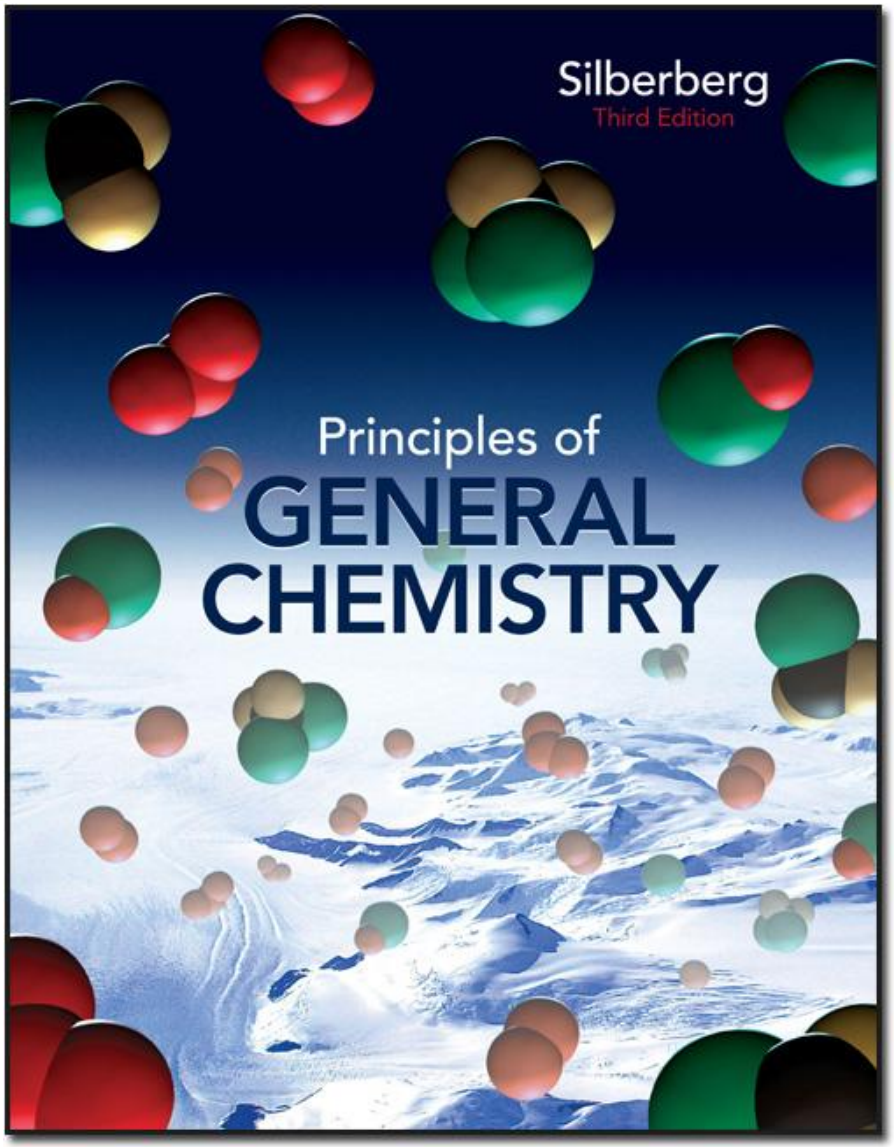


Chapter 17

Lecture Outline

See separate *Image PowerPoint* slides for all figures and tables pre-inserted into PowerPoint without notes.

Chapter 17

Equilibrium: The Extent of Chemical Reactions

Equilibrium: The Extent of Chemical Reactions

17.1 The Equilibrium State and the Equilibrium Constant

17.2 The Reaction Quotient and the Equilibrium Constant

17.3 Expressing Equilibria with Pressure Terms: Relation between K_c and K_p

17.4 Comparing Q and K to Determine Reaction Direction

17.5 How to Solve Equilibrium Problems

17.6 Reaction Conditions and Equilibrium: Le Châtelier's Principle

The Equilibrium State

All reactions are ***reversible*** and under suitable conditions will reach a state of ***equilibrium***.

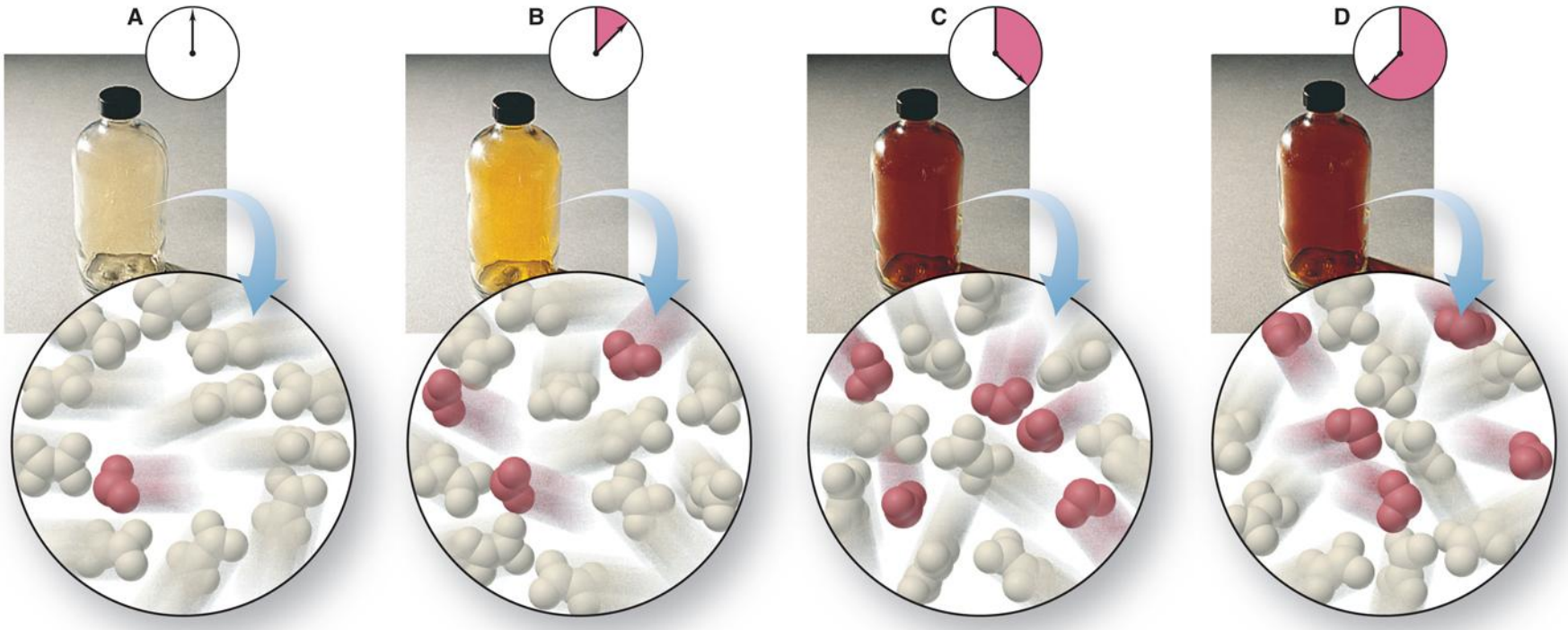
At equilibrium, the concentrations of products and reactants no longer change because the ***rates*** of the forward and reverse reactions are equal.

At equilibrium: $\text{rate}_{\text{forward}} = \text{rate}_{\text{reverse}}$

Chemical equilibrium is a ***dynamic*** state because reactions continue to occur, but because they occur at the same rate, no net change is observed on the macroscopic level.

Figure 17.1 Reaching equilibrium on the macroscopic and molecular levels.

$$N_2O_4(g) \text{ colorless} \rightleftharpoons {}_2NO_2(g) \text{ Brown}$$



The Equilibrium Constant

Consider the reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

At equilibrium $\text{rate}_{fwd} = \text{rate}_{rev}$

$$\text{so } k[N_2O_4]_{eq} = k[NO_2]^2_{eq}$$

$$\text{then } \frac{k_{fwd}}{k_{rev}} = \frac{[NO_2]^2_{eq}}{[N_2O_4]_{eq}}$$

The ratio of constants gives a new constant, the **equilibrium constant *K***:

$$K = \frac{k_{fwd}}{k_{rev}} = \frac{[NO_2]^2_{eq}}{[N_2O_4]_{eq}}$$

K and the extent of reaction

K reflects a particular ratio of **product** concentrations to **reactant** concentrations for a reaction at particular temp.

K therefore indicates the ***extent*** of a reaction, i.e., how far a reaction proceeds towards the products at a given temperature.

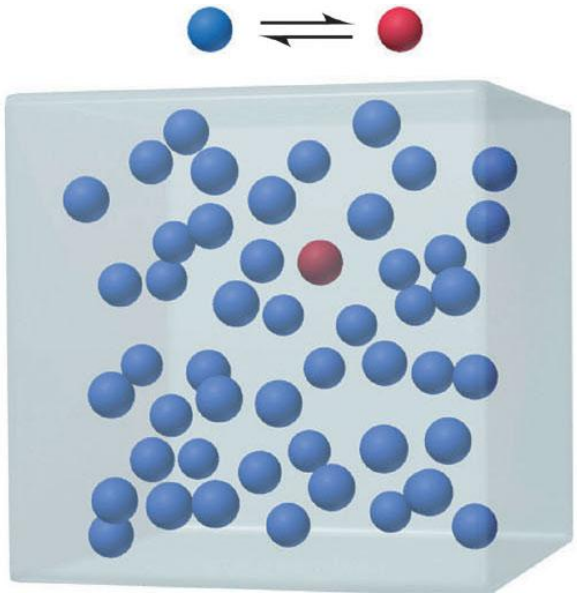
1- A ***small*** value for *K* indicates that the reaction yields little product before reaching equilibrium. The reaction favors the ***reactants***. $N_{2\,(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$ $K = 1 \times 10^{-30}$

2- A ***large*** value for *K* indicates that the reaction reaches equilibrium with very little reactant remaining. The reaction favors the ***products***. $2CO_{(g)} + O_{2(g)} \rightleftharpoons 2CO_{2(g)}$ $K = 2.2 \times 10^{22}$

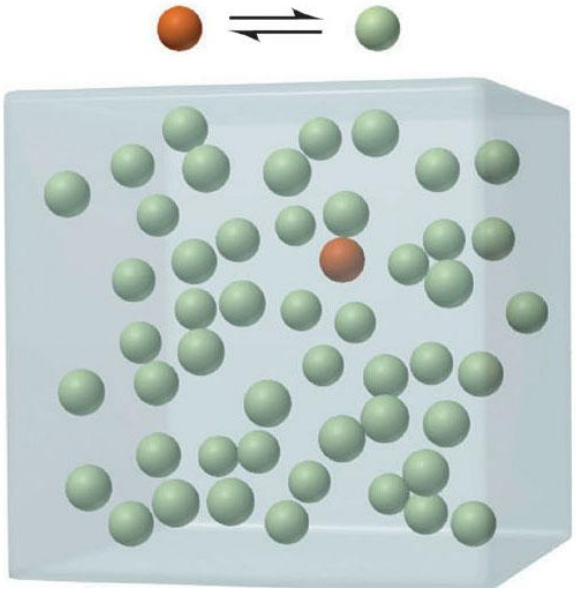
3- Intermediate K when significant amount of both reactant and product are present in equilibrium, K has an intermediate value.

$2\,BrCl_{(g)} \rightleftharpoons Br_{2\,(g)} + Cl_{2\,(g)}$ $K = 5$

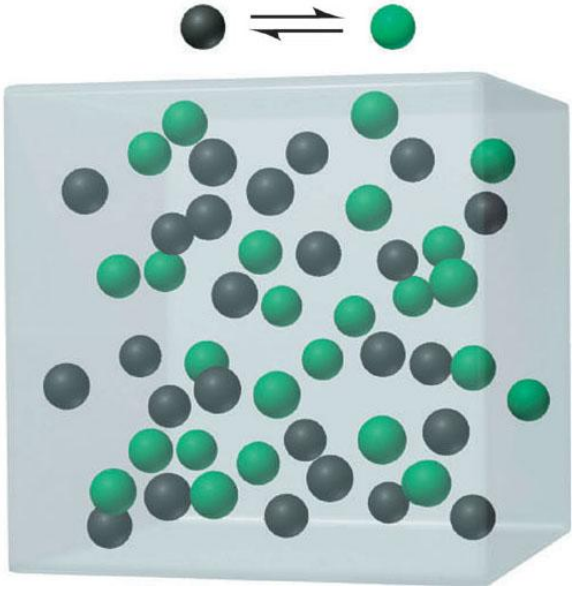
Figure 17.2 The range of equilibrium constants.



small K
The reaction mixture contains mostly reactants.



large K
The reaction mixture contains mostly products.



intermediate K

The Reaction Quotient *Q*

For the general reaction $aA + bB \rightleftharpoons cC + dD$

the reaction quotient (mass action expression) $Q = \frac{[C]^c[D]^d}{[A]^a[B]^b}$

Q gives the ratio of product concentrations to reactant concentrations ***at any point*** in a reaction.

At equilibrium: *Q* = *K* $\quad$ Q_c *If it based on concentration*

For a particular system and temperature, ***the same equilibrium state is attained regardless of starting concentrations***. The value of *Q* indicates how close the reaction is to equilibrium, and in which direction it must proceed to reach equilibrium.

Figure 17.3 The change in Q during the N_2O_4-NO_2 reaction.

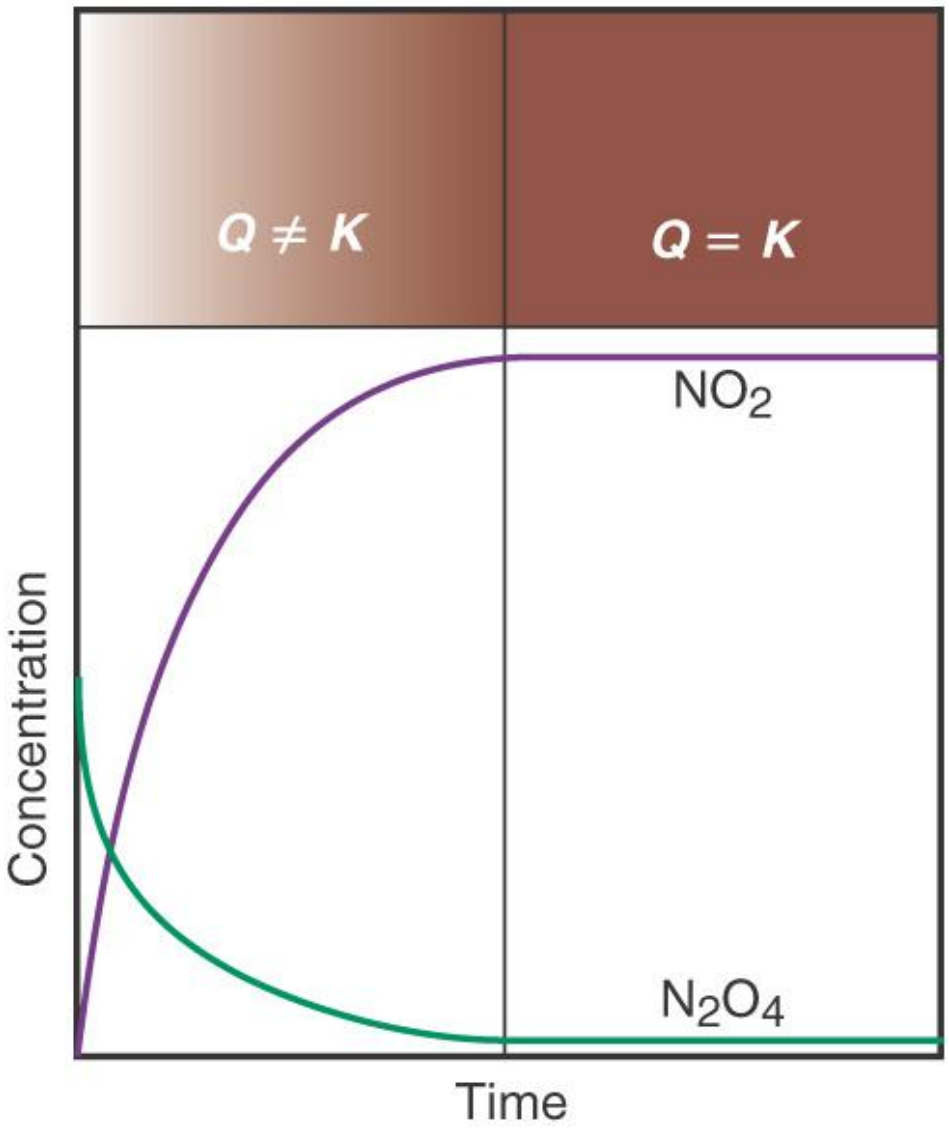


Table 17.1 Initial and Equilibrium Concentration Ratios for the N_2O_4-NO_2 System at 200°C (473 K)

	Initial			Equilibrium		
Expt	$[N_2O_4]$	$[NO_2]$	$Q, \frac{[NO_2]^2}{[N_2O_4]}$	$[N_2O_4]_{eq}$	$[NO_2]_{eq}$	$K, \frac{[NO_2]^2_{eq}}{[N_2O_4]_{eq}}$
1	0.1000	0.0000	0.0000	0.0357	0.193	10.4
2	0.0000	0.1000	∞	0.000924	0.0982	10.4
3	0.0500	0.0500	0.0500	0.00204	0.146	10.4
4	0.0750	0.0250	0.0833	0.00275	0.170	10.5

Sample Problem 17.1 **Writing the Reaction Quotient from the Balanced Equation**

PROBLEM: Write the reaction quotient, Q_c, for each of the following reactions:

(a) The decomposition of dinitrogen pentaoxide, $N_2O_5(g) \rightleftharpoons NO_2(g) + O_2(g)$

(b) The combustion of propane, $C_3H_8(g) + O_2(g) \rightleftharpoons CO_2(g) + H_2O(g)$

PLAN: We balance the equations and then construct the reaction quotient.

SOLUTION:

(a) $2N_2O_5(g) \rightleftharpoons 4NO_2(g) + O_2(g)$ $\qquad Q_c = \dfrac{[NO_2]^4[O_2]}{[N_2O_5]^2}$

(b) $C_3H_8(g) + 5\ O_2(g) \rightleftharpoons 3\ CO_2(g) + 4\ H_2O(g)$ $\qquad Q_c = \dfrac{[CO_2]^3[H_2O]^4}{[C_3H_8][O_2]^5}$

Forms of *K* and *Q*

For an overall reaction that is the ***sum*** of two more individual reactions:

$Q_{overall} = Q_1 \times Q_2 \times Q_3 \times \ldots\ldots$ and

$K_{overall} = K_1 \times K_2 \times K_3 \times \ldots\ldots$

The form of *Q* and *K* depend on the ***direction*** in which the balanced equation is written:

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

$$Q_{c(rev)} = \frac{1}{Q_{c(fwd)}} \qquad K_{c(rev)} = \frac{1}{K_{c(fwd)}}$$

Q and *K* are unitless

Forms of *K* and *Q*

If the coefficients of a balanced equation are multiplied by a common factor,

$$Q' = Q^n = \left(\frac{[C]^c[D]^d}{[A]^a[B]^b}\right)^n \qquad \text{and } K' = K^n$$

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

If Multiplying by 1/2

$SO_2(g) + 1\backslash 2\ O_2(g) \rightleftharpoons SO_3(g)$

$$Q_c = \frac{[SO_3]}{[SO_2]\ [O_2]^{1\backslash 2}} \qquad Q'_{c(fwd)} = Q^{1/2}{}_{c(fwd)} = Q_c = \left(\frac{[SO_3]^2}{[SO_2]^2\ [O_2]}\right)^{1\backslash 2}$$

Sample Problem 17.2 Writing the Reaction Quotient and Finding *K* for an Overall Reaction

PROBLEM: Nitrogen dioxide is a toxic pollutant that contributes to photochemical smog. One way it forms is through the following sequence:

$$(1)\ N_2(g) + O_2(g) \rightleftharpoons 2NO(g) \quad K_{c1} = 4.3\times10^{-25}$$

$$(2)\ 2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g) \quad K_{c2} = 6.4\times10^{9}$$

(a) Show that the overall Q_c for this reaction sequence is the same as the product of the Q_c's of the individual reactions.

(b) Given that both reactions occur at the same temperature, find K_c for the overall reaction.

PLAN: We first write the overall reaction by adding the individual reactions and then write the overall Q_c. Then we write the Q_c for each step. We add the steps and multiply their Q_c's, canceling common terms. We can then calculate the overall K_c.

Sample Problem 17.2

SOLUTION:

(a) (1) $N_2(g) + O_2(g) \rightleftharpoons \cancel{2NO(g)}$ $K_{c1} = 4.3\times10^{-25}$

(2) $\cancel{2NO(g)} + O_2(g) \rightleftharpoons 2NO_2(g)$ $K_{c2} = 6.4\times10^{9}$

$N_2(g) + 2O_2(g) \rightleftharpoons 2NO_2(g)$

$$Q_{c(overall)} = \frac{[NO_2]^2}{[N_2][O_2]^2} \qquad Q_{c1} = \frac{[NO]^2}{[N_2][O_2]} \qquad Q_{c2} = \frac{[NO_2]^2}{[NO]^2[O_2]}$$

$$Q_{c1} \times Q_{c2} = \frac{\cancel{[NO]^2}}{[N_2][O_2]} \times \frac{[NO_2]^2}{\cancel{[NO]^2}[O_2]} = \frac{[NO_2]^2}{[N_2][O_2]^2}$$

(b) $K_c = K_{c1} \times K_{c2} = (4.3\times10^{-25}) \times (6.4\times10^{9})$ **$= 2.8\times10^{-15}$**

K and *Q* for hetereogeneous equilibrium

A ***hetereogeneous*** equilibrium involves reactants and/or products in different phases.

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

A pure **solid** or **liquid** always has the same "concentration", i.e., the same number of moles per liter of solid or liquid.

The expressions for *Q* and *K* include only species whose concentrations ***change*** as the reaction approaches equilibrium.

Pure solids and liquids are omitted from the expression for *Q* or *K*.

For the above reaction, $Q_c = [CO_2]$

Table 17.2 Ways of Expressing Q and Calculating K

Form of Chemical Equations	Form of Q	Value of K
Reference reaction: $A \rightleftharpoons B$	$Q_{(ref)} = \dfrac{[B]}{[A]}$	$K_{(ref)} = \dfrac{[B]_{eq}}{[A]_{eq}}$
Reference reaction: $B \rightleftharpoons A$	$Q = \dfrac{1}{Q_{(ref)}} = \dfrac{[A]}{[B]}$	$K = \dfrac{1}{K_{(ref)}}$
Reaction as sum of two steps: (1) $A \rightleftharpoons C$	$Q_1 = \dfrac{[C]}{[A]}; Q_2 = \dfrac{[B]}{[C]}$	
(2) $C \rightleftharpoons B$	$Q_{overall} = Q_1 \times Q_2 = Q_{(ref)}$ $= \dfrac{\cancel{[C]}}{[A]} \times \dfrac{[B]}{\cancel{[C]}} = \dfrac{[B]}{[A]}$	$K_{overall} = K_1 \times K_2 = K_{(ref)}$
Coefficients multiplied by n	$Q = Q_{(ref)}^{n}$	$K = K_{(ref)}^{n}$
Reaction with pure solid or liquid component, such as $A(s)$	$Q = Q_{(ref)}[A] = [B]$	$K = K_{(ref)}[A] = [B]$

Expressing Equilibria with Pressure Terms K_c and K_p

K for a reaction may be expressed using partial pressures of gaseous reactants instead of molarity.

The partial pressure of each gas is directly proportional to its molarity.

$PV = \mathbf{nRT}$

$$\frac{P}{RT} = \frac{n}{V}$$

Substitute in (1)

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$

$$Q_p = \frac{P_{NO_2}^2}{P_{NO}^2 \times P_{O_2}}$$

$$Q_c = \frac{[NO_2]^2}{[NO]^2\,[O_2]} \quad \ldots.(1) \longrightarrow Q_C = \frac{P_{NO_2}^2}{P_{NO}^2 \times P_{O_2}} \times RT$$

$$\boxed{Q_c = Q_p\,(RT)} \rightarrow \boxed{K_c = K_p\,(RT)} \rightarrow \boxed{K_p = \frac{K_c}{RT}} \longrightarrow \boxed{K_p = K_c\,(RT)^{-1}}$$

$$\boxed{K_p = K_c\,(RT)^{\Delta n(gas)}}$$

$$\boxed{\Delta n_{gas} = n_{(g)}\ \text{product} - n_{(g)}\ \text{reactant}}$$

If the amount (mol) of gas does not change in the reaction, $\Delta n_{gas} = 0$ and $K_p = K_c$.

Sample Problem 17.4 Converting Between K_c and K_p

PROBLEM: A chemical engineer injects limestone ($CaCO_3$) into the hot flue gas of a coal-burning power plant for form lime (CaO), which scrubs SO_2 from the gas and forms gypsum ($CaSO_4 \cdot 2H_2O$). Find K_c for the following reaction, if CO_2 pressure is in atmospheres.

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g) \qquad K_p = 2.1\text{x}10^{-4} \text{ (at 1000 K)}$$

PLAN: We know K_p, so to convert between K_p, we must first determine Δn_{gas} from the balanced equation before we calculate K_c. Since pressure is in atmospheres, $R = 0.0821$ L·atm/mol·K.

SOLUTION: $\Delta n_{gas} = 1 - 0$ since there is one gaseous product and no gaseous reactants.

$$K_p = K_c(RT)^{\Delta n} \quad K_c = K_p/(RT)^{\Delta n} = (2.1\text{x}10^{-4})(0.0821\text{x}1000)^{-1}$$

$$= 2.6\text{x}10^{-6}$$

Determining the Direction of Reaction

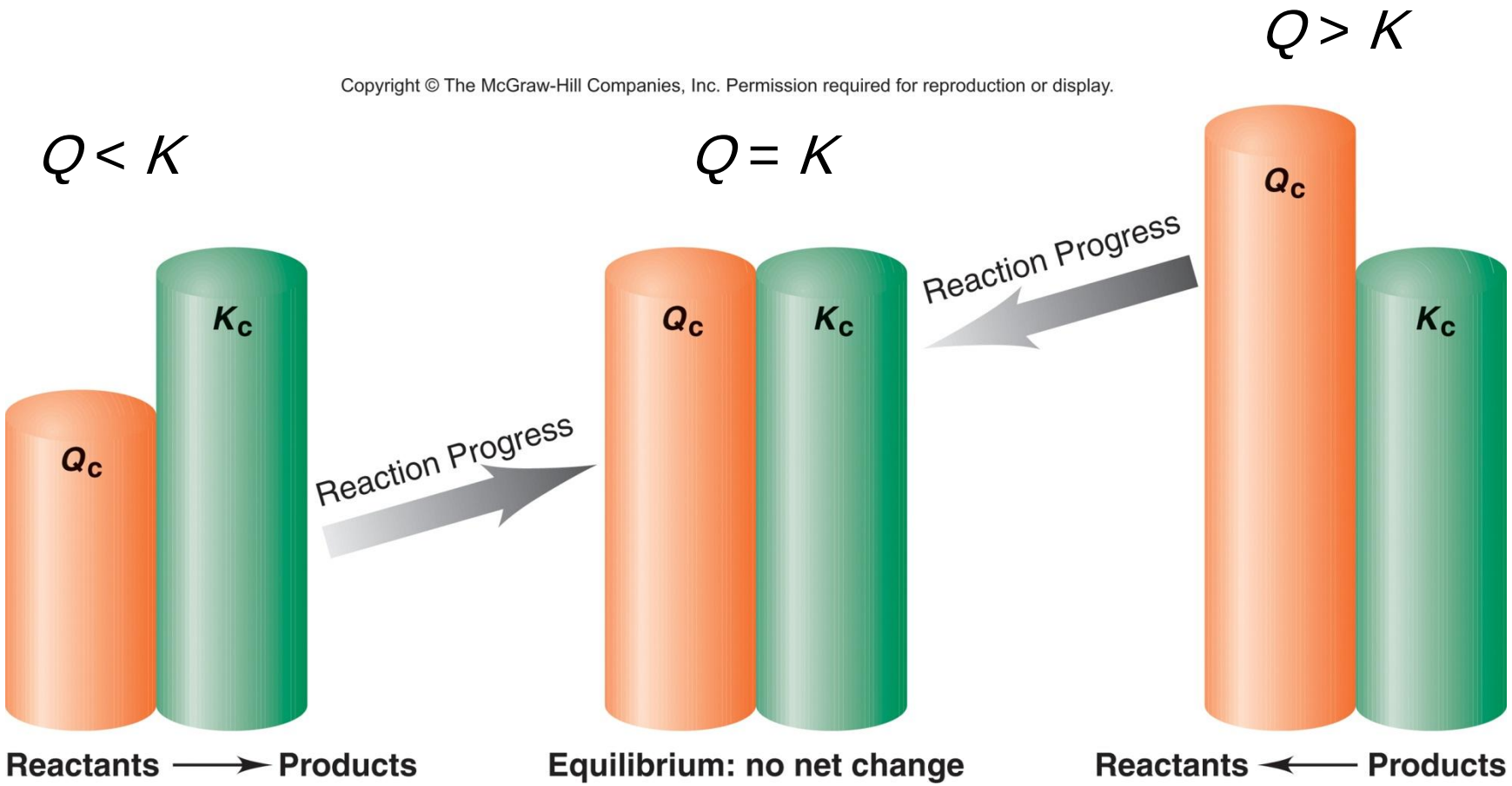
The value of Q indicates the direction in which a reaction must proceed to reach equilibrium.

If $Q < K$, the reactants must decrease and the products increase; reactants → products until equilibrium is reached.

If $Q > K$, the reactants must increase and the products decrease; products → reactants until equilibrium is reached.

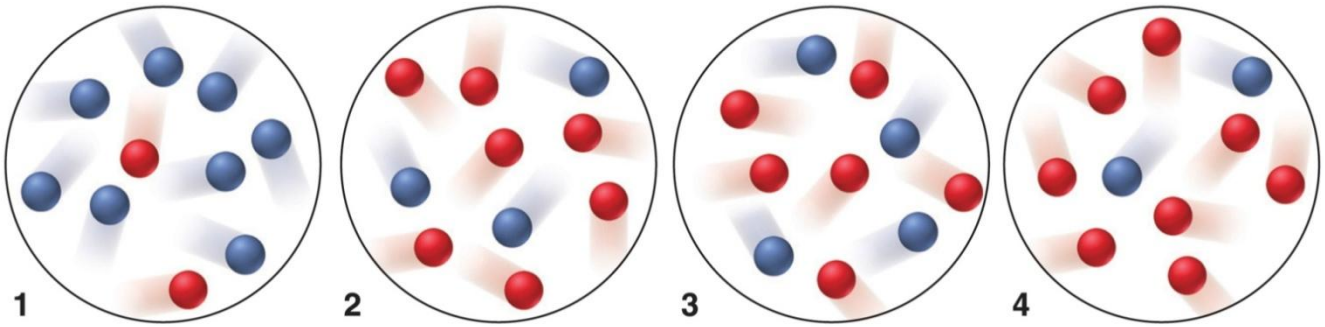
If $Q = K$, the system is at equilibrium and no further net change takes place.

Figure 17.4 Reaction direction and the relative sizes of *Q* and *K*.



Sample Problem 17.4 Using Molecular Scenes to Determine Reaction Direction

PROBLEM: For the reaction A(*g*) $\rightleftharpoons$ B(*g*), the equilibrium mixture at 175°C is [A] = 2.8×10^{-4} *M* and [B] = 1.2×10^{-4} *M*. The molecular scenes below represent mixtures at various times during runs 1-4 of this reaction (A is *red*; B is *blue*). Does the reaction progress to the right or left or not at all for each mixture to reach equilibrium?



PLAN: We must compare Q_c with K_c to determine the reaction direction, so we use the given equilibrium concentrations to find K_c. Then we count spheres and calculate Q for each mixture.

Sample Problem 17.4

SOLUTION:

$$K_c = \frac{[B]}{[A]} = \frac{1.2\text{x}10^{-4}}{2.8\text{x}10^{-4}} = 0.43$$

Counting the red and blue spheres to calculate Q_c for each mixture:

1. $Q_c = 8/2 = 4.0$ 2. $Q_c = 3/7 = 0.43$
3. $Q_c = 4.6 = 0.67$ 4. $Q_c = 2/8 = 0.25$

Comparing Q_c with K_c to determine reaction direction:

1. **$Q_c > K_c$; reaction proceeds to the left.**
2. **$Q_c = K_c$; no net change.**
3. **$Q_c > K_c$; reaction proceeds to the left.**
4. **$Q_c < K_c$; reaction proceeds to the right.**

Solving Equilibrium Problems

If equilibrium quantities are given, we simply substitute these into the expression for K_c to calculate its value.

If only some equilibrium quantities are given, we use a ***reaction table*** to calculate them and find K_c.

A reaction table shows

- the balanced equation,
- the *initial* quantities of reactants and products,
- the *changes* in these quantities during the reaction, and
- the *equilibrium* quantities.

Example: In a study of carbon oxidation, an evacuated vessel containing a small amount of powdered graphite is heated to 1080 K. Gaseous CO_2 is added to a pressure of 0.458 atm and CO forms. At equilibrium, the total pressure is 0.757 atm. Calculate K_p.

$$CO_2(g) + C(\text{graphite}) \rightleftharpoons 2CO(g)$$

Pressure (atm)	**$CO_2(g)$ +**	**C(graphite)** $\rightleftharpoons$	**$2CO(g)$**
Initial	0.458	-	0
Change	$-x$	-	$+2x$
Equilibrium	$0.458 - x$	-	$2x$

The amount of CO_2 will **decrease**. If we let the decrease in CO_2 be x, then the increase in CO will be $+2x$.

Equilibrium amounts are calculated by adding the change to the initial amount.

Once we have the equilibrium amounts expressed in terms of x, we use the other information given in the problem to solve for x.

The total pressure at equilibrium is 0.757 atm = $P_{CO_2(eq)} + P_{CO(eq)}$

$$0.757 \text{ atm} = 0.458 - x + 2x \qquad \text{(from reaction table)}$$

$$0.757 \text{ atm} = 0.458 + x$$
$$x = 0.757 - 0.458 = 0.299 \text{ atm}$$

At equilibrium $P_{CO_2(eq)} = 0.458 - x = 0.458 - 0.299 = 0.159$ atm

$$P_{CO} = 2x = 2(0.299) = 0.598 \text{ atm}$$

$$K_p = \frac{P^2_{CO_2(eq)}}{P_{CO(eq)}} = \frac{0.598^2}{0.159} = 2.25$$

Sample Problem 17.6 Calculating K_c from Concentration Data

PROBLEM: In order to study hydrogen halide decomposition, a researcher fills an evacuated 2.00-L flask with 0.200 mol of HI gas and allows the reaction to proceed at 453°C.

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

At equilibrium, [HI] = 0.078 *M*. Calculate K_c.

PLAN: To calculate K_c we need equilibrium concentrations. We can find the initial [HI] from the amount and the flask volume, and we are given [HI] at equilibrium. From the balanced equation, when $2x$ mol of HI reacts, x mol of H_2 and x mol of I_2 form. We use this information to set up a reaction table.

SOLUTION: Calculating [HI]:

$$[HI] = \frac{0.200 \text{ mol}}{2.00 \text{ L}} = 0.100 \ M$$

Sample Problem 17.6

Concentration (*M*)	$2HI(g) \rightleftharpoons$	$H_2(g)$ +	$I_2(g)$
Initial	0.100	0	0
Change	$-2x$	$+x$	$+x$
Equilibrium	$0.100 - 2x$	x	x

$[HI] = 0.078 = 0.100 - 2x; \quad x = 0.011\ M$

$$Q_c = \frac{[H_2]\,[I_2]}{[HI]^2} = \frac{(0.011)(0.011)}{(0.078)^2}$$

$= 0.020 = K_c$

Sample Problem 17.7 **Determining Equilibrium Concentrations from K_c**

PROBLEM: In a study of the conversion of methane to other fuels, a chemical engineer mixes gaseous CH_4 and H_2O in a 0.32-L flask at 1200 K. At equilibrium the flask contains 0.26 mol of CO, 0.091 mol of H_2, and 0.041 mol of CH_4. What is the $[H_2O]$ at equilibrium? $K_c = 0.26$ for this process at 1200 K.

PLAN: First we write the balanced equation and the expression for Q_c. We calculate the equilibrium concentrations from the given numbers of moles and the flask volume. We then use the value of K_c to solve for $[H_2O]$.

SOLUTION: $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$

$$[CH_4]_{eq} = \frac{0.041 \text{ mol}}{0.32 \text{ L}} = 0.13\ M \qquad [CO]_{eq} = \frac{0.26 \text{ mol}}{0.32 \text{ L}} = 0.81\ M$$

$$[H_2]_{eq} = \frac{0.091 \text{ mol}}{0.32 \text{ L}} = 0.28\ M$$

Sample Problem 17.7

$$Q_c = \frac{[CO][H_2]^3}{[CH_4][H_2O]}$$

$$[H_2O] = \frac{[CO][H_2]^3}{[CH_4]\,K_c} = \frac{(0.81)(0.28)^3}{(0.13)(0.26)}$$

= 0.53 *M*

Sample Problem 17.8 Determining Equilibrium Concentrations from Initial Concentrations and K_c

PROBLEM: Fuel engineers use the extent of the change from CO and H_2O to CO_2 and H_2 to regulate the proportions of synthetic fuel mixtures. If 0.250 mol of CO and 0.250 mol of H_2O are placed in a 125-mL flask at 900 K, what is the composition of the equilibrium mixture? At this temperature, K_c is 1.56.

PLAN: We have to find the concentrations of all species at equilibrium and then substitute into a K_c expression. First we write a balanced equation, calculate initial concentrations and set up a reaction table.

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

Calculating initial concentrations, $[CO] = [H_2O] = \dfrac{0.250 \text{ mol}}{0.125 \text{ L}} = 2.00\ M$


Sample Problem 17.8

Concentration (*M*)	$CO(g)$	+	$H_2O(g)$	⇌	$CO_2(g)$	+	$H_2(g)$
Initial	2.00		2.00		0		0
Change	$-x$		$-x$		$+x$		$+x$
Equilibrium	$2.00 - x$		$2.00 - x$		x		x

$$Q_c = K_c = \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{(x)(x)}{(2.00 - x)(2.00 - x)} = \frac{(x)^2}{(2.00 - x)^2}$$

$$\sqrt{1.56} = \frac{x}{2.00 - x} = \pm 1.25 \qquad x = 1.11\ M \qquad 2.00 - x = 0.89\ M$$

$[CO] = [H_2O] = 0.89\ M$ **$[CO_2] = [H_2] = 1.11\ M$**

Sample Problem 17.9 **Making a Simplifying Assumption to Calculate Equilibrium Concentrations**

PROBLEM: Phosgene is a potent chemical warfare agent that is now outlawed by international agreement. It decomposes by the reaction $COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$; $K_c = 8.3 \times 10^{-4}$ at 360°C. Calculate [CO], [Cl_2], and [$COCl_2$] when the following amounts of phosgene decompose and reach equilibrium in a 10.0-L flask.

(a) 5.00 mol $COCl_2$ **(b)** 0.100 mol $COCl_2$

PLAN: We know from the balanced equation that when x mol of $COCl_2$ decomposes, x mol of CO and x mol of Cl_2 form. We calculate initial concentrations, define x, set up a reaction table, and substitute the values into the expression for Q_c. Since K_c is very small, we can assume that x is negligible, which simplifies the expression. We must check this assumption when we have solved for x.

Sample Problem 17.9

SOLUTION:

(a) Calculating initial concentrations, $[COCl_2] = \frac{0.500 \text{ mol}}{10.0 \text{ L}} = 0.500\ M$

Let x = amount of $COCl_2$ that reacts:

Concentration (*M*)	**$COCl_2$ (*g*)** $\rightleftharpoons$	**CO(*g*)** +	**Cl_2(*g*)**
Initial	0.500	0	0
Change	$-x$	$+x$	$+x$
Equilibrium	$0.500 - x$	x	x

$$K_c = \frac{[CO][Cl_2]}{[COCl_2]} = \frac{x^2}{0.500 - x} = 8.3 \times 10^{-4}$$

Sample Problem 17.9

Since K_c is very small, the reaction does not proceed very far to the right, so let's assume that x can be neglected when we calculate $[COCl_2]_{eqm}$:

$$K_c = 8.3\text{x}10^{-4} \approx \frac{x^2}{0.500} \qquad x^2 \approx (8.3\text{x}10^{-4})(0.500)$$

$$\text{so } x \approx 2.0\text{x}10^{-2}$$

At equilibrium, $\mathbf{[COCl_2]} = 0.500 - 2.0\text{x}10^{-2} = \mathbf{7.5\text{x}10^{-3}}$ ***M***
and $\mathbf{[Cl_2] = [CO] = 2.0\text{x}10^{-2}}$ ***M***

Check that the assumption is justified:

$$\frac{x}{[COCl_2]_{init}} \text{ x } 100 = \frac{2.0\text{x}10^{-2}}{0.500} \text{ x } 100 = 4\%, \text{ which is } < 5\%, \text{ so the assumption is justified.}$$

Sample Problem 17.9

(b) Calculating initial concentrations, $[COCl_2] = \frac{0.100 \text{ mol}}{10.0 \text{ L}} = 0.0100\ M$

$$K_c = \frac{[CO][Cl_2]}{[COCl_2]} = \frac{x^2}{0.0100 - x} = 8.3 \times 10^{-4}$$

If we assume that $0.0100 - x \approx 0.100$

then $K_c = 8.3 \times 10^{-4} \approx \frac{x^2}{0.0100}$ and $x \approx 2.9 \times 10^{-3}$

Checking the assumption:

$\frac{2.9 \times 10^{-3}}{0.0100} \times 100 = 29\%$, which is > 5%, so the assumption is *not* justified.

Sample Problem 17.9

Using the quadratic formula we get

$x^2 + (8.3\text{x}10^{-4})x - (8.3\text{x}10^{-6}) = 0$

$x = 2.5\text{x}10^{-3}$ and $0.0100 - x = 7.5\text{x}10^{-3}$ *M*

$[CO] = [Cl_2] = 2.5\text{x}10^{-3}$ *M*

$[COCl_2] = 7.5\text{x}10^{-3}$ *M*

The Simplifying Assumption

We assume that x([A]$_{reacting}$ can be neglected if

- K_c is relatively small and/or
- [A]$_{init}$ is relatively large.

If $\frac{[A]_{init}}{K_c} > 400$, the assumption is justified; neglecting x introduces an error < 5%.

If $\frac{[A]_{init}}{K_c} < 400$, the assumption is not justified; neglecting x introduces an error > 5%.

Sample Problem 17.10 Predicting Reaction Direction and Calculating Equilibrium Concentrations

PROBLEM: The research and development unit of a chemical company is studying the reaction of CH_4 and H_2S, two components of natural gas: $CH_4(g) + 2H_2S(g) \rightleftharpoons CS_2(g) + 4H_2(g)$

In one experiment, 1.00 mol of CH_4, 1.00 mol of CS_2, 2.00 mol of H_2S, and 2.00 mol of H_2 are mixed in a 250-mL vessel at 960°C. At this temperature, $K_c = 0.036$.

(a) In which direction will the reaction proceed to reach equilibrium?

(b) If $[CH_4] = 5.56\ M$ at equilibrium, what are the equilibrium concentrations of the other substances?

PLAN: **(a)** To find the direction of reaction we determine the initial concentrations from the given amounts and volume, calculate Q_c and compare it with K_c.

(b) Based on this information, we determine the sign of each concentration change for the reaction table and hence calculate equilibrium concentrations.

Sample Problem 17.10

SOLUTION:

(a) Calculating initial concentrations, $[CH_4] = \dfrac{1.00 \text{ mol}}{0.250 \text{ L}} = 4.00\ M$

$[H_2S] = 8.00\ M$, $[CS_2] = 4.00\ M$ and $[H_2] = 8.00\ M$

$$Q_c = \frac{[CS_2][H_2]^4}{[CH_4][H_2S]^2} = \frac{(4.0)(8.0)^4}{(4.0)(8.0)^2} = 64$$

Since $Q_c > K_c$, the reaction will proceed to the left. The reactant concentrations will increase and the product concentrations will decrease.

Sample Problem 17.10

(b) We use this information to construct our reaction table.

Concentration (*M*)	$CH_4(g)$	+ $2H_2S(g)$	⇌ $CS_2(g)$	+ $4H_2(g)$
Initial	4.00	8.00	4.00	8.00
Change	$+x$	$+2x$	$-x$	$-4x$
Equilibrium	$4.00 + x$	$8.00 + 2x$	$4.00 - x$	$8.00 - 4x$

At equilibrium $[CH_4] = 5.56\ M$, so $4.00 + x = 5.56$ and $x = 1.56$

$[H_2S] = 8.00 + 2x = 11.12\ M$

$[CS_2] = 4.00 - x = 2.44\ M$

$[H_2] = 8.00 - 4x = 1.76\ M$

Figure 17.5 Steps in solving equilibrium problems.

PRELIMINARY SETTING UP

1. Write the balanced equation.
2. Write the reaction quotient, *Q*.
3. Convert all amounts into the correct units (*M* or atm).

WORKING ON THE REACTION TABLE

4. When reaction direction is not known, compare *Q* with *K*.
5. Construct a reaction table.

✓ Check the sign of x, the change in the concentration (or pressure).

Figure 17.5 continued

SOLVING FOR x AND EQUILIBRIUM QUANTITIES

6. Substitute the quantities into Q.

7. To simplify the math, assume that x is negligible:

$$([A]_{init} - x = [A]_{eq} \approx [A]_{init})$$

8. Solve for x.

✓ Check that assumption is justified (<5% error). If not, solve quadratic equation for x.

9. Find the equilibrium quantities.

✓ Check to see that calculated values give the known K.

Le Châtelier's Principle

When a chemical system at equilibrium is disturbed, it reattains equilibrium by undergoing a ***net reaction*** that ***reduces*** the effect of the disturbance.

A system is disturbed when a change in conditions forces it temporarily out of equilibrium.

The system responds to a disturbance by a ***shift*** in the equilibrium ***position***.

A shift ***to the left*** is a net reaction from product to reactant.

A shift ***to the right*** is a net reaction from reactant to product.

The Effect of a Change in Concentration

If the concentration of A increases, the system reacts to consume some of it.

- If a reactant is added, the equilibrium position shifts to the right.
- If a product is added, the equilibrium position shifts to the left.

If the concentration of B decreases, the system reacts to consume some of it.

- If a reactant is removed, the equilibrium position shifts to the left.
- If a product is removed, the equilibrium position shifts to the right.

Only substances that appear in the expression for Q can have an effect.

A change in concentration has ***no effect*** on the value of K.

Figure 17.6 The effect of a change in concentration.

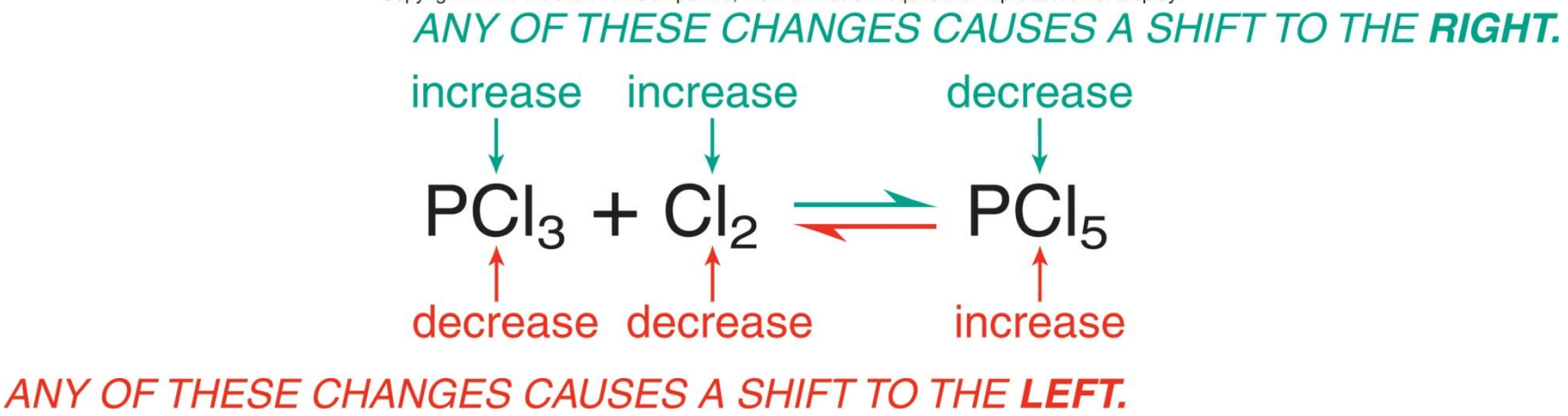
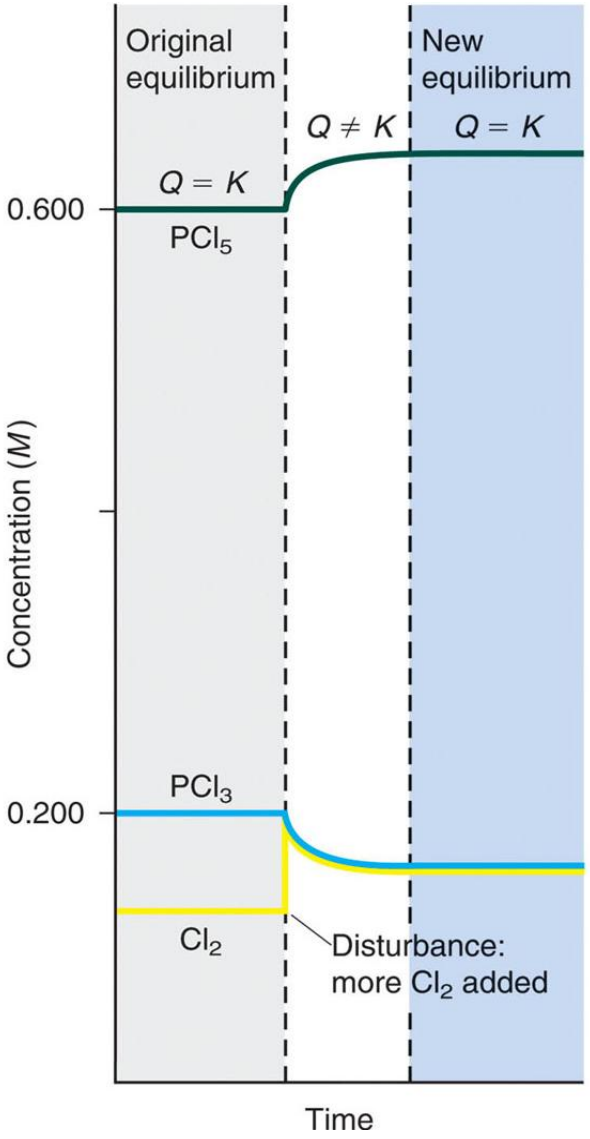


Table 17.3 The Effect of Added Cl_2 on the PCl_3-Cl_2-PCl_5 System

Concentration (M)	$PCl_3(g)$ +	$Cl_2(g)$	$\rightleftharpoons$	$PCl_3(g)$
Original equilibrium	0.200	0.125		0.600
Disturbance		+0.075		
New initial	0.200	0.200		0.600
Change	$-x$	$-x$		$+x$
New equilibrium	0.200 - x	0.200 - x		0.600 + x (0.637)*

*Experimentally determined value

Figure 17.7 The effect of added Cl_2 on the PCl_3-Cl_2-PCl_5 system.



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

When Cl_2 (*yellow curve*) is added, its concentration increases instantly (*vertical part of yellow curve*) and then falls gradually as it reacts with PCl_3 to form more PCl_5. Equilibrium is re-established at new concentrations but with the **same value of *K***.

Sample Problem 17.11

Predicting the Effect of a Change in Concentration on the Equilibrium Position

PROBLEM: To improve air quality and obtain a useful product, chemists often remove sulfur from coal and natural gas by treating the contaminant hydrogen sulfide with O_2:

$$2H_2S(g) + O_2(g) \rightleftharpoons 2S(s) + 2H_2O(g)$$

What happens to

(a) $[H_2O]$ if O_2 is added? **(b)** $[H_2S]$ if O_2 is added?

(c) $[O_2]$ if H_2S is removed? **(d)** $[H_2S]$ if sulfur is added?

PLAN: We write the reaction quotient to see how Q_c is affected by each disturbance, relative to K_c. This effect tells us the direction in which the reaction proceeds for the system to reattain equilibrium and how each concentration changes.

Sample Problem 17.12

SOLUTION: $$Q_c = \frac{[H_2O]^2}{[H_2S]^2[O_2]}$$

(a) When O_2 is added, Q decreases and the reaction proceeds to the right until $Q_c = K_c$ again, so **$[H_2O]$ increases.**

(b) When O_2 is added, Q decreases and the reaction proceeds to the right until $Q_c = K_c$ again, so **$[H_2S]$ decreases.**

(c) When H_2S is removed, Q increases and the reaction proceeds to the left until $Q_c = K_c$ again, so **$[O_2]$ increases.**

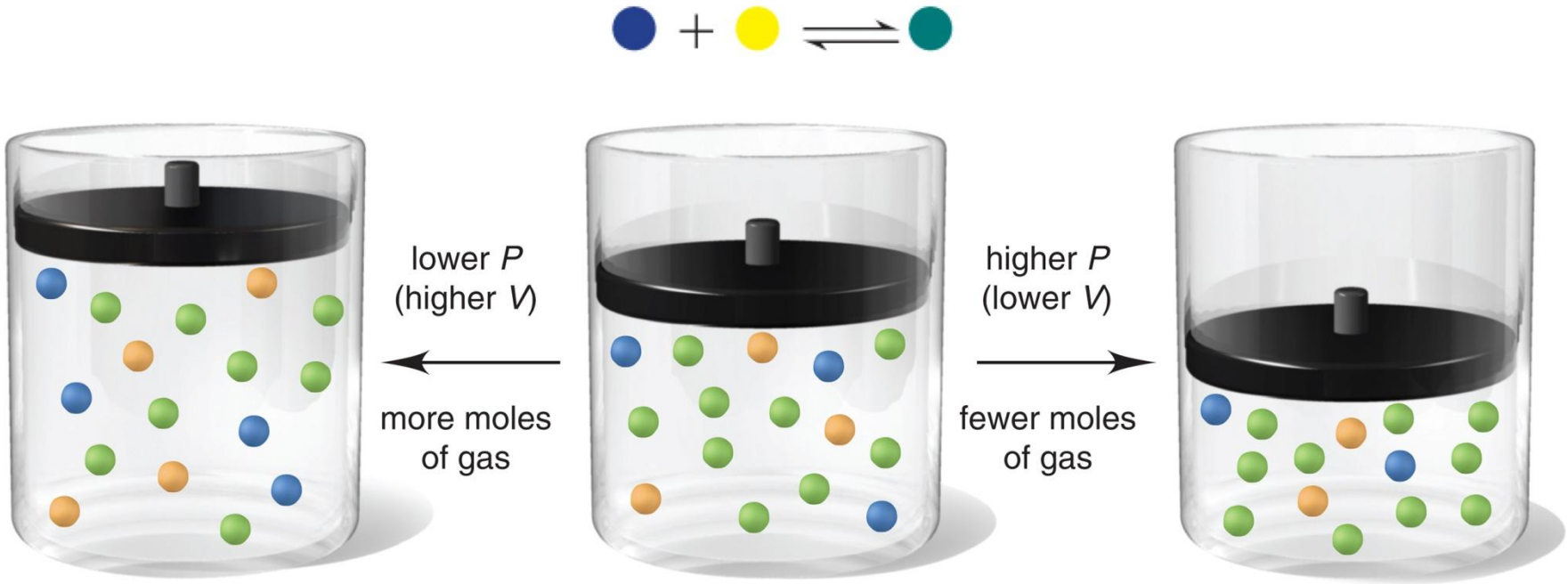
(d) The concentration of solid S is unchanged as long as some is present, so it does not appear in the reaction quotient. Adding more S has no effect, so **$[H_2S]$ is unchanged.**

The Effect of a Change in Pressure (Volume)

Changes in pressure affect equilibrium systems containing gaseous components.

- Changing the concentration of a gaseous component causes the equilibrium to shift accordingly.
- Adding an inert gas has ***no effect*** on the equilibrium position, as long as the volume does not change.
  - This is because all concentrations and partial pressures remain unchanged.
- Changing the volume of the reaction vessel will cause equilibrium to shift if $\Delta n_{gas} \neq 0$.
- Changes in pressure (volume) have ***no effect*** on the value of *K*.

Figure 17.8 **The effect of a change in pressure (volume) on a system at equilibrium.**



Sample Problem 17.12 Predicting the Effect of a Change in Volume (Pressure) on the Equilibrium Position

PROBLEM: How would you change the volume of each of the following reactions to *increase* the yield of the products?

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

(b) $S(s) + 3F_2(g) \rightleftharpoons SF_6(g)$

(c) $Cl_2(g) + I_2(g) \rightleftharpoons 2ICl(g)$

PLAN: Whenever gases are present, a change in volume causes a change in concentration. For reactions in which the number of moles of gas changes, a decrease in volume (pressure increase) causes an equilibrium shift to lower the pressure by producing fewer moles of gas. A volume increase (pressure decrease) has the opposite effect.

Sample Problem 17.12

SOLUTION:

(a) CO_2 is the only gas present. To increase its yield, we should **increase the volume** (decrease the pressure).

(b) There are more moles of gaseous reactants than products, so we should **decrease the volume** (increase the pressure) to shift the equilibrium to the right.

(c) The number of moles of gas is the same in both the reactants and the products; therefore **a change in volume will have no effect**.

The Effect of a Change in Temperature

To determine the effect of a change in temperature on equilibrium, heat is considered a component of the system.

Heat is a ***product*** in an ***exothermic*** reaction ($\Delta H^\circ_{rxn} < 0$).

Heat is a ***reactant*** in an ***endothermic*** reaction ($\Delta H^\circ_{rxn} > 0$).

An ***increase*** in temperature ***adds*** heat, which favors the ***endothermic*** reaction.

A ***decrease*** in temperature ***removes*** heat, which favors the ***exothermic*** reaction.

Temperature and *K*

The only factor that affects the value of *K* for a given equilibrium system is ***temperature***.

For a reaction with $\Delta H^\circ_{rxn} > 0$, an ***increase*** in temperature will cause *K* to ***increase***.

For a reaction with $\Delta H^\circ_{rxn} < 0$, an ***increase*** in temperature will cause *K* to ***decrease***.

The van't Hoff equation shows this relationship:

$$\ln \frac{K_2}{K_1} = -\frac{\Delta H^\circ_{rxn}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$R = 8.314$ J/mol·K

K_1 is the equilibrium constant at T_1

Sample Problem 17.13 **Predicting the Effect of a Change in Temperature on the Equilibrium Position**

PROBLEM: How does an *increase* in temperature affect the equilibrium concentration of the underlined substance and *K* for each of the following reactions?

(a) $CaO(s) + H_2O(l) \rightleftharpoons Ca(OH)_2(aq)$ $\Delta H^\circ = -82$ kJ

(b) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ $\Delta H^\circ = 178$ kJ

(c) $SO_2(g) \rightleftharpoons S(s) + O_2(g)$ $\Delta H^\circ = 297$ kJ

PLAN: We write each equation to show heat as a reactant or product. The temperature increases when we add heat, so the system shifts to absorb the heat; that is, the endothermic reaction is favored. Thus, *K* will increase if the forward reaction is endothermic and decrease if it is exothermic.

Sample Problem 17.13

SOLUTION:

(a) $CaO(s) + H_2O(l) \rightleftharpoons Ca(OH)_2(aq) + \text{heat}$

An increase in temperature will shift the reaction to the left, so **$[Ca(OH)_2]$ and *K* will decrease.**

(b) $CaCO_3(s) + \text{heat} \rightleftharpoons CaO(s) + CO_2(g)$

An increase in temperature will shift the reaction to the right, so **$[CO_2]$ and *K* will increase.**

(c) $SO_2(g) + \text{heat} \rightleftharpoons S(s) + O_2(g)$

An increase in temperature will shift the reaction to the right, so **$[SO_2]$ will decrease**.

Catalysts and Equilibrium

A catalyst speeds up a reaction by lowering its activation energy. A catalyst therefore speeds up the forward and reverse reactions to the same extent.

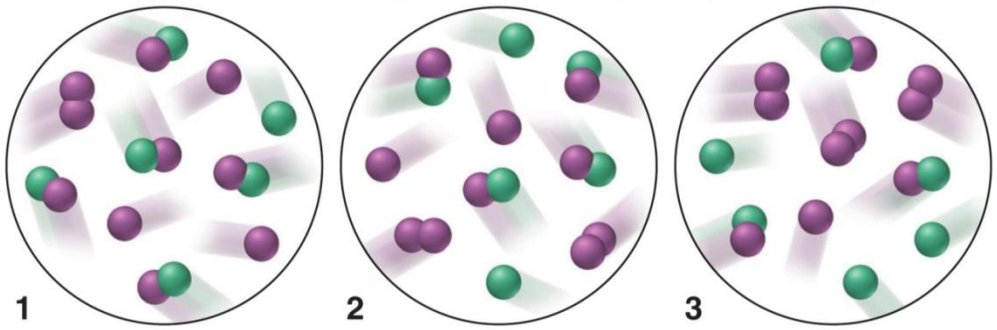
A catalyst causes a reaction to reach equilibrium more quickly, but has ***no effect*** on the equilibrium position.

Table 17.4 Effects of Various Disturbances on a System at Equilibrium

Disturbance	Effect on Equilibrium Position	Effect on Value of K
Concentration		
Increase [reactant]	Toward formation of product	None
Decrease [reactant]	Toward formation of reactant	None
Increase [product]	Toward formation of reactant	None
Decrease [product]	Toward formation of product	None
Pressure		
Increase P (decrease V)	Toward formation of fewer moles of gas	None
Decrease P (increase V)	Toward formation of more moles of gas	None
Increase P (add inert gas, no change in V)	None; concentrations unchanged	None
Temperature		
Increase T	Toward absorption of heat	Increases if $\Delta H^\circ_{rxn} > 0$ Decreases if $\Delta H^\circ_{rxn} < 0$
Decrease T	Toward release of heat	Increases if $\Delta H^\circ_{rxn} < 0$ Decreases if $\Delta H^\circ_{rxn} > 0$
Catalyst added	None; forward and reverse rates increase equally; equilibrium attained sooner	None

Sample Problem 17.14 Determining Equilibrium Parameters from Molecular Scenes

PROBLEM: For the reaction $X(g) + Y_2(g) \rightleftharpoons XY(g) + Y(g)$ $\Delta H > 0$ the following molecular scenes depict different reaction mixtures. (X = *green*, Y = *purple*):



(a) If $K = 2$ at the temperature of the reaction, which scene represents the mixture at equilibrium?

(b) Will the reaction mixtures in the other two scenes proceed toward reactant or toward products to reach equilibrium?

(c) For the mixture at equilibrium, how will a rise in temperature affect $[Y_2]$?

Sample Problem 17.14

PLAN: To select the scene that represents the reaction at equilibrium, we first write the expression for Q. We count the particles for each scene and calculate the value of Q. The scene that gives $Q = K$ represents equilibrium. For the other two scenes, we compare Q to K and determine the direction of reaction.

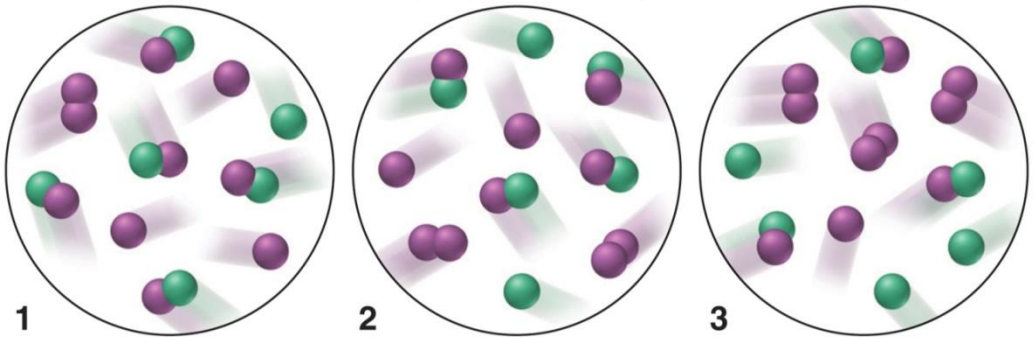
SOLUTION: For the reaction, we have $Q = \dfrac{[XY][Y]}{[X][Y_2]}$

For scene 1: $Q_c = \dfrac{5 \times 3}{1 \times 1} = 15$

For scene 2: $Q_c = \dfrac{4 \times 2}{2 \times 2} = 2$

For scene 3: $Q_c = \dfrac{3 \times 1}{3 \times 3} = \frac{1}{3}$

Sample Problem 17.14



$Q = 15$ $Q = 2.0$ $Q = 0.33$

(a) In scene 2, $Q = K$, so it represents the system at equilibrium.

(b) In scene 1, $Q > K$, so the system will proceed toward the reactants to reach equilibrium. In scene 3, $Q < K$, so the system will proceed toward the products.

(c) If $\Delta H > 0$, heat is a reactant (endothermic). A rise in temperature will favor the products and $[Y_2]$ will decrease as the system shifts toward the products.

The Synthesis of Ammonia

Ammonia is synthesized industrially via the **Haber process**:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \quad \Delta H^\circ_{rxn} = -91.8 \text{ kJ}$$

There are three ways to maximize the yield of NH_3:

- Decrease [NH_3] by removing NH_3 as it forms.
- Decrease the volume (increase the pressure).
- Decrease the temperature.

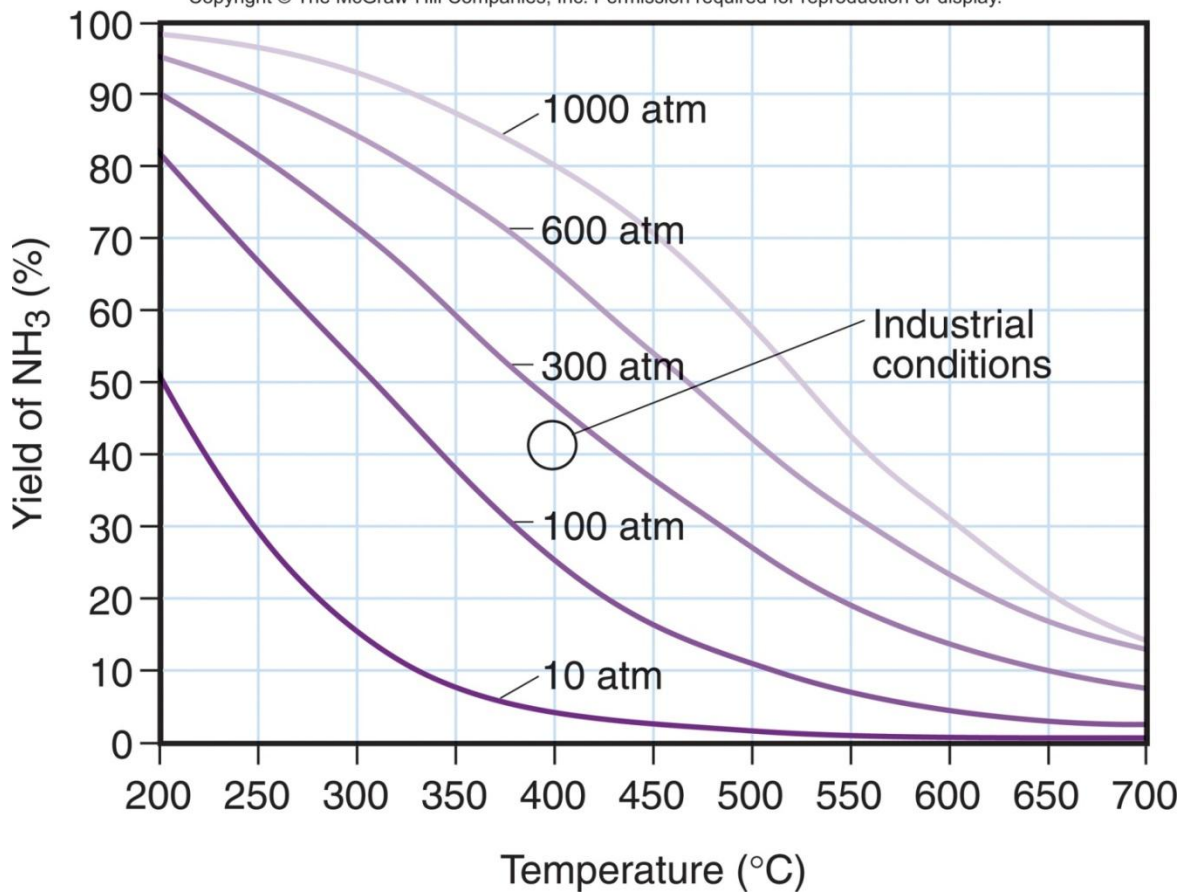
Table 17.5 Effect of Temperature on K_c for Ammonia Synthesis

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \quad \Delta H°_{rxn} = -91.8 \text{ kJ}$$

T (K)	K_c
200.	7.17×10^{15}
300.	2.69×10^{8}
400.	3.94×10^{4}
500.	1.72×10^{2}
600.	4.53×10^{0}
700.	2.96×10^{-1}
800.	3.96×10^{-2}

An increase in temperature causes the equilibrium to shift towards the reactants, since the reaction is exothermic.

Figure 17.9 Percent yield of ammonia vs. temperature at five different pressures.



At very high *P* and low *T* (*top left*), the yield is high, but the rate is low. Industrial conditions (*circle*) are between 200 and 300 atm at about 400°C.