{\circ}} \qquad a_{SO_3} = \frac{P_{O2}}{P^{\circ}}$$

$$K_P = \left(\frac{(P_{SO_3})^2}{(P_{SO_2})^2(P_{O_2})} \right) P^{\circ}$$

General Chemistry: Chapter 15

Gases: The Equilibrium Constant, K_C

In *concentration* we can do another substitution

$$2\ SO_2(g) + O_2(g) \rightleftharpoons 2\ SO_3(g)$$
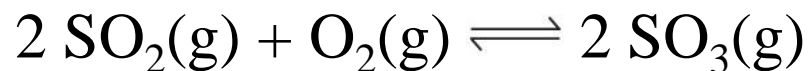
$$[SO_3] = \frac{n_{SO3}}{V} = \frac{P_{SO3}}{RT} \qquad [SO_2] = \frac{P_{SO2}}{RT} \qquad [O_2] = \frac{P_{O2}}{RT}$$

$$(a_X) = \frac{[X]}{c^\circ} = \frac{\frac{P_X}{RT}}{c^\circ} \qquad\qquad P_X = [X]\,RT$$

General Chemistry: Chapter 15

Gases: The Equilibrium Constant, K_C

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

$$K_P = \frac{(a_{SO_3})^2}{(a_{SO_2})^2(a_{O_2})} = P^{\circ}\left(\frac{(P_{SO_3})^2}{(P_{SO_2})^2(P_{O_2})}\right) \qquad P_X = [X]\ RT$$

$$= \left(\frac{([SO_3]\ RT)^2}{([SO_2]\ RT)^2([O_2]\ RT)}\right)P^{\circ}$$

$$= \frac{P^{\circ}}{RT}\left(\frac{([SO_3])^2}{([SO_2])^2([O_2])}\right) = \frac{K_C}{RT} \qquad \text{Where } P^{\circ} = 1 \text{ bar}$$

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An Alternative Derivation

$$2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g)$$
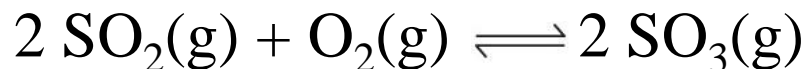
Where $P^\circ = 1$ bar

$$K_c = \frac{[SO_3]}{[SO_2]^2[O_2]} = \frac{\left(\dfrac{P_{SO_3}}{RT}\right)^2}{\left(\dfrac{P_{SO_2}}{RT}\right)^2 \dfrac{P_{O_2}}{RT}} = \frac{P_{SO_3}^2}{P_{SO_2}^2\,P_{O_2}}\,RT$$

$$K_c = K_P(RT) \qquad\qquad K_P = K_c(RT)^{-1}$$

In general terms: $\quad K_P = K_c(RT)^{\Delta n}$

General Chemistry: Chapter 15

EXAMPLE 15-3   Illustrating the Dependence of K on the Reference State

Complete the calculation of K_p for reaction (15.11) knowing that $K_c = 2.8 \times 10^2$ (at 1000 K).

Analyze

We use equation (15.16), with $R = 0.08314$ bar L K^{-1} mol^{-1}. For reasons outlined on page 666, units are omitted from our calculations.

Solve

Write the equation relating the two equilibrium constants with different reference states.

$$K_c = RT \times K_p$$

Rearrange the expression to obtain the quantity desired, K_p.

$$K_p = \frac{K_c}{RT}$$

Substitute the given data and solve.

$$K_p = \frac{2.8 \times 10^2}{0.08314 \times 1000} = 3.4$$

General Chemistry: Chapter 15

Pure Liquids and Solids

Equilibrium constant expressions do not contain concentration terms for solid or liquid phases of a single component (that is, pure solids or liquids).

$$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$$
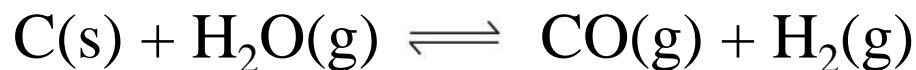
$$K_c = \frac{[CO][H_2]}{[H_2O]^2} = \frac{P_{CO}P_{H_2}}{P_{H_2O}^2}(RT)^1$$

General Chemistry: Chapter 15

EXAMPLE 15-4   Writing Equilibrium Constant Expressions for Reactions Involving Pure Solids or Liquids

At equilibrium in the following reaction at 60 °C, the partial pressures of the gases are found to be $P_{HI} = 3.70 \times 10^{-3}$ bar and $P_{H_2S} = 1.01$ bar. What is the value of K for the reaction?
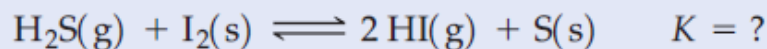
$$H_2S(g) + I_2(s) \rightleftharpoons 2\,HI(g) + S(s) \qquad K = ?$$

Analyze

We need to first write the equilibrium constant expression in terms of activities, and then eliminate the activities of pure solids and pure liquids by setting their activities to 1.

Solve

Write the equilibrium constant expression in terms of activities. Note that activities for the iodine and sulfur are not included, since the activity of a pure solid is 1.

$$K = \frac{(a_{HI})^2}{(a_{H_2S})}$$

The partial pressures are given in bar. The activity of each gas is equal to the numerical value of its partial pressure.

$$a_{HI} = 3.70 \times 10^{-3} \text{ and } a_{H_2S} = 1.01$$

Substitute the given equilibrium data into the equilibrium constant expression.

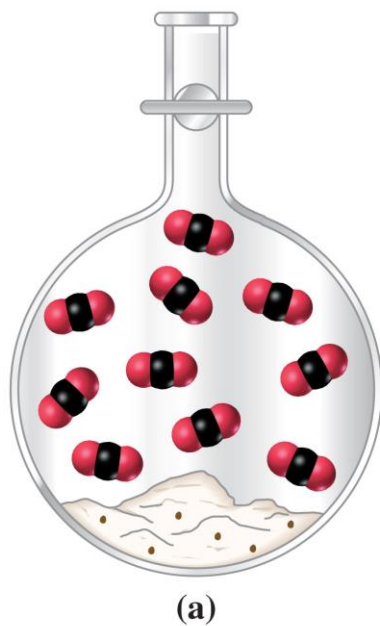$$K = \frac{(3.70 \times 10^{-3})^2}{1.01} = 1.36 \times 10^{-5}$$

General Chemistry: Chapter 15

Burnt Lime

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

$$K_c = [CO_2] \qquad K_P = P_{CO_2}(RT)$$

(a)   (b)

General Chemistry: Chapter 15

15-4 The Significance of the Magnitude of the Equilibrium Constant.

TABLE 15.3   Equilibrium Constants of Some Common Reactions

Reaction	Equilibrium constant, K_p
$2 H_2(g) + O_2(g) \rightleftharpoons 2 H_2O(l)$	1.4×10^{83} at 298 K
$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$	1.9×10^{-23} at 298 K 1.0 at about 1200 K
$2 SO_2(g) + O_2(g) \rightleftharpoons 2 SO_3(g)$	3.4 at 1000 K
$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$	1.6×10^{-21} at 298 K 10.0 at about 1100 K

General Chemistry: Chapter 15

$$CO(g) + 2\ H_2(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CH_3OH(g)$$

Equilibrium can be approached various ways.

Qualitative determination of change of initial conditions as equilibrium is approached is needed.

$$Q_c = \frac{[G]_t^{\ g}[H]_t^{\ h}}{[A]_t^{\ m}[B]_t^{\ n}}$$ At equilibrium $Q_c = K_c$

Reaction Quotient

	(a)	**(b)**	**(c)**	**(d)**	**(e)**
Initial condition:	Pure reactants	"Left" of equilibrium	Equilibrium	"Right" of equilibrium	Pure products
Reaction quotient,	$Q_c = 0$	$< K_c$	$= K_c$	$> K_c$	$= \infty$
Reaction proceeds	$\longrightarrow$ to the right	$\longrightarrow$		$\longleftarrow$	$\longleftarrow$ to the left

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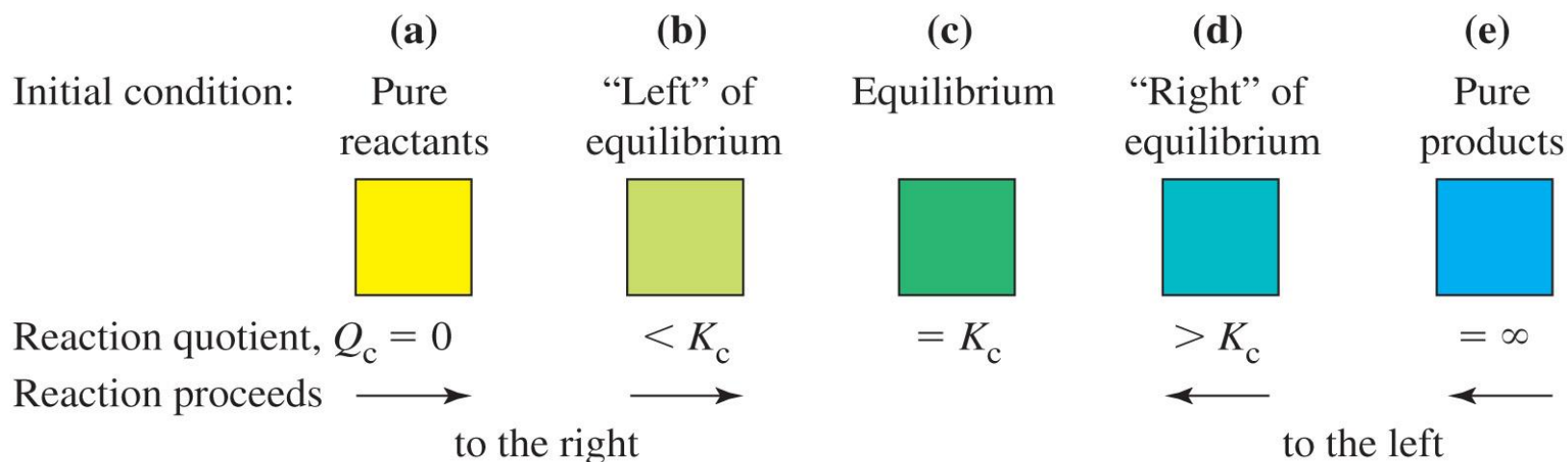
EXAMPLE 15-5   Predicting the Direction of a Net Chemical Change in Establishing Equilibrium

To increase the yield of $H_2(g)$ in the water–gas reaction—the reaction of $C(g)$ and $H_2O(g)$ to form $CO(g)$ and $H_2(g)$—a follow-up reaction called the "water–gas shift reaction" is generally used. In this reaction, some of the $CO(g)$ of the water gas is replaced by $H_2(g)$.

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

$K_c = 1.00$ at about 1100 K. The following amounts of substances are brought together and allowed to react at this temperature: 1.00 mol CO, 1.00 mol H_2O, 2.00 mol CO_2, and 2.00 mol H_2. Compared with their initial amounts, which of the substances will be present in a greater amount and which in a lesser amount when equilibrium is established?

Analyze
Our task is to determine the direction of net change by evaluating Q_c and comparing it to K_c.

Solve
Write down the expression for Q_c.

$$Q_c = \frac{[CO_2][H_2]}{[CO][H_2O]}$$

Substitute concentrations into the expression for Q_c, by assuming an arbitrary volume V (which cancels out in the calculation).

$$Q_c = \frac{(2.00/V)(2.00/V)}{(1.00/V)(1.00/V)} = 4.00$$
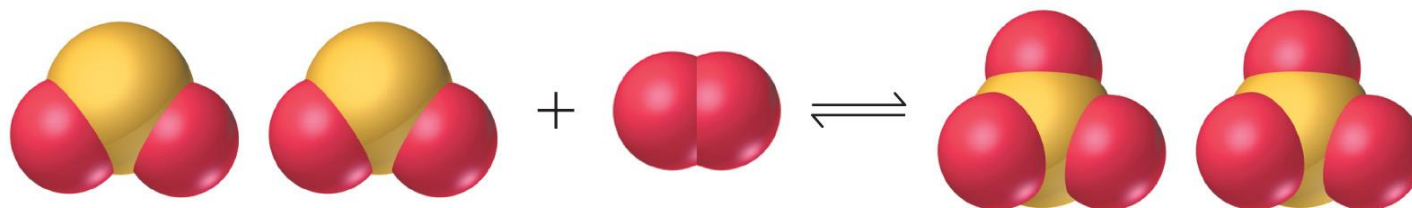
Compare Q_c to K_c.

$$4.00 > 1.00$$

Because $Q_c > K_c$ (that is, $4.00 > 1.00$), a net change occurs to the *left*. When equilibrium is established, the amounts of CO and H_2O will be greater than the initial quantities and the amounts of CO_2 and H_2 will be less.
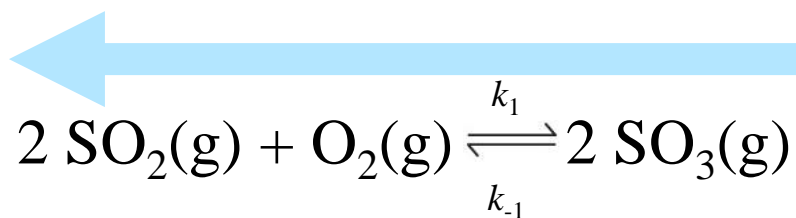
15-6 Altering Equilibrium Conditions:
Le Châtelier's Principle

When an equilibrium system is subjected to a change in temperature, pressure, or concentration of a reacting species, the system responds by attaining a new equilibrium that *partially* offsets the impact of the change.

What happens if we add SO_3 to this equilibrium?

General Chemistry: Chapter 15

Le Châtelier's Principle

$$2\ SO_2(g) + O_2(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2\ SO_3(g)$$

$K_c = 2.8 \times 10^2$ at 1000K

Add:

1.00 mol SO$_3$

(b)

0.68 mol SO$_3$

0.32 mol SO$_2$

0.16 mol O$_2$

10.0 L

(a)

1.46 mol SO$_3$

10.0 L

(c)

0.54 mol SO$_2$

0.27 mol O$_2$

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

$$Q > K_c$$

General Chemistry: Chapter 15
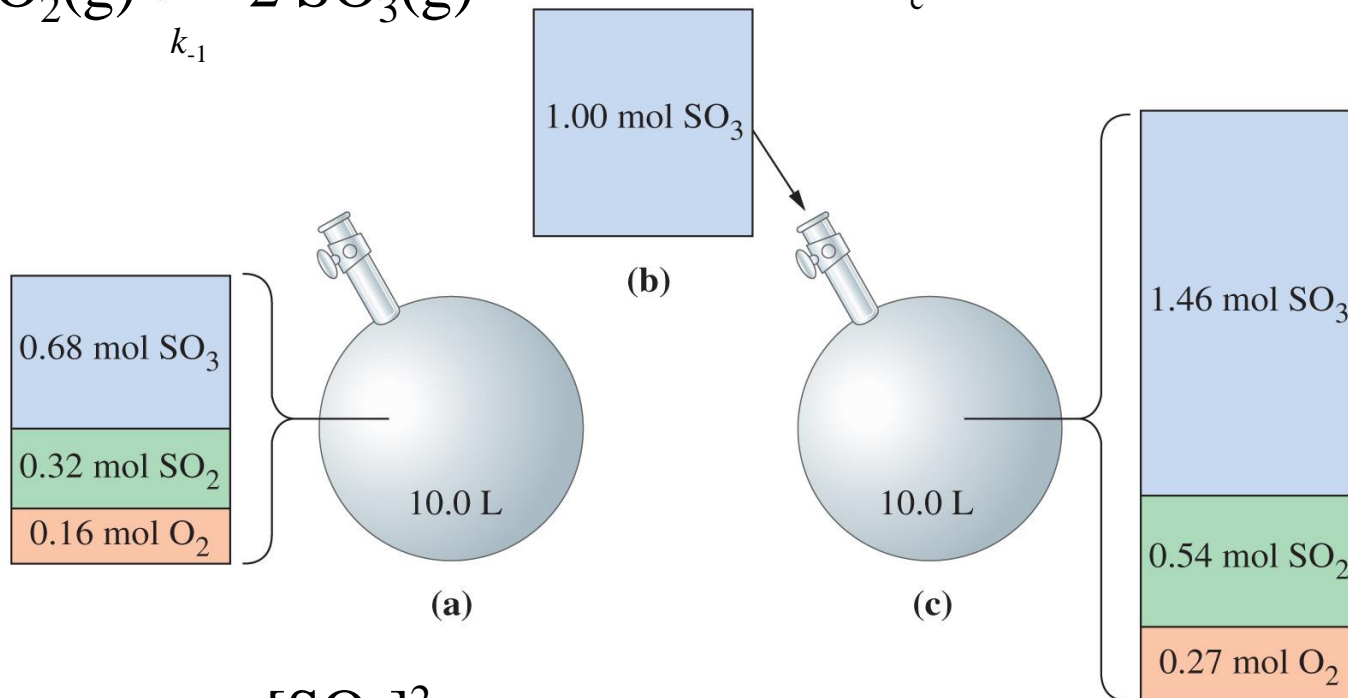
Effect of Condition Changes

Adding a gaseous reactant or product changes P_{gas}.

Adding an inert gas changes the total pressure.

 Relative partial pressures are unchanged.

Changing the volume of the system causes a change in the equilibrium position.

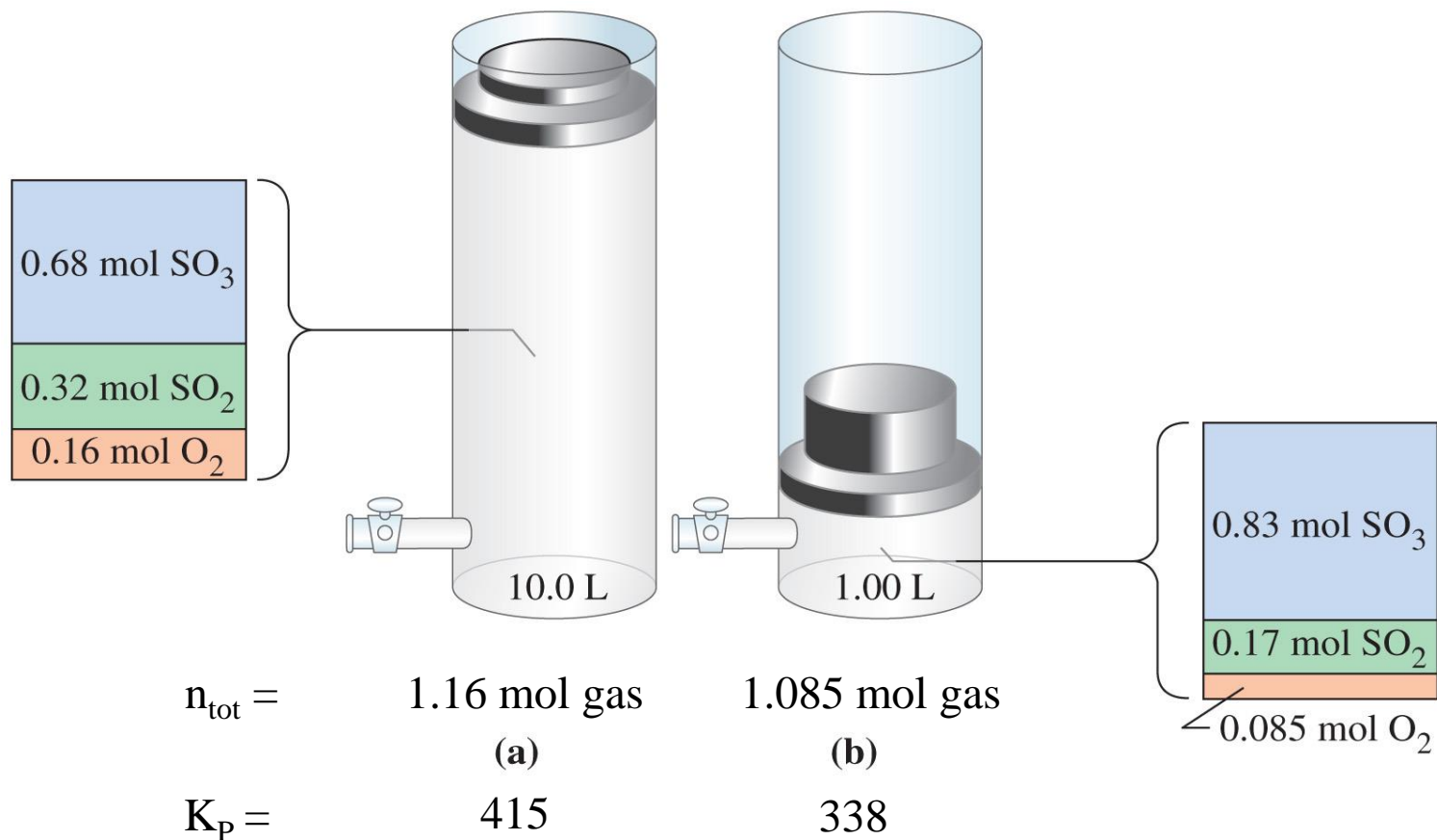$$K_c = \frac{[SO_3]}{[SO_2]^2[O_2]} = \frac{\left(\dfrac{n_{SO_3}}{V}\right)^2}{\left(\dfrac{n_{SO_2}}{V}\right)^2 \dfrac{n_{O_2}}{V}} = \frac{n_{SO_3}^2}{n_{SO_2}^2\, n_{O_2}}\, V$$

General Chemistry: Chapter 15

Effect of Change in Volume

$$K_c = \frac{[G]^g[H]^h}{[C]^c[D]^d} = \frac{n_G^g \; n_H^h}{n_A^a \; n_B^a} V^{(a+b)-(g+h)}$$

$$= \frac{n_G^g \; n_H^h}{n_A^a \; n_B^a} V^{-\Delta n}$$

When the volume of an equilibrium mixture of gases is *reduced*, a net change occurs in the direction that produces *fewer moles of gas*. When the volume is *increased*, a net change occurs in the direction that produces *more moles of gas*.

General Chemistry: Chapter 15

Effect of the Change of Volume

0.68 mol SO_3

0.32 mol SO_2

0.16 mol O_2

10.0 L

1.00 L

0.83 mol SO_3

0.17 mol SO_2

0.085 mol O_2

$n_{tot} =$ 1.16 mol gas 1.085 mol gas

(a) (b)

$K_P =$ 415 338

General Chemistry: Chapter 15

EXAMPLE 15-7   Applying Le Châtelier's Principle: The Effect of Changing Volume

An equilibrium mixture of $N_2(g)$, $H_2(g)$, and $NH_3(g)$ is transferred from a 1.50 L flask to a 5.00 L flask. In which direction does a net change occur to restore equilibrium?

$$N_2(g) + 3 H_2(g) \rightleftharpoons 2 NH_3(g)$$
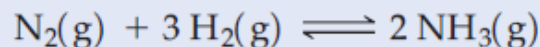
Analyze

Because the volume has increased, the reaction will move in the direction that increases the number of moles of gas.

Solve

When the gaseous mixture is transferred to the larger flask, the partial pressure of each gas and the total pressure drop. Whether we think in terms of a decrease in pressure or an increase in volume, we reach the same conclusion. Equilibrium shifts in such a way as to produce a larger number of moles of gas. Some of the NH_3 originally present decomposes back to N_2 and H_2. A net change occurs in the direction of the reverse reaction—to the left—in restoring equilibrium.

Effect of Temperature on Equilibrium

Raising the temperature of an equilibrium mixture shifts the equilibrium condition in the *direction of the endothermic* reaction.

Lowering the temperature causes a shift in the *direction of the exothermic* reaction.

General Chemistry: Chapter 15

EXAMPLE 15-8   Applying Le Châtelier's Principle: Effect of Temperature on Equilibrium

Consider the reaction

$$2 SO_2(g) + O_2(g) \rightleftharpoons 2 SO_3(g) \qquad \Delta H° = -197.8 \text{ kJ}$$
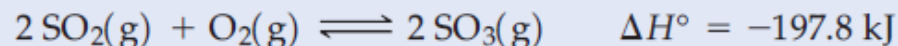
Will the amount of $SO_3(g)$ formed from given amounts of $SO_2(g)$ and $O_2(g)$ be greater at high or low temperatures?

Analyze

We must think of the impact made by changing the temperature. In general, an increase in temperature causes a shift in the direction of the endothermic reaction.

Solve

The sign of $\Delta H°$ tells us that the forward reaction is exothermic. Thus, the reverse reaction is endothermic. In this case, increasing the temperature will favor the reverse reaction and lowering the temperature will favor the forward reaction. The conversion of SO_2 to SO_3 is favored at *low* temperatures.

General Chemistry: Chapter 15

Effect of a Catalyst on Equilibrium

A catalyst changes the mechanism of a reaction to one with a lower activation energy.

A catalyst has no effect on the condition of equilibrium.

But does affect the *rate* at which equilibrium is attained.

General Chemistry: Chapter 15

EXAMPLE 15-9 Determining a Value of K_c from the Equilibrium Quantities of Substances

Dinitrogen tetroxide, $N_2O_4(l)$, is an important component of rocket fuels—for example, as an oxidizer of liquid hydrazine in the Titan rocket. At 25 °C, N_2O_4 is a colorless gas that partially dissociates into NO_2, a red-brown gas. The color of an equilibrium mixture of these two gases depends on their relative proportions, which in turn depends on the temperature (Fig. 15-8).

Equilibrium is established in the reaction $N_2O_4(g) \rightleftharpoons 2 NO_2(g)$ at 25 °C. The quantities of the two gases present in a 3.00 L vessel are 7.64 g N_2O_4 and 1.56 g NO_2. What is the value of K_c for this reaction?

Analyze

We are given the equilibrium amounts (in terms of mass) of the reactants and products, along with the volume of the reaction vessel. We use these values to determine the equilibrium concentrations and plug them into the equilibrium constant expression.

Solve

Convert the mass of N_2O_4 to moles.

$$\text{mol } N_2O_4 = 7.64 \text{ g } N_2O_4 \times \frac{1 \text{ mol } N_2O_4}{92.01 \text{ g } N_2O_4} = 8.303 \times 10^{-2} \text{ mol}$$

Convert moles of N_2O_4 to mol/L.

$$[N_2O_4] = \frac{8.303 \times 10^2 \text{ mol}}{3.00 \text{ L}} = 0.0277 \text{ M}$$

Convert the mass of NO_2 to moles.

$$\text{mol } NO_2 = 1.56 \text{ g } NO_2 \times \frac{1 \text{ mol } NO_2}{46.01 \text{ g } NO_2} = 3.391 \times 10^{-2} \text{ mol}$$

Convert moles of NO_2 to mol/L.

$$[NO_2] = \frac{3.391 \times 10^{-2}}{3.00 \text{ L}} = 0.0113 \text{ M}$$

Write the equilibrium constant expression, substitute the equilibrium concentrations, and solve for K_c.

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} = \frac{(0.0113)^2}{(0.0277)} = 4.61 \times 10^{-3}$$

General Chemistry: Chapter 15

(a)   (b)

▲ FIGURE 15-8
The equilibrium $N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$
(a) At dry ice temperatures, N_2O_4 exists as a solid.
The gas in equilibrium with the solid is mostly
colorless N_2O_4, with only a trace of brown NO_2.
(b) When warmed to room temperature and above,
the N_2O_4 melts and vaporizes. The proportion of
$NO_2(g)$ at equilibrium increases over that at low
temperatures, and the equilibrium mixture of
$N_2O_4(g)$ and $NO_2(g)$ has a red-brown color.
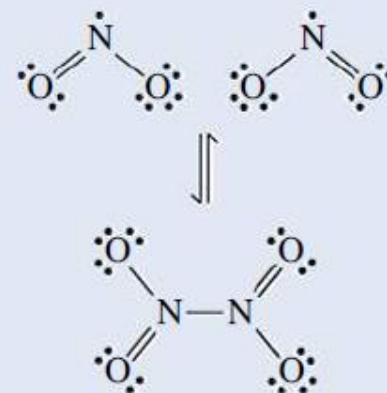
▲ **The Lewis structures of N_2O_4 and $NO_2(g)$**
Nitrogen dioxide is a free radical that combines
exothermically to form dinitrogen tetroxide.

General Chemistry: Chapter 15

EXAMPLE 15-10   **Determining a Value of K_p from Initial and Equilibrium Amounts of Substances: Relating K_c and K_p**

The equilibrium condition for $SO_2(g)$, $O_2(g)$, and $SO_3(g)$ is important in sulfuric acid production. When a 0.0200 mol sample of SO_3 is introduced into an evacuated 1.52 L vessel at 900 K, 0.0142 mol SO_3 is present at equilibrium. What is the value of K_p for the dissociation of $SO_3(g)$ at 900 K?

$$2 SO_3(g) \rightleftharpoons 2 SO_2(g) + O_2(g) \qquad K_p = ?$$
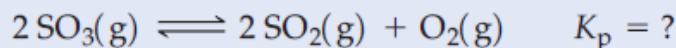
Analyze

Let's first determine K_c and then convert to K_p by using equation (15.16). In the ICE table below, the key term leading to the other data is the change in amount of SO_3: In progressing from 0.0200 mol SO_3 to 0.0142 mol SO_3, 0.0058 mol SO_3 is dissociated. The *negative sign* (−0.0058 mol) indicates that this amount of SO_3 is consumed in establishing equilibrium. In the row labeled "changes," the changes in amounts of SO_2 and O_2 must be related to the change in amount of SO_3. For this, we use the stoichiometric coefficients from the balanced equation: 2, 2, and 1. That is, *two* moles of SO_2 and *one* mole of O_2 are produced for every *two* moles of SO_3 that dissociate.

Solve

| The reaction:	$2 SO_3(g)$	$\rightleftharpoons$	$2 SO_2(g)$	+	$O_2(g)$
initial amounts:	0.0200 mol		0.00 mol		0.00 mol
changes:	−0.0058 mol		+0.0058 mol		+0.0029 mol
equil amounts:	0.0142 mol		0.0058 mol		0.0029 mol
equil concns:	$[SO_3] = \dfrac{0.0142 \text{ mol}}{1.52 \text{ L}};$		$[SO_2] = \dfrac{0.0058 \text{ mol}}{1.52 \text{ L}};$		$[O_2] = \dfrac{0.0029 \text{ mol}}{1.52 \text{ L}}$
	$[SO_3] = 9.34 \times 10^{-3} \text{ M};$		$[SO_2] = 3.8 \times 10^{-3} \text{ M};$		$[O_2] = 1.9 \times 10^{-3} \text{ M}$

$$K_c = \frac{[SO_2]^2[O_2]}{[SO_3]^2} = \frac{(3.8 \times 10^{-3})^2(1.9 \times 10^{-3})}{(9.34 \times 10^{-3})^2} = 3.1 \times 10^{-4}$$

$$K_p = K_c(RT)^{\Delta n_{gas}} = 3.1 \times 10^{-4}(0.0821 \times 900)^{(2+1)-2}$$
$$= 3.1 \times 10^{-4}(0.0821 \times 900)^1 = 2.3 \times 10^{-2}$$

General Chemistry: Chapter 15

EXAMPLE 15-11   Determining Equilibrium Partial and Total Pressures from a Value of K_p

Ammonium hydrogen sulfide, $NH_4HS(s)$, used as a photographic developer, is unstable and dissociates at room temperature.

$$NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g) \qquad K_p = 0.108 \text{ at } 25\,°C$$
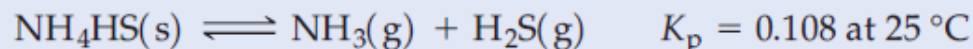
A sample of $NH_4HS(s)$ is introduced into an evacuated flask at $25\,°C$. What is the total gas pressure at equilibrium?

Analyze

We begin by writing the equilibrium constant expression in terms of pressure. The key step is to recognize that the pressure of ammonia is equal to the pressure of hydrogen sulfide. This will then allow us to determine the pressure of ammonia and hydrogen sulfide.

Solve

K_p for this reaction is just the product of the equilibrium partial pressures of $NH_3(g)$ and $H_2S(g)$, each stated in atmospheres. (There is no term for NH_4HS because it is a solid.) Because these gases are produced in equimolar amounts, $P_{NH_3} = P_{H_2S}$.

$$K_p = (P_{NH_3})(P_{H_2S}) = 0.108$$
$$K_p = (P_{NH_3})(P_{H_2S}) = (P_{NH_3})(P_{NH_3}) = (P_{NH_3})^2 = 0.108$$

Find P_{NH_3}. (Note that the unit atm appears because in the equilibrium expression the reference pressure $P°$ was implicitly included.)

$$P_{NH_3} = \sqrt{0.108} = 0.329 \text{ atm} \qquad P_{H_2S} = P_{NH_3} = 0.329 \text{ atm}$$

The total pressure is

$$P_{tot} = P_{NH_3} + P_{H_2S} = 0.329 \text{ atm} + 0.329 \text{ atm} = 0.658 \text{ atm}$$

General Chemistry: Chapter 15

EXAMPLE 15-12   Calculating Equilibrium Concentrations from Initial Conditions

A 0.0240 mol sample of $N_2O_4(g)$ is allowed to come to equilibrium with $NO_2(g)$ in a 0.372 L flask at 25 °C. Calculate the amount of N_2O_4 present at equilibrium (Fig. 15-10).

$$N_2O_4(g) \rightleftharpoons 2 NO_2(g) \qquad K_c = 4.61 \times 10^{-3} \text{ at } 25 \text{ °C}$$

(a)

$\underset{}{} = N_2O_4$

$\underset{}{} = NO_2$

(b)
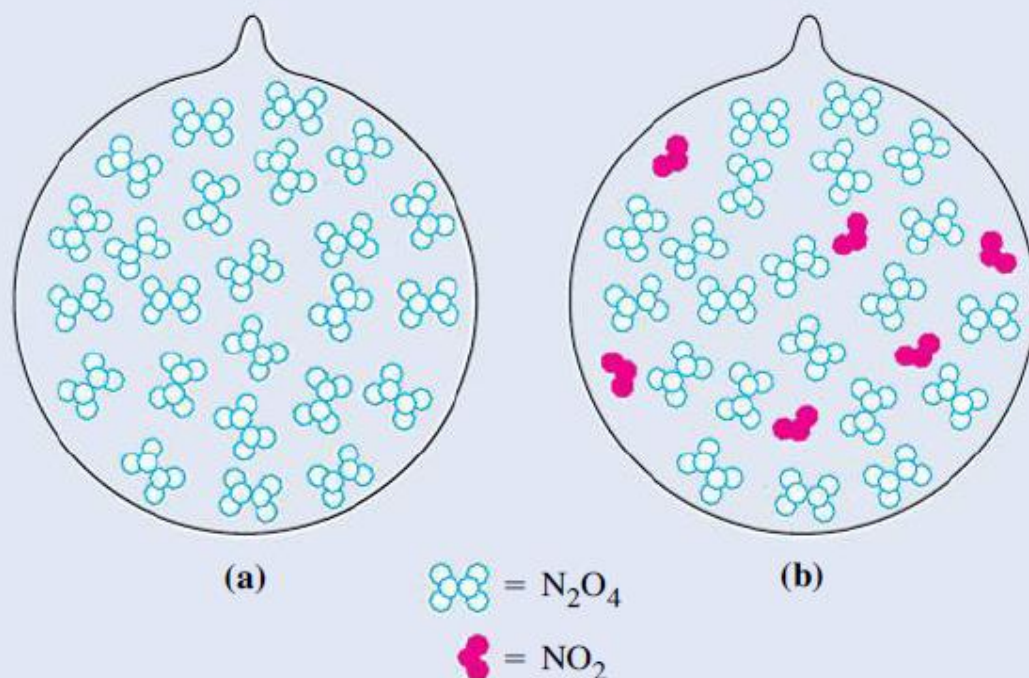
◀ FIGURE 15-10
Equilibrium in the reaction

$$N_2O_4(g) \rightleftharpoons 2 NO_2(g)$$

at 25 °C—Example 15-12 illustrated
Each "molecule" illustrated represents 0.001 mol. **(a)** Initially, the bulb contains 0.024 mol N_2O_4, represented by 24 "molecules." **(b)** At equilibrium, some "molecules" of N_2O_4 have dissociated to NO_2. The 21 "molecules" of N_2O_4 and 6 of NO_2 correspond to 0.021 mol N_2O_4 and 0.006 mol NO_2 at equilibrium.

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Solve

The reaction:	$N_2O_4(g)$	$\rightleftharpoons$	$2\,NO_2(g)$
initial amounts:	0.0240 mol		0.00 mol
changes:	$-x$ mol		$+2x$ mol
equil amounts:	$(0.0240 - x)$ mol		$2x$ mol
equil concns:	$[N_2O_4] = (0.0240 - x)\,\text{mol}/0.372\,\text{L}$		$[NO_2] = 2x\,\text{mol}/0.372\,\text{L}$

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} = \frac{\left(\dfrac{2x}{0.372}\right)^2}{\left(\dfrac{0.0240 - x}{0.372}\right)} = \frac{4x^2}{0.372(0.0240 - x)} = 4.61 \times 10^{-3}$$

$$4x^2 = 4.12 \times 10^{-5} - (1.71 \times 10^{-3})x$$

$$x^2 + (4.28 \times 10^{-4})x - 1.03 \times 10^{-5} = 0$$

$$x = \frac{-4.28 \times 10^{-4} \pm \sqrt{(4.28 \times 10^{-4})^2 + 4 \times 1.03 \times 10^{-5}}}{2}$$

$$= \frac{-4.28 \times 10^{-4} \pm \sqrt{(1.83 \times 10^{-7}) + 4.12 \times 10^{-5}}}{2}$$

$$x = \frac{-4.28 \times 10^{-4} \pm \sqrt{4.14 \times 10^{-5}}}{2}$$

$$= \frac{-4.28 \times 10^{-4} \pm 6.43 \times 10^{-3}}{2}$$

$$= 3.00 \times 10^{-3}\,\text{mol}\,N_2O_4$$

The amount of N_2O_4 at equilibrium is $(0.0240 - x) = (0.0240 - 0.0030) = 0.0210\,\text{mol}\,N_2O_4$.

General Chemistry: Chapter 15

EXAMPLE 15-13   Using the Reaction Quotient, Q_c, in an Equilibrium Calculation

Solid silver is added to a solution with these initial concentrations: $[Ag^+] = 0.200$ M, $[Fe^{2+}] = 0.100$ M, and $[Fe^{3+}] = 0.300$ M. The following reversible reaction occurs.

$$Ag^+(aq) + Fe^{2+}(aq) \rightleftharpoons Ag(s) + Fe^{3+}(aq) \qquad K_c = 2.98$$
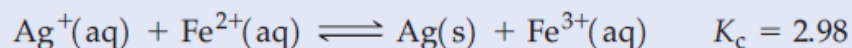
What are the ion concentrations when equilibrium is established?

Analyze

Because all reactants and products are present initially, we need to use the reaction quotient Q_c to determine the direction in which a net change occurs.

$$Q_c = \frac{[Fe^{3+}]}{[Ag^+][Fe^{2+}]} = \frac{0.300}{(0.200)(0.100)} = 15.0$$

Because Q_c (15.0) is larger than K_c (2.98), a net change must occur in the direction of the reverse reaction, *to the left*. Let's define x as the change in molarity of Fe^{3+}. Because the net change occurs *to the left*, we designate the changes for the species on the left side of the equation as positive and those on the right side as negative.

Solve

The reaction:	$Ag^+(aq)$	+	$Fe^{2+}(aq)$	$\rightleftharpoons$ $Ag(s)$ +	$Fe^{3+}(aq)$
initial concns:	0.200 M		0.100 M		0.300 M
changes:	$+x$ M		$+x$ M		$-x$ M
equil concns:	$(0.200 + x)$ M		$(0.100 + x)$ M		$(0.300 - x)$ M

$$K_c = \frac{[Fe^{3+}]}{[Ag^+][Fe^{2+}]} = \frac{(0.300 - x)}{(0.200 + x)(0.100 + x)} = 2.98$$

This equation, which is solved in Appendix A-3, is a quadratic equation for which the acceptable root is $x = 0.11$. To obtain the equilibrium concentrations, we substitute this value of x into the terms shown in the table of data.

$$[Ag^+]_{equil} = 0.200 + 0.11 = 0.31 \text{ M}$$
$$[Fe^{2+}]_{equil} = 0.100 + 0.11 = 0.21 \text{ M}$$
$$[Fe^{3+}]_{equil} = 0.300 - 0.11 = 0.19 \text{ M}$$

General Chemistry: Chapter 15