

CHAPTER SEVENTENTH

THE EQUILIBRIUM STATE AND THE EQUILIBRIUM CONSTANT

Reaction chemistry has two fundamental aspects:

- **Kinetics**; applies to the *speed* of a reaction, the concentration of product that appears (or of reactant that disappears) per unit time.
- **Equilibrium**; applies to the *extent* of a reaction, the concentration of product that has appeared after an unlimited time, or once no further change occurs.

In this chapter, we consider equilibrium principles in systems of gases and pure liquids and solids; we'll discuss various solution equilibria in the next two chapters.

17.1 THE EQUILIBRIUM STATE AND THE EQUILIBRIUM CONSTANT

In a state of equilibrium, the system reaches equilibrium; reactant and product concentrations stop changing because the forward and reverse rates have become equal:

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

Example:



When we introduce some $\text{N}_2\text{O}_4(\text{l})$ into a sealed flask kept at 200°C , a change

occurs immediately. The liquid vaporizes (bp = 21°C) and the gas begins to turn pale brown. The color darkens, and after a few moments, the color stops changing (Figure 17.1).

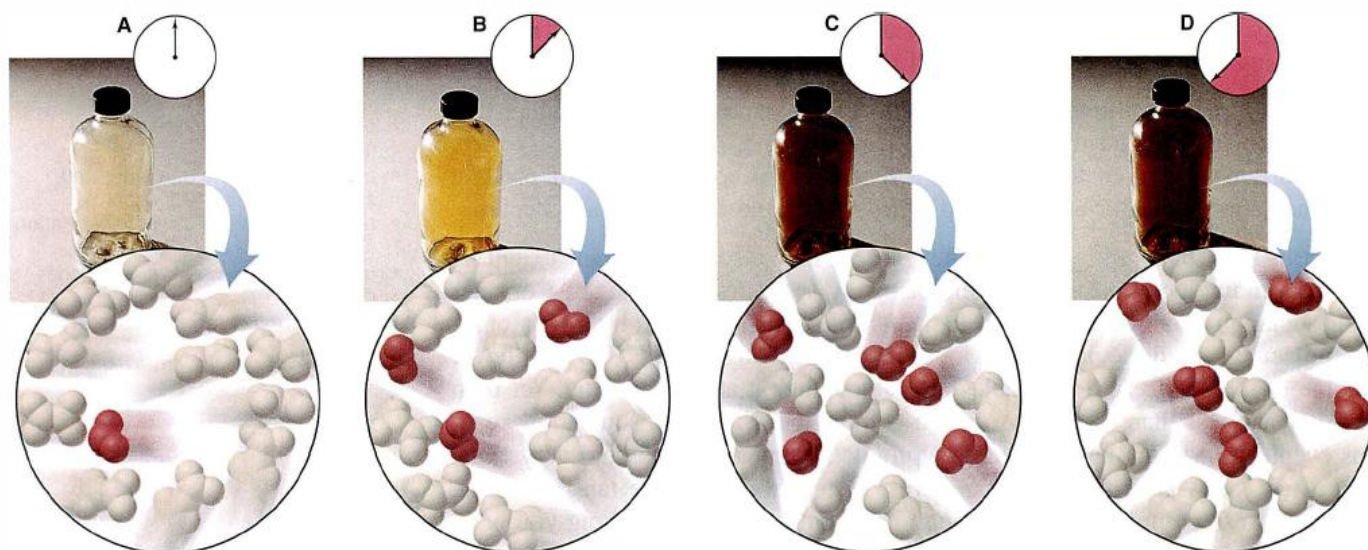


Figure 17.1 Reaching equilibrium on the macroscopic and molecular levels. A, When the experiment begins, the reaction mixture consists mostly of colorless N_2O_4 . B, As N_2O_4 decomposes to reddish brown NO_2 , the color of the mixture becomes pale brown. C, When equilibrium is reached, the concentrations of NO_2 and N_2O_4 are constant, and the color reaches its final intensity. D, Because the reaction continues in the forward and reverse directions at equal rates, the concentrations (and color) remain constant.

At equilibrium, we have

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

In this case, both forward and reverse reactions are elementary steps (Section 16.7), so we can write their rate laws directly from the balanced equation:

$$k_{\text{fwd}}[\text{N}_2\text{O}_4]_{\text{eq}} = k_{\text{rev}}[\text{NO}_2]_{\text{eq}}^2$$

By rearranging,

we set the ratio of the rate constants equal to the ratio of the concentration terms:

$$k_{\text{fwd}}/k_{\text{rev}} = [\text{NO}_2]_{\text{eq}}^2/[\text{N}_2\text{O}_4]_{\text{eq}}$$

The ratio of constants gives rise to a new overall constant called the **equilibrium constant (K)**:

$$K = \frac{k_{\text{fwd}}}{k_{\text{rev}}} = \frac{[\text{NO}_2]_{\text{eq}}^2}{[\text{N}_2\text{O}_4]_{\text{eq}}}$$

The magnitude of K is an indication of *how far a reaction proceeds* toward product at a given temperature.

Three examples of different magnitudes of K (Figure 17.2):

1. **Small K .** If a reaction yields very little product before reaching equilibrium, it has a small K , and we may even say there is "no reaction." For example, the oxidation of nitrogen barely proceeds at 1000 K:



2. **Large K .** Conversely, if a reaction reaches equilibrium with very little reactant remaining, it has a large K , and we say it "goes to completion." The oxidation of carbon monoxide goes to completion at 1000 K:



3. **Intermediate K .** When significant amounts of both reactant and product are present at equilibrium, K has an intermediate value, as when bromine monochloride breaks down to its elements at 1000 K:

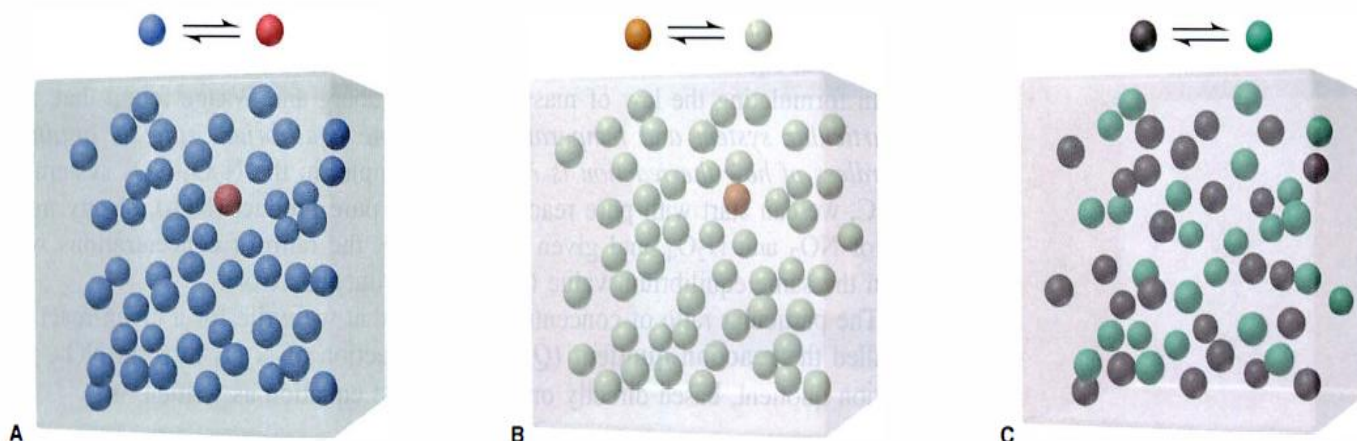
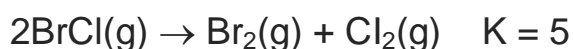


Figure 17.2 The range of equilibrium constants. A, A system that reaches equilibrium with very little product has a small K . For this reaction, $K = 1/49 = 0.020$. B, A system that reaches equilibrium with nearly all product has a large K . For this reaction, $K = 49/1 = 49$. C, A system that reaches equilibrium with significant concentrations of reactant and product has an intermediate K . For this reaction, $K = 25/25 = 1.0$.

17.2 THE REACTION QUOTIENT AND THE EQUILIBRIUM CONSTANT

In 1864, two Norwegian chemists, Cato Guldberg and Peter Waage, observed that *at a given temperature, a chemical system reaches a state in which a particular ratio of reactant and product concentrations has a constant value*. This is one way of stating the **law of chemical equilibrium**, or the **law of mass action**.

The particular ratio of concentration terms that we write for a given reaction is called the **reaction quotient (Q)**. For the reaction of N_2O_4 to form NO_2 , the reaction quotient, based directly on the balanced equation as written, is:

$$Q = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}$$

As the reaction proceeds toward the equilibrium state, the ratio of concentrations, and consequently the value of Q, changes. When equilibrium is reached, the value of Q no longer changes, and it becomes equal to K, at the given temperature:

$$\text{At equilibrium: } Q = K$$

Table 17.1 presents four experiments, each a different run of the N_2O_4 - NO_2 reaction at 200°C . There are two essential points to note:

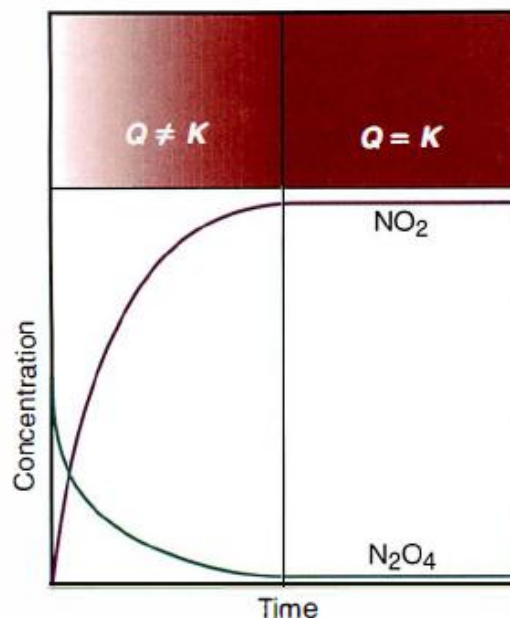
- The ratio of initial concentrations varies widely but always gives the same ratio of equilibrium concentrations.
- The individual equilibrium concentrations are different in each case, but the ratio of these equilibrium concentrations is constant.

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

Exp't.	Initial		Ratio (Q)	Equilibrium		Ratio (K)
	$[\text{N}_2\text{O}_4]$	$[\text{NO}_2]$	$[\text{NO}_2]^2/[\text{N}_2\text{O}_4]$	$[\text{N}_2\text{O}_4]_{\text{eq}}$	$[\text{NO}_2]_{\text{eq}}$	$[\text{NO}_2]_{\text{eq}}^2/[\text{N}_2\text{O}_4]_{\text{eq}}$
1	0.1000	0.0000	0.0000	0.00357	0.193	10.4
2	0.0000	0.1000	∞	9.24×10^{-4}	9.82×10^{-2}	10.4
3	0.0500	0.0500	0.0500	0.00204	0.146	10.4
4	0.0750	0.0250	0.00833	0.00275	0.170	10.5

The curves in Figure 17.3 show experiment 1 in Table 17.1. Note that for any given chemical system, K is a special value of Q that occurs when the reactant and product terms have their equilibrium values.

Figure 17.3 The change in Q during the N_2O_4 - NO_2 reaction. The curved plots and the darkening brown screen above them show that $[\text{N}_2\text{O}_4]$ and $[\text{NO}_2]$, and therefore the value of Q , change with time. Before equilibrium is reached, the concentrations are changing continuously, so $Q \neq K$. Once equilibrium is reached (vertical line) and any time thereafter, $Q = K$.



Writing the Reaction Quotient

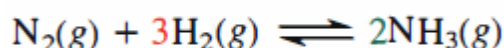
For the general balanced equation;



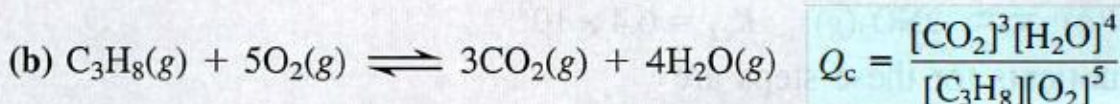
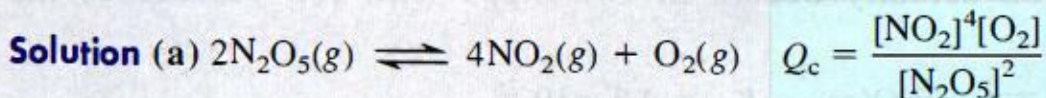
where a , b , c , and d are the stoichiometric coefficients, the reaction quotient is

$$Q_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

For example:



$$Q_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$$

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, $\text{N}_2\text{O}_5(\text{g}) \rightleftharpoons \text{NO}_2(\text{g}) + \text{O}_2(\text{g})$ (b) The combustion of propane gas, $\text{C}_3\text{H}_8(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{g})$ **Plan** We balance the equations and then construct the reaction quotient (Equation 17.4).**Check** Always be sure that the exponents in Q are the same as the balancing coefficients. A good check is to reverse the process: turn the numerator into products and the denominator into reactants, and change the exponents to coefficients.**FOLLOW-UP PROBLEM 17.1** Write a reaction quotient, Q_c , for each of the following reactions (unbalanced):(a) The first step in nitric acid production, $\text{NH}_3(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons \text{NO}(\text{g}) + \text{H}_2\text{O}(\text{g})$ (b) The disproportionation of nitric oxide, $\text{NO}(\text{g}) \rightleftharpoons \text{N}_2\text{O}(\text{g}) + \text{NO}_2(\text{g})$ **Variations in the Form of the Reaction Quotient**

The reaction quotient Q is a collection of terms based on the balanced equation exactly as written for a given reaction. Therefore, the value of Q and the value of K also depend on how the balanced equation is written.

Units for Q and K

The values of Q and K are shown as unitless numbers. This is because each term in the reaction quotient represents the ratio of the measured quantity of the substance (molar concentration or pressure) to the thermodynamic *standard-state* quantity of the substance. These standard states are 1 M for a substance in solution, 1 atm for gases, and the pure substance for a liquid or solid. Thus, a 1.20 M concentration of 1.20 M becomes $1.20 \text{ M}/1.00 \text{ M} = 1.20$; similarly, a pressure of 0.53 atm becomes $0.53 \text{ atm}/1.00 \text{ atm} = 0.53$. With such quantity terms unitless, the ratio of terms we use to find the value of Q (or K) is also unitless.

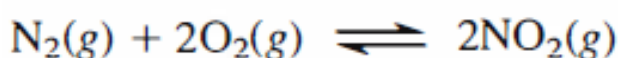
Form of Q for an Overall Reaction

If an overall reaction is the sum of two or more reactions, the overall reaction quotient (or equilibrium constant) is the product of the reaction quotients (or equilibrium constants) for the steps:

$$Q_{\text{overall}} = Q_1 \times Q_2 \times Q_3 \times \cdots$$

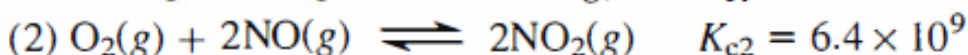
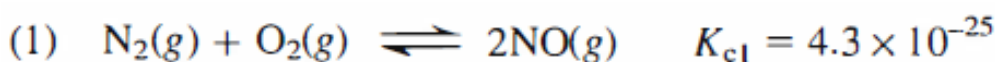
$$K_{\text{overall}} = K_1 \times K_2 \times K_3 \times \cdots$$

For example;



$$Q_{\text{c(overall)}} = \frac{[\text{NO}_2]^2}{[\text{N}_2][\text{O}_2]^2}$$

The overall reaction actually occurs in two steps with NO as the intermediate:



$$Q_{\text{c1}} = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]} \quad \text{and} \quad Q_{\text{c2}} = \frac{[\text{NO}_2]^2}{[\text{O}_2][\text{NO}]^2}$$

The overall reaction quotient is the product of Q_{c1} and Q_{c2} :

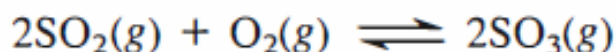
$$\frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]} \times \frac{[\text{NO}_2]^2}{[\text{O}_2][\text{NO}]^2} = \frac{[\text{NO}_2]^2}{[\text{N}_2][\text{O}_2]^2} = Q_{\text{c(overall)}}$$

Similarly, the equilibrium constant for the overall reaction is:

$$K_{\text{c(overall)}} = K_{\text{c1}} \times K_{\text{c2}} = (4.3 \times 10^{-25})(6.4 \times 10^9) = 2.8 \times 10^{-15}$$

Form of Q for a Forward and Reverse Reaction

The form of the reaction quotient depends on the direction in which the balanced equation is written. Consider, for example:



The reaction quotient for this equation as written is:

$$Q_{c(\text{fwd})} = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]}$$

If we had written the reverse reaction, the decomposition of sulfur trioxide,



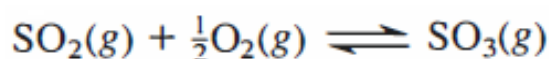
$$Q_{c(\text{rev})} = \frac{[\text{SO}_2]^2[\text{O}_2]}{[\text{SO}_3]^2} = \frac{1}{Q_{c(\text{fwd})}}$$

Thus, a reaction quotient (or equilibrium constant) for a forward reaction is the reciprocal of the reaction quotient (or equilibrium constant) for the reverse reaction:

$$Q_{c(\text{fwd})} = \frac{1}{Q_{c(\text{rev})}} \quad \text{and} \quad K_{c(\text{fwd})} = \frac{1}{K_{c(\text{rev})}}$$

Form of Q for a Reaction with Coefficients Multiplied by a Common Factor

Multiplying all the coefficients of the equation by some factor also changes the form of Q. For example, multiplying all the coefficients in the previous equation for the formation of SO_3 by $\frac{1}{2}$ gives:



$$Q'_{c(\text{fwd})} = \frac{[\text{SO}_3]}{[\text{SO}_2][\text{O}_2]^{1/2}}$$

$$Q'_{c(\text{fwd})} = Q_{c(\text{fwd})}^{1/2} = \left(\frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]} \right)^{1/2} = \frac{[\text{SO}_3]}{[\text{SO}_2][\text{O}_2]^{1/2}}$$

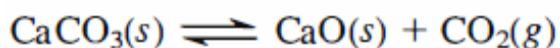
In general,



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

Form of Q for a Reaction Involving Pure Liquids and Solids

When the components are in different phases, the system reaches heterogeneous equilibrium. Consider the decomposition of limestone to lime and carbon dioxide:



$$Q_c = \frac{[\text{CaO}][\text{CO}_2]}{[\text{CaCO}_3]}$$

A pure solid, however, such as CaCO_3 or CaO , always has the same 'concentration' at a given temperature, that is, the same number of moles per liter of its volume, just as it has the same density (g/cm^3) at a given temperature. Therefore, the concentration of a pure solid is constant, as is the concentration of a pure liquid.

Because we are concerned only with concentrations that change as they approach equilibrium, we *eliminate the terms for pure liquids and solids* from the reaction quotient.

$$Q'_c = Q_c \frac{[\text{CaCO}_3]}{[\text{CaO}]} = [\text{CO}_2]$$

Table 17.2 Ways of Expressing Q and Calculating K

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

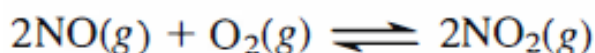
17.3 EXPRESSING EQUILIBRIA WITH PRESSURE TERMS: RELATION BETWEEN K_c AND K_p

It is easier to measure the pressure of a gas than its concentration and, as long as the gas behaves nearly ideally under the conditions of the experiment, the ideal gas law allows us to relate these variables to each other:

$$PV = nRT, \quad \text{so} \quad P = \frac{n}{V}RT \quad \text{or} \quad \frac{P}{RT} = \frac{n}{V}$$

Thus, at constant temperature, pressure is directly proportional to molar concentration.

For example, in the reaction between gaseous NO and O₂,



$$Q_p = \frac{P_{\text{NO}_2}^2}{P_{\text{NO}}^2 \times P_{\text{O}_2}}$$

The equilibrium constant obtained when all components are present at their equilibrium partial pressures is designated K_p , the equilibrium constant based on pressures.

How to convert the terms in Q_c for the reaction above to those in Q_p ?

$$\Delta n_{\text{gas}} = \text{moles of gaseous product} - \text{moles of gaseous reactant} = 2 - 3 = -1$$

The reaction quotient based on concentrations is:

$$Q_c = \frac{\frac{n_{\text{NO}_2}^2}{V^2}}{\frac{n_{\text{NO}}^2}{V^2} \times \frac{n_{\text{O}_2}}{V}} = \frac{\frac{P_{\text{NO}_2}^2}{(RT)^2}}{\frac{P_{\text{NO}}^2}{(RT)^2} \times \frac{P_{\text{O}_2}}{RT}} = \frac{P_{\text{NO}_2}^2}{P_{\text{NO}}^2 \times P_{\text{O}_2}} \times \frac{\frac{1}{(RT)^2}}{\frac{1}{(RT)^2} \times \frac{1}{RT}} = \frac{P_{\text{NO}_2}^2}{P_{\text{NO}}^2 \times P_{\text{O}_2}} \times RT$$

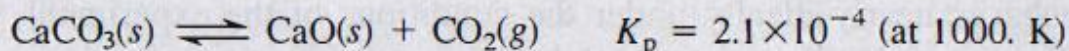
$$Q_c = Q_p(RT)$$

Thus, in general, we have:

$$K_p = K_c(RT)^{\Delta n_{\text{gas}}}$$

SAMPLE PROBLEM 17.2 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 to form lime (CaO), which scrubs SO_2 from the gas and forms gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). Find K_c for the following reaction, if CO_2 pressure is in atmospheres:



Plan We know K_p (2.1×10^{-4}), so to convert between K_p and K_c , we must first determine Δn_{gas} from the balanced equation. Then we rearrange Equation 17.8. With gas pressure in atmospheres, R is $0.0821 \text{ atm}\cdot\text{L}/\text{mol}\cdot\text{K}$.

Solution Determining Δn_{gas} : There is 1 mol of gaseous product and no gaseous reactant, so $\Delta n_{\text{gas}} = 1 - 0 = 1$.

Rearranging Equation 17.8 and calculating K_c :

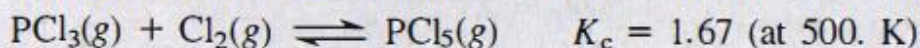
$$K_p = K_c(RT)^{\Delta n_{\text{gas}}} \quad \text{so} \quad K_c = K_p(RT)^{-\Delta n_{\text{gas}}}$$

$$K_c = (2.1 \times 10^{-4})(0.0821 \times 1000.)^{-1} = 2.6 \times 10^{-6}$$

Check Work backward to see whether you obtain the given K_p :

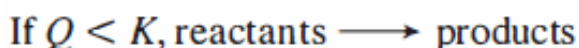
$$K_p = (2.6 \times 10^{-6})(0.0821 \times 1000.) = 2.1 \times 10^{-4}$$

FOLLOW-UP PROBLEM 17.2 Calculate K_p for the following reaction:

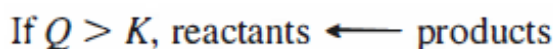
**17.4 REACTION DIRECTION: COMPARING Q AND K**

Because the value of Q can change, depending on the initial concentrations, Q can be smaller than K , larger than K , or, when the system reaches equilibrium, equal to K . The three possible relative sizes of Q and K are shown in Figure 17.4.

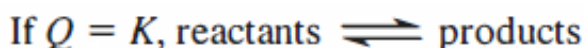
- $Q < K$; for Q to become equal to K , the reactants must decrease and the products increase. In other words, the reaction will progress toward products, until equilibrium is reached:



- $Q > K$; the reaction will progress to the left, toward reactants:



- $Q = K$; this situation corresponds to equilibrium.



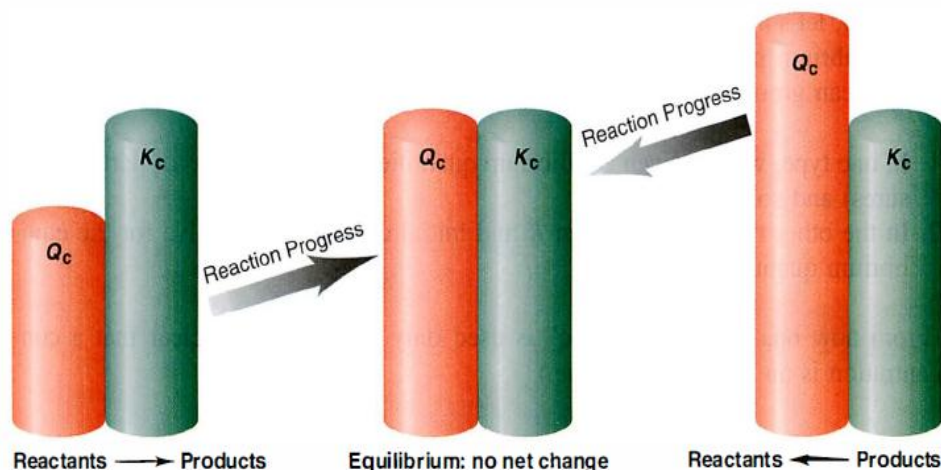


Figure 17.4 Reaction direction and the relative sizes of Q and K . When Q_c is smaller than K_c , the equilibrium of the reaction system shifts to the right, that is, toward products. When Q_c is larger than K_c , the equilibrium of the reaction system shifts to the left. Both shifts continue until $Q_c = K_c$. Note that the size of K_c remains the same throughout.

SAMPLE PROBLEM 17.3 Comparing Q and K to Determine Reaction Direction

Problem For the reaction $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$, $K_c = 0.21$ at 100°C . At a point during the reaction, $[\text{N}_2\text{O}_4] = 0.12 \text{ M}$ and $[\text{NO}_2] = 0.55 \text{ M}$. Is the reaction at equilibrium? If not, in which direction is it progressing?

Plan We write the expression for Q_c , find its value by substituting the given concentrations, and then compare its value with the given K_c .

Solution Writing the reaction quotient and solving for Q_c :

$$Q_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = \frac{0.55^2}{0.12} = 2.5$$

With $Q_c > K_c$, the reaction is not at equilibrium and will proceed to the left until $Q_c = K_c$.

Check With $[\text{NO}_2] > [\text{N}_2\text{O}_4]$, we expect to obtain a value for Q_c that is greater than 0.21. If $Q_c > K_c$, the numerator will decrease and the denominator will increase until $Q_c = K_c$; that is, this reaction will proceed toward reactants.

FOLLOW-UP PROBLEM 17.3 Chloromethane forms by the reaction



At 1500 K , $K_p = 1.6 \times 10^4$. In the reaction mixture, $P_{\text{CH}_4} = 0.13 \text{ atm}$, $P_{\text{Cl}_2} = 0.035 \text{ atm}$, $P_{\text{CH}_3\text{Cl}} = 0.24 \text{ atm}$, and $P_{\text{HCl}} = 0.47 \text{ atm}$. Is CH_3Cl or CH_4 forming?

SECTION SUMMARY

We compare the values of Q and K to determine the direction in which a reaction will proceed toward equilibrium.

- If $Q_c < K_c$, more product forms.
- If $Q_c > K_c$, more reactant forms.
- If $Q_c = K_c$, there is no net change.

17.5 HOW TO SOLVE EQUILIBRIUM PROBLEMS

Many kinds of equilibrium problems arise in the real world, as well as on chemistry exams, but we can group most of them into two types:

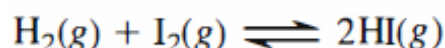
1. In one type, we are given equilibrium quantities (concentrations or partial pressures) and solve for K .
2. In the other type, we are given K and initial quantities and solve for the equilibrium quantities.

Using Quantities to Determine the Equilibrium Constant

Substituting Given Equilibrium Quantities into Q to Find K

In the straightforward case, we are given the equilibrium quantities and we must calculate K .

Suppose, for example, that equal amounts of gaseous hydrogen and iodine are injected into a 1.50-L reaction flask at a fixed temperature. In time, the following equilibrium is attained:



At equilibrium, analysis shows that the flask contains 1.80 mol of H_2 , 1.80 mol of I_2 , and 0.520 mol of HI .

We first have to convert the amounts (mol) to concentrations (mol/L), using the flask volume of 1.50 L:

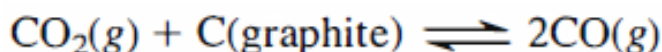
$$[\text{H}_2] = \frac{1.80 \text{ mol}}{1.50 \text{ L}} = 1.20 \text{ M}$$

Similarly, $[\text{I}_2] = 1.20 \text{ M}$, and $[\text{HI}] = 0.347 \text{ M}$. Substituting these values into the expression for K_c :

$$K_c = \frac{(0.347)^2}{(1.20)(1.20)} = 8.36 \times 10^{-2}$$

Using a Reaction Table to Determine Equilibrium Quantities and Find K

In a study of carbon oxidation, an evacuated vessel containing a small amount of powdered graphite is heated to 1080 K, and then CO₂ is added to a pressure of 0.458 atm. Once the CO₂ is added, the system starts to produce CO. After equilibrium has been reached, the total pressure inside the vessel is 0.757 atm. Calculate K_p.



$$Q_p = \frac{P_{\text{CO}}^2}{P_{\text{CO}_2}}$$



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

To find x, we use P_{total},

$$P_{\text{total}} = 0.757 \text{ atm} = P_{\text{CO}_2} + P_{\text{CO}} = (0.458 \text{ atm} - x) + 2x$$

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

$$\boxed{x = 0.299 \text{ atm}}$$

With x known, we determine the equilibrium partial pressures:

$$P_{\text{CO}_2} = 0.458 \text{ atm} - x = 0.458 \text{ atm} - 0.299 \text{ atm} = 0.159 \text{ atm}$$

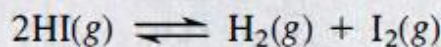
$$P_{\text{CO}} = 2x = 2(0.299 \text{ atm}) = 0.598 \text{ atm}$$

Now, we substitute these values into the expression for Q_p to find K_p:

$$Q_p = \frac{P_{\text{CO}}^2}{P_{\text{CO}_2}} = \frac{0.598^2}{0.159} = 2.25 = K_p$$

SAMPLE PROBLEM 17.4 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:



At equilibrium, $[\text{HI}] = 0.078 \text{ M}$. Calculate K_c .

Plan To calculate K_c , we need the equilibrium concentrations. We can find the initial $[\text{HI}]$ from the amount (0.200 mol) and the flask volume (2.00 L), and we are given $[\text{HI}]$ at equilibrium (0.078 M). From the balanced equation, when $2x$ mol of HI reacts, x mol of H_2 and x mol of I_2 form. We set up a reaction table, use the known $[\text{HI}]$ at equilibrium to solve for x (the change in $[\text{H}_2]$ or $[\text{I}_2]$), and substitute the concentrations into Q_c .

Solution Calculating initial $[\text{HI}]$:

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

Setting up the reaction table, with $x = [\text{H}_2]$ or $[\text{I}_2]$ that forms and $2x = [\text{HI}]$ that reacts:

Concentration (M)	$2\text{HI}(g)$	\rightleftharpoons	$\text{H}_2(g)$	+	$\text{I}_2(g)$
Initial	0.100		0		0
Change	$-2x$		$+x$		$+x$
Equilibrium	$0.100 - 2x$		x		x

Solving for x , using the known $[\text{HI}]$ at equilibrium:

$$[\text{HI}] = 0.100 \text{ M} - 2x = 0.078 \text{ M}$$

$$x = 0.011 \text{ M}$$

Therefore, the equilibrium concentrations are

$$[\text{H}_2] = [\text{I}_2] = 0.011 \text{ M} \quad \text{and} \quad [\text{HI}] = 0.078 \text{ M}$$

Substituting into the reaction quotient:

$$Q_c = \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2}$$

Thus,

$$K_c = \frac{(0.011)(0.011)}{0.078^2} = 0.020$$

Check Rounding gives $\sim 0.01^2/0.08^2 = 0.02$. Because the initial $[\text{HI}]$ of 0.100 M fell slightly at equilibrium to 0.078 M, relatively little product formed; so we expect $K_c < 1$.

FOLLOW-UP PROBLEM 17.4 The atmospheric oxidation of nitrogen monoxide, $2\text{NO}(g) + \text{O}_2(g) \rightleftharpoons 2\text{NO}_2(g)$, was studied at 184°C with initial pressures of 1.000 atm of NO and 1.000 atm of O_2 . At equilibrium, $P_{\text{O}_2} = 0.506 \text{ atm}$. Calculate K_p .

Using the Equilibrium Constant to Determine Quantities

Like the type of problem that involves finding K , the type that involves finding equilibrium concentrations (or pressures) has several variations.

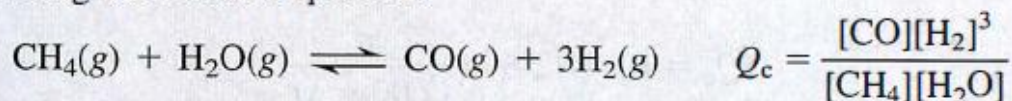
SAMPLE PROBLEM 17.5 Determining Equilibrium Concentrations from K_c

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 $[\text{H}_2\text{O}]$ at equilibrium? $K_c = 0.26$ for the equation



Plan First, we use the balanced equation to write the reaction quotient. We can calculate the equilibrium concentrations from the given numbers of moles and the flask volume (0.32 L). Substituting these into Q_c and setting it equal to the given K_c (0.26), we solve for the unknown equilibrium concentration, $[\text{H}_2\text{O}]$.

Solution Writing the reaction quotient:



Determining the equilibrium concentrations:

$$[\text{CH}_4] = \frac{0.041 \text{ mol}}{0.32 \text{ L}} = 0.13 \text{ M}$$

Similarly, $[\text{CO}] = 0.81 \text{ M}$ and $[\text{H}_2] = 0.28 \text{ M}$.

Calculating $[\text{H}_2\text{O}]$ at equilibrium: Since $Q_c = K_c$, rearranging gives

$$[\text{H}_2\text{O}] = \frac{[\text{CO}][\text{H}_2]^3}{[\text{CH}_4]K_c} = \frac{(0.81)(0.28)^3}{(0.13)(0.26)} = 0.53 \text{ M}$$

Check Always check by substituting the concentrations into Q_c to confirm K_c :

$$Q_c = \frac{[\text{CO}][\text{H}_2]^3}{[\text{CH}_4][\text{H}_2\text{O}]} = \frac{(0.81)(0.28)^3}{(0.13)(0.53)} = 0.26 = K_c$$

FOLLOW-UP PROBLEM 17.5 Nitrogen monoxide, oxygen, and nitrogen react by the following equation: $2\text{NO}(g) \rightleftharpoons \text{N}_2(g) + \text{O}_2(g)$; $K_c = 2.3 \times 10^{30}$ at 298 K. In the atmosphere, $P_{\text{O}_2} = 0.209 \text{ atm}$ and $P_{\text{N}_2} = 0.781 \text{ atm}$. What is the equilibrium partial pressure of NO in the air we breathe? [*Hint*: You need K_p to find the partial pressure.]

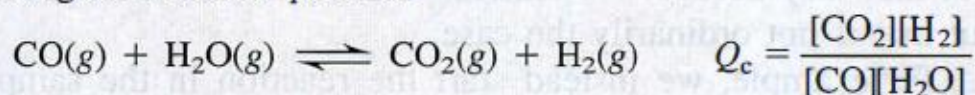
SAMPLE PROBLEM 17.6 Determining Equilibrium Concentrations from Initial Concentrations and K_c

Problem Fuel engineers use the extent of the change from CO and H₂O to CO₂ and H₂ to regulate the proportions of synthetic fuel mixtures. If 0.250 mol of CO and 0.250 mol of H₂O 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 for the equation



Plan We have to find the “composition” of the equilibrium mixture, in other words, the equilibrium concentrations. As always, we use the balanced equation to write the reaction quotient. We find the initial [CO] and [H₂O] from the given amounts (0.250 mol of each) and volume (0.125 L), use the balanced equation to define x and set up a reaction table, substitute into Q_c , and solve for x , from which we calculate the concentrations.

Solution Writing the reaction quotient:



Calculating initial reactant concentrations:

$$[\text{CO}] = [\text{H}_2\text{O}] = \frac{0.250 \text{ mol}}{0.125 \text{ L}} = 2.00 \text{ M}$$

Setting up the reaction table, with $x = [\text{CO}]$ and $[\text{H}_2\text{O}]$ that react:

Concentration (M)	CO(g)	+	H ₂ O(g)	\rightleftharpoons	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

Substituting into the reaction quotient and solving for x :

$$Q_c = \frac{[\text{CO}_2][\text{H}_2]}{[\text{CO}][\text{H}_2\text{O}]} = \frac{(x)(x)}{(2.00 - x)(2.00 - x)} = \frac{x^2}{(2.00 - x)^2}$$

At equilibrium, we have

$$Q_c = K_c = 1.56 = \frac{x^2}{(2.00 - x)^2}$$

We can apply the following math shortcut in this case *but not in general*: Because the right side of the equation is a perfect square, we take the square root of both sides:

$$\sqrt{1.56} = \frac{x}{2.00 - x} = \pm 1.25$$

A positive number (1.56) has a positive *and* a negative square root, but *only the positive root has any chemical meaning*, so we ignore the negative root:*

$$1.25 = \frac{x}{2.00 - x} \quad \text{or} \quad 2.50 - 1.25x = x$$

So $2.50 = 2.25x$; therefore, $x = 1.11 M$

Calculating equilibrium concentrations:

$$[\text{CO}] = [\text{H}_2\text{O}] = 2.00 M - x = 2.00 M - 1.11 M = 0.89 M$$

$$[\text{CO}_2] = [\text{H}_2] = x = 1.11 M$$

Check From the intermediate size of K_c , it makes sense that the changes in concentration are moderate. It's a good idea to check that the sign of x in the reaction table makes sense—only reactants were initially present, so the change had to proceed to the right: x is the change in concentration, so it has a negative sign for reactants and a positive sign for products. Also check that the equilibrium concentrations give the known K_c :

$$\frac{(1.11)(1.11)}{(0.89)(0.89)} = 1.56.$$

FOLLOW-UP PROBLEM 17.6 The decomposition of HI at low temperature was studied by injecting 2.50 mol of HI into a 10.32-L vessel at 25°C. What is $[\text{H}_2]$ at equilibrium for the reaction $2\text{HI}(g) \rightleftharpoons \text{H}_2(g) + \text{I}_2(g)$; $K_c = 1.26 \times 10^{-3}$?

*The negative root gives $-1.25 = \frac{x}{2.00 - x}$, or $-2.50 + 1.25x = x$.

So $-2.50 = -0.25x$, and $x = 10. M$

This value has no chemical meaning because we started with 2.00 M of each reactant, so it is impossible for 10. M to react. Moreover, the square root of an equilibrium constant is another equilibrium constant, which cannot have a negative value.

Using the Quadratic Formula to Solve for the Unknown

Suppose, for example, that we start the reaction in the sample problem 17.6 with the initial concentrations of 2.00 M CO and 1.00 M H₂O.

The reaction table is:

Concentration (M)	CO(g)	+	H ₂ O(g)	\rightleftharpoons	CO ₂ (g)	+	H ₂ (g)
Initial	2.00		1.00		0		0
Change	-x		-x		+x		+x
Equilibrium	2.00 - x		1.00 - x		x		x

$$Q_c = \frac{[\text{CO}_2][\text{H}_2]}{[\text{CO}][\text{H}_2\text{O}]} = \frac{(x)(x)}{(2.00 - x)(1.00 - x)} = \frac{x^2}{x^2 - 3.00x + 2.00}$$

$$1.56 = \frac{x^2}{x^2 - 3.00x + 2.00}$$

$$a x^2 + b x + c = 0$$

$$0.56x^2 - 4.68x + 3.12 = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$x = \frac{4.68 \pm \sqrt{(-4.68)^2 - 4(0.56)(3.12)}}{2(0.56)}$$

$$x = 7.6 \text{ M} \quad \text{and} \quad x = 0.73 \text{ M}$$

Note that only one of the values for x makes sense chemically. The larger value gives negative concentrations at equilibrium. Therefore, $x = 0.73 \text{ M}$, and we have

$$[\text{CO}] = 2.00 \text{ M} - x = 2.00 \text{ M} - 0.73 \text{ M} = 1.27 \text{ M}$$

$$[\text{H}_2\text{O}] = 1.00 \text{ M} - x = 0.27 \text{ M}$$

$$[\text{CO}_2] = [\text{H}_2] = x = 0.73 \text{ M}$$

Checking to see if these values give the known K_c , we have

$$K_c = \frac{(0.73)(0.73)}{(1.27)(0.27)} = 1.6 \text{ (within rounding of 1.56)}$$

Simplifying Assumptions for Finding an Unknown Quantity

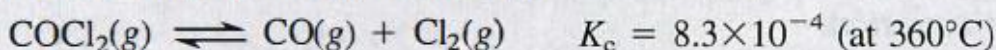
In many cases, we can use chemical "common sense" to make an assumption that avoids the use of the quadratic formula to find x . In general, if a reaction has a relatively small K and a relatively large initial reactant concentration, the concentration change (x) can often be neglected without introducing significant error.

$$[\text{reactant}]_{\text{init}} - x = [\text{reactant}]_{\text{eq}} \approx [\text{reactant}]_{\text{init}}$$

For the assumption that x is negligible to be justified, you must check that the error introduced is not significant. One common criterion is the 5% rule: if the assumption results in a change (error) in a concentration that is less than 5%, the error is not significant, and the assumption is justified.

SAMPLE PROBLEM 17.7 Calculating Equilibrium Concentrations with Simplifying Assumptions

Problem Phosgene is a potent chemical warfare agent that is now outlawed by international agreement. It decomposes by the reaction



Calculate $[\text{CO}]$, $[\text{Cl}_2]$, and $[\text{COCl}_2]$ when each of the following amounts of phosgene decomposes and reaches equilibrium in a 10.0-L flask:

(a) 5.00 mol of COCl_2 (b) 0.100 mol of 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 convert amount (5.00 mol or 0.100 mol) to concentration, define x and set up the reaction table, and substitute the values into Q_c . Before using the quadratic formula, we simplify the calculation by assuming that x is negligibly small. After solving for x , we check the assumption and find the concentrations. If the assumption is not justified, we must use the quadratic formula to find x .

Solution (a) For 5.00 mol of COCl_2 . Writing the reaction quotient:

$$Q_c = \frac{[\text{CO}][\text{Cl}_2]}{[\text{COCl}_2]}$$

Calculating initial $[\text{COCl}_2]$:

$$[\text{COCl}_2]_{\text{init}} = \frac{5.00 \text{ mol}}{10.0 \text{ L}} = 0.500 \text{ M}$$

Setting up the reaction table, with $x = [\text{COCl}_2]_{\text{reacting}}$:

Concentration (M)	$\text{COCl}_2(g)$	\rightleftharpoons	$\text{CO}(g)$	+	$\text{Cl}_2(g)$
Initial	0.500		0		0
Change	$-x$		$+x$		$+x$
Equilibrium	$0.500 - x$		x		x

If we use the equilibrium values in Q_c , we obtain

$$Q_c = \frac{[\text{CO}][\text{Cl}_2]}{[\text{COCl}_2]} = \frac{x^2}{0.500 - x} = K_c = 8.3 \times 10^{-4}$$

Because K_c is small, the reaction does not proceed very far to the right, so let's assume that x (the $[\text{COCl}_2]$ that reacts) is so much smaller than the initial concentration, 0.500 M , that the equilibrium concentration is nearly the same. Therefore,

$$0.500\text{ M} - x \approx 0.500\text{ M}$$

Using this assumption, we substitute and solve for x :

$$K_c = 8.3 \times 10^{-4} \approx \frac{x^2}{0.500}$$

$$x^2 \approx (8.3 \times 10^{-4})(0.500) \quad \text{so} \quad x \approx 2.0 \times 10^{-2}$$

Checking the assumption by finding the percent error:

$$\frac{2.0 \times 10^{-2}}{0.500} \times 100 = 4\% \quad (\text{less than } 5\%, \text{ so the assumption is justified})$$

Solving for the equilibrium concentrations:

$$\begin{aligned} [\text{CO}] &= [\text{Cl}_2] = x = 2.0 \times 10^{-2}\text{ M} \\ [\text{COCl}_2] &= 0.500\text{ M} - x = 0.480\text{ M} \end{aligned}$$

(b) For 0.100 mol of COCl_2 . The calculation in this case is the same as the calculation in part (a), except that $[\text{COCl}_2]_{\text{init}} = 0.100\text{ mol}/10.0\text{ L} = 0.0100\text{ M}$. Thus, at equilibrium, we have

$$\begin{aligned} Q_c &= \frac{[\text{CO}][\text{Cl}_2]}{[\text{COCl}_2]} = \frac{x^2}{0.0100 - x} \\ &= K_c = 8.3 \times 10^{-4} \end{aligned}$$

Making the assumption that $0.0100\text{ M} - x \approx 0.0100\text{ M}$ and solving for x :

$$\begin{aligned} K_c &= 8.3 \times 10^{-4} \approx \frac{x^2}{0.0100} \\ x &\approx 2.9 \times 10^{-3} \end{aligned}$$

Checking the assumption:

$$\frac{2.9 \times 10^{-3}}{0.0100} \times 100 = 29\% \quad (\text{more than } 5\%, \text{ so the assumption is not justified})$$

We must solve the quadratic equation, $x^2 + (8.3 \times 10^{-4})x - (8.3 \times 10^{-6}) = 0$, for which the only meaningful value of x is 2.5×10^{-3} (see Appendix A).

Solving for the equilibrium concentrations:

$$\begin{aligned} [\text{CO}] &= [\text{Cl}_2] = 2.5 \times 10^{-3}\text{ M} \\ [\text{COCl}_2] &= 1.00 \times 10^{-2}\text{ M} - x = 7.5 \times 10^{-3}\text{ M} \end{aligned}$$

Check Once again, the best check is to use the calculated values to be sure you obtain the given K_c .

Comment Note that the assumption was justified at the high initial concentration, but *not* at the low initial concentration.

FOLLOW-UP PROBLEM 17.7 In a study of the effect of temperature on halogen decomposition, 0.50 mol of I_2 was heated in a 2.5-L vessel, and the following reaction occurred: $\text{I}_2(\text{g}) \rightleftharpoons 2\text{I}(\text{g})$.

(a) Calculate $[\text{I}_2]$ and $[\text{I}]$ at equilibrium at 600 K ; $K_c = 2.94 \times 10^{-10}$.

(b) Calculate $[\text{I}_2]$ and $[\text{I}]$ at equilibrium at 2000 K ; $K_c = 0.209$.

Mixtures of Reactants and Products: Determining Reaction Direction

Suppose, we start with a mixture of reactants and products. Whenever the reaction direction is not obvious, we first compare the value of Q with K to find the direction in which the reaction proceeds to reach equilibrium. This tells us the sign of x , the unknown change in concentration.

SAMPLE PROBLEM 17.8 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:



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 $[\text{CH}_4] = 5.56 \text{ M}$ at equilibrium, what are the equilibrium concentrations of the other substances?

Plan (a) To find the direction, we convert the given initial amounts and volume (0.250 L) to concentrations, calculate Q_c , and compare it with K_c . (b) Based on the results from (a), we determine the sign of each concentration change for the reaction table and then use the known $[\text{CH}_4]$ at equilibrium (5.56 M) to determine x and the other equilibrium concentrations.

Solution (a) Calculating the initial concentrations:

$$[\text{CH}_4] = \frac{1.00 \text{ mol}}{0.250 \text{ L}} = 4.00 \text{ M}$$

Similarly, $[\text{H}_2\text{S}] = 8.00 \text{ M}$, $[\text{CS}_2] = 4.00 \text{ M}$, and $[\text{H}_2] = 8.00 \text{ M}$.

Calculating the value of Q_c :

$$Q_c = \frac{[\text{CS}_2][\text{H}_2]^4}{[\text{CH}_4][\text{H}_2\text{S}]^2} = \frac{(4.00)(8.00)^4}{(4.00)(8.00)^2} = 64.0$$

Comparing Q_c and K_c : $Q_c > K_c$ ($64.0 > 0.036$), so the reaction goes to the left. Therefore, concentrations of reactants increase and those of products decrease.

(b) Setting up a reaction table, with $x = [\text{CS}_2]$ that reacts, which equals $[\text{CH}_4]$ that forms:

Concentration (M)	$\text{CH}_4(g)$	+	$2\text{H}_2\text{S}(g)$	\rightleftharpoons	$\text{CS}_2(g)$	+	$4\text{H}_2(g)$
Initial	4.00		8.00		4.00		8.00
Change	+ x		+ $2x$		- x		- $4x$
Equilibrium	$4.00 + x$		$8.00 + 2x$		$4.00 - x$		$8.00 - 4x$

Solving for x : At equilibrium,

$$[\text{CH}_4] = 5.56 \text{ M} = 4.00 \text{ M} + x$$

So, $x = 1.56 \text{ M}$

Thus, $[\text{H}_2\text{S}] = 8.00 \text{ M} + 2x = 8.00 \text{ M} + 2(1.56 \text{ M}) = 11.12 \text{ M}$

$$[\text{CS}_2] = 4.00 \text{ M} - x = 2.44 \text{ M}$$

$$[\text{H}_2] = 8.00 \text{ M} - 4x = 1.76 \text{ M}$$

Check The comparison of Q_c and K_c showed the reaction proceeding to the left. The given data from part (b) confirm this because $[\text{CH}_4]$ increases from 4.00 M to 5.56 M during the reaction. Check that the concentrations give the known K_c :

$$\frac{(2.44)(1.76)^4}{(5.56)(11.12)^2} = 0.0341, \text{ which is close to } 0.036$$

FOLLOW-UP PROBLEM 17.8 An inorganic chemist studying the reactions of phosphorus halides mixes 0.1050 mol of PCl_5 with 0.0450 mol of Cl_2 and 0.0450 mol of PCl_3 in a 0.5000-L flask at 250°C : $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$; $K_c = 4.2 \times 10^{-2}$.

(a) In which direction will the reaction proceed?

(b) If $[\text{PCl}_5] = 0.2065 \text{ M}$ at equilibrium, what are the equilibrium concentrations of the other components?

17.6 REACTION CONDITIONS AND THE EQUILIBRIUM STATE: LE CHATELIER'S PRINCIPLE

Le Chatelier'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.

There are three common disturbances are:

- a change in concentration of a component (that appears in Q),
- a change in pressure (caused by a change in volume),
- or a change in temperature.

In the following discussions, we focus on the reversible gaseous reaction:



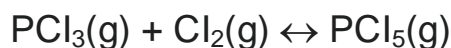
However, the basis of Le Chatelier's principle holds for any system at equilibrium.

The Effect of a Change in Concentration

At 523 K, the $\text{PCl}_3\text{-Cl}_2\text{-PCl}_5$ system reaches equilibrium when

$$Q_c = \frac{[\text{PCl}_5]}{[\text{PCl}_3][\text{Cl}_2]} = 24.0 = K_c$$

What happens if we now inject some Cl_2 gas?



The system will reduce the increase in reactant by proceeding toward the product side, until eventually Q_c again equals K_c .

The concentrations of the components have changed, however: the concentrations of Cl_2 and PCl_5 are higher than in the original equilibrium position, and the concentration of PCl_3 is lower. Nevertheless, the ratio of values gives the same K_c .

To summarize the effects of concentration changes (Figure 17.6):

- The equilibrium position shifts to the right if a reactant is added or a product is removed: [reactant] increases or [product] decreases.
- The equilibrium position shifts to the left if a reactant is removed or a product is added: [reactant] decreases or [product] increases.

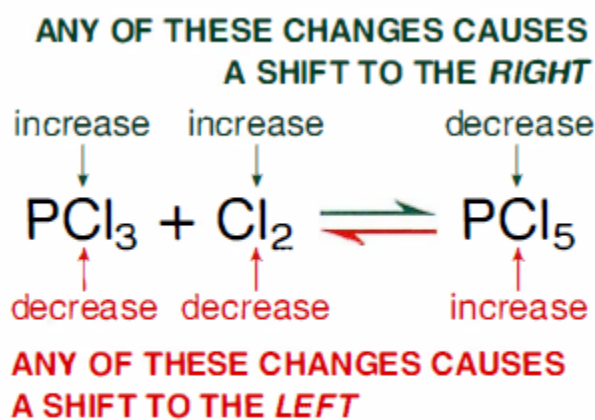


Figure 17.6 The effect of a change in concentration.

Consider the case in which we added Cl_2 to the system at equilibrium. Suppose the original equilibrium position was established with the following concentrations: $[\text{PCl}_3] = 0.200 \text{ M}$, $[\text{Cl}_2] = 0.125 \text{ M}$, and $[\text{PCl}_5] = 0.600 \text{ M}$. Thus,

$$Q_c = \frac{[\text{PCl}_5]}{[\text{PCl}_3][\text{Cl}_2]} = \frac{0.600}{(0.200)(0.125)} = 24.0 = K_c$$

Now we add enough Cl_2 to increase its concentration by 0.075 M .

Table 17.3 shows a reaction table of the entire process. Figure 17.7 depicts the process.

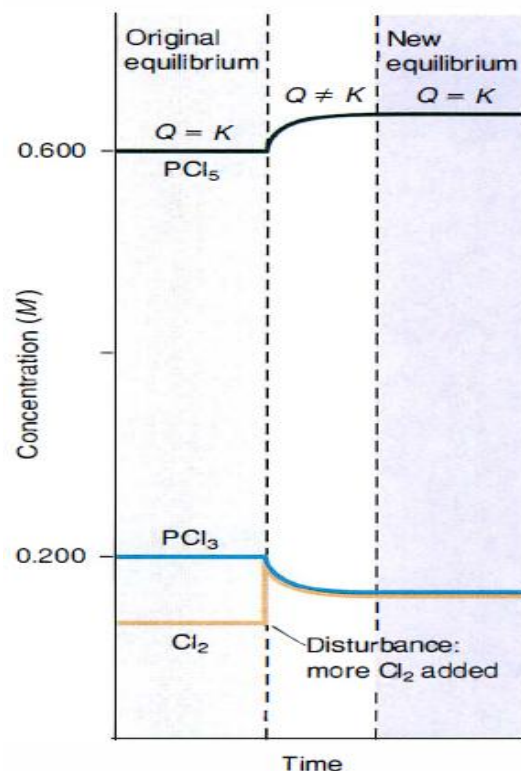
Table 17.3 The Effect of Added Cl_2 on the $\text{PCl}_3\text{-Cl}_2\text{-PCl}_5$ System

Concentration (M)	$\text{PCl}_3(\text{g})$	+	$\text{Cl}_2(\text{g})$	\rightleftharpoons	$\text{PCl}_5(\text{g})$
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 $\text{PCl}_3\text{-Cl}_2\text{-PCl}_5$ system. In the original equilibrium (gray region), all concentrations are constant. When Cl_2 (yellow curve) is added, its concentration jumps and then starts to fall as Cl_2 reacts with some PCl_3 to form more PCl_5 . After a period of time, equilibrium is re-established at new concentrations (blue region) but with the same K .



From Table 17.3,

$$\begin{aligned} [\text{PCl}_5] &= 0.600 \text{ M} + x = 0.637 \text{ M}, & \text{so } x &= 0.037 \text{ M} \\ [\text{PCl}_3] &= [\text{Cl}_2] = 0.200 \text{ M} - x = 0.163 \text{ M} \end{aligned}$$

Therefore, at equilibrium,

$$K_{c(\text{original})} = \frac{0.600}{(0.200)(0.125)} = 24.0$$

$$K_{c(\text{new})} = \frac{0.637}{(0.163)(0.163)} = 24.0$$

SAMPLE PROBLEM 17.9 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 fuel contaminant hydrogen sulfide with O_2 :



What happens to

- (a) $[\text{H}_2\text{O}]$ if O_2 is added? (b) $[\text{H}_2\text{S}]$ if O_2 is added?
 (c) $[\text{O}_2]$ if H_2S is removed? (d) $[\text{H}_2\text{S}]$ 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.

Solution Writing the reaction quotient: $Q_c = \frac{[\text{H}_2\text{O}]^2}{[\text{H}_2\text{S}]^2[\text{O}_2]}$

(a) When O_2 is added, the denominator of Q_c increases, so $Q_c < K_c$. The reaction proceeds to the right until $Q_c = K_c$ again, so $[\text{H}_2\text{O}]$ increases.

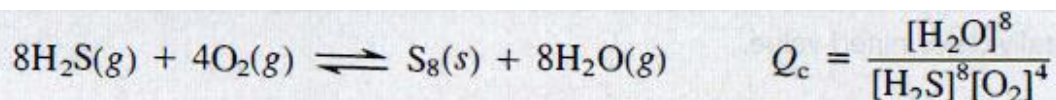
(b) As in part (a), when O_2 is added, $Q_c < K_c$. Some H_2S reacts with the added O_2 as the reaction proceeds to the right, so $[\text{H}_2\text{S}]$ decreases.

(c) When H_2S is removed, the denominator of Q_c decreases, so $Q_c > K_c$. As the reaction proceeds to the left to re-form H_2S , more O_2 is produced as well, so $[\text{O}_2]$ 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 $[\text{H}_2\text{S}]$ is unchanged (but see Comment 2 below).

Check Apply Le Châtelier's principle to see that the reaction proceeds in the direction that lowers the increased concentration or raises the decreased concentration.

Comment 1. As you know, sulfur exists most commonly as S_8 . How would this change in formula affect the answers? The balanced equation and Q_c would be



The value of K_c is different for this equation, but the changes described in the problem have the same effects. For example, in (a), if O_2 were added, the denominator of Q_c would increase, so $Q_c < K_c$. As above, the reaction would proceed to the right until $Q_c = K_c$ again. In other words, changes predicted by Le Châtelier's principle for a given reaction are not affected by a change in the balancing coefficients.

2. In (d), you saw that adding a solid has no effect on the concentrations of other components: because *the concentration of the solid cannot change*, it does not appear in Q . But *the amount of solid can change*. Adding H_2S shifts the reaction to the right, and more S forms.

FOLLOW-UP PROBLEM 17.9 In a study of the chemistry of glass etching, an inorganic chemist examines the reaction between sand (SiO_2) and hydrogen fluoride at a temperature above the boiling point of water:



Predict the effect on $[\text{SiF}_4]$ when (a) $\text{H}_2\text{O}(g)$ is removed; (b) some liquid water is added; (c) HF is removed; (d) some sand is removed.

The Effect of a Change in Pressure (Volume)

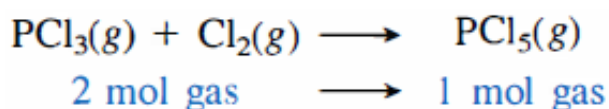
Changes in pressure have significant effects only on equilibrium systems with gaseous components. A change in pressure has a negligible effect on liquids and solids because they are nearly incompressible.

Pressure changes can occur in three ways:

- Changing the concentration of a gaseous component
- Adding an inert gas (one that does not take part in the reaction)
- Changing the volume of the reaction vessel

Adding an inert gas does not change the volume, so all reactant and product concentrations remain the same. In other words, the volume and the number of moles of the reactant and product gases do not change, so their partial pressures do not change. Because we use these (unchanged) partial pressures in the reaction quotient, the equilibrium position cannot change. Moreover, the inert gas does not appear in Q , so it cannot have an effect.

On the other hand, changing the pressure by changing the volume often causes a large shift in the equilibrium position. Suppose we let the $\text{PCl}_3\text{-Cl}_2\text{-PCl}_5$ system come to equilibrium in a cylinder-piston assembly. Then, we press down on the piston to halve the volume: the gas pressure immediately doubles. To reduce this increase in gas pressure, the system responds by reducing the number of gas molecules, by shifting the reaction toward the side with fewer moles of gas, in this case, toward the product side:

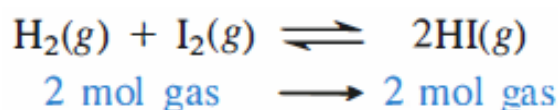


Because it is just another way to change the concentration, a change in pressure due to a change in volume does not alter K_c .

Thus, for a system that contains gases at equilibrium, in which the amount (mol) of gas, n_{gas} , changes during the reaction (Figure 17.8):

- If the volume becomes smaller (pressure is higher), the reaction shifts so that the total number of gas molecules decreases.
- If the volume becomes larger (pressure is lower), the reaction shifts so that the total number of gas molecules increases.

In many cases, however, n_{gas} does not change ($\Delta n_{\text{gas}} = 0$). For example,

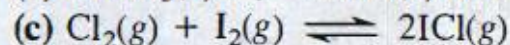
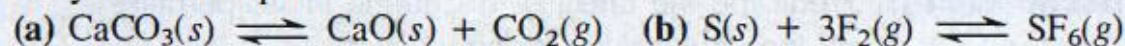


$$Q_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{[\text{HI}][\text{HI}]}{[\text{H}_2][\text{I}_2]}$$

Therefore, a change in volume has the same effect on the numerator and denominator. Thus, *if $\Delta n_{\text{gas}} = 0$, there is no effect on the equilibrium position.*

SAMPLE PROBLEM 17.10 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?



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, if the volume decreases (pressure increases), the equilibrium position shifts to relieve the pressure by reducing the number of moles of gas. A volume increase (pressure decrease) has the opposite effect.

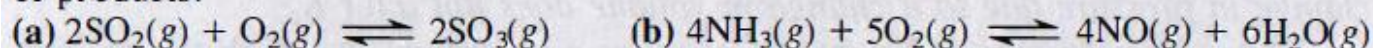
Solution (a) The only gas is the product CO_2 . To make the system produce more CO_2 , we increase the volume (decrease the pressure).

(b) With 3 mol of gas on the left and only 1 mol on the right, we decrease the volume (increase the pressure) to form more SF_6 .

(c) The number of moles of gas is the same on both sides of the equation, so a change in volume (pressure) will have no effect on the yield of ICl .

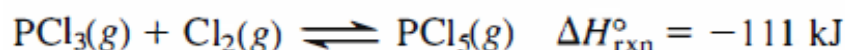
Check Let's predict the relative values of Q_c and K_c . In (a), $Q_c = [\text{CO}_2]$, so increasing the volume will make $Q_c < K_c$, and the system will make more CO_2 . In (b), $Q_c = [\text{SF}_6]/[\text{F}_2]^3$. Lowering the volume increases $[\text{F}_2]$ and $[\text{SF}_6]$ proportionately, but Q_c decreases because of the exponent 3 in the denominator. To make $Q_c = K_c$ again, $[\text{SF}_6]$ must increase. In (c), $Q_c = [\text{ICl}]^2/[\text{Cl}_2][\text{I}_2]$. A change in volume (pressure) affects the numerator (2 mol) and denominator (2 mol) equally, so it will have no effect.

FOLLOW-UP PROBLEM 17.10 Would you increase or decrease the pressure (via a volume change) of each of the following reaction mixtures to *decrease* the yield of products?

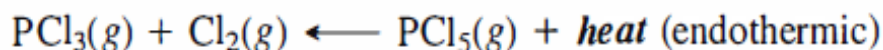
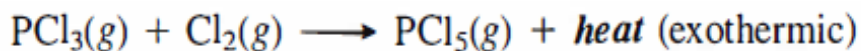


The Effect of a Change in Temperature

Of the three types of disturbances—a change in concentration, in pressure, or in temperature—**only temperature changes alter K**. To see why, we must take the heat of reaction into account:



The forward reaction is exothermic (releases heat; $\Delta H^\circ < 0$), so the reverse reaction is endothermic (absorbs heat; $\Delta H^\circ > 0$):



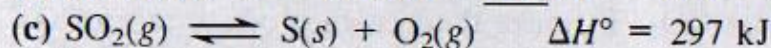
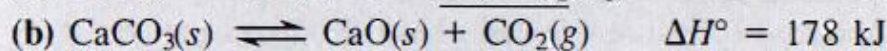
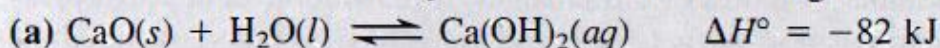
If we consider heat as a component of the equilibrium system, then a temperature increase (adding heat) favors the endothermic (heat-absorbing) direction, and a temperature decrease (removing heat) favors the exothermic (heat-releasing) direction.

Thus,

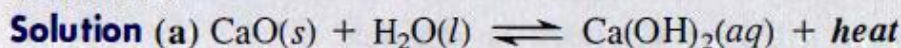
- A temperature rise will increase K_c for a system with a positive $\Delta H^\circ_{\text{rxn}}$.
- A temperature rise will decrease K_c for a system with a negative $\Delta H^\circ_{\text{rxn}}$.

SAMPLE PROBLEM 17.11 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_c for each of the following reactions?



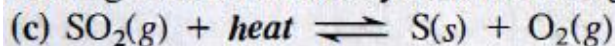
Plan We write each equation to show heat as a reactant or product. Increasing the temperature adds heat, so the system shifts to absorb the heat; that is, the endothermic reaction occurs. K_c will increase if the forward reaction is endothermic and decrease if it is exothermic.



Adding heat shifts the system to the left: $[\text{Ca(OH)}_2]$ and K_c will decrease.



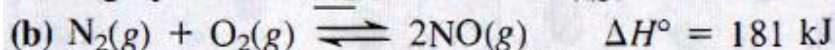
Adding heat shifts the system to the right: $[\text{CO}_2]$ and K_c will increase.



Adding heat shifts the system to the right: $[\text{SO}_2]$ will decrease and K_c will increase.

Check You can check your answers by going through the reasoning for a *decrease* in temperature: heat is removed and the exothermic direction is favored. All the answers should be opposite.

FOLLOW-UP PROBLEM 17.11 How does a *decrease* in temperature affect the partial pressure of the underlined substance and the value of K_p for each of the following reactions?



The Lack of Effect of a Catalyst

Recall from Chapter 16 that a catalyst speeds up a reaction by providing an alternative mechanism with a lower activation energy, thereby increasing the forward and reverse rates to the same extent.

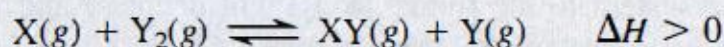
If, for instance, we add a catalyst to a mixture of PCl_3 and Cl_2 at 523 K, the system will attain the same equilibrium concentrations of PCl_3 , Cl_2 , and PCl_5 more quickly than it did without the catalyst. Nevertheless, a catalyst often plays a key role in optimizing the yield of a reaction system. The industrial production of ammonia, described in the following subsection, provides an example of a catalyzed improvement of yield. **(The last section is assigned for reading)**

Table 17.4 Effect of Various Disturbances on a System at Equilibrium

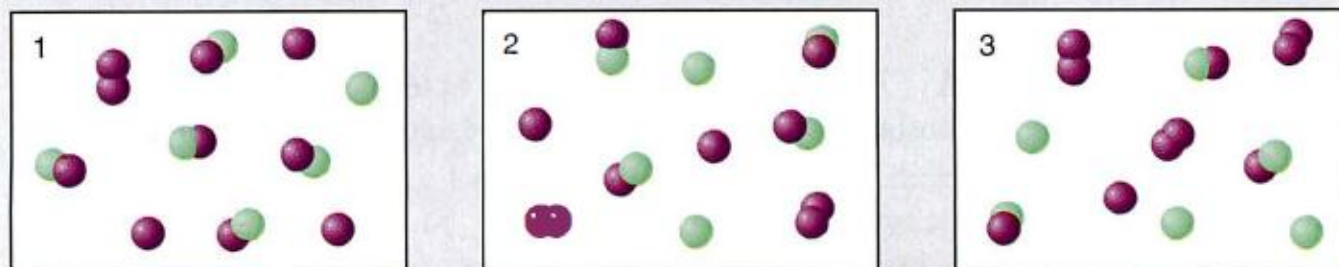
Disturbance	Net Direction of Reaction	Effect on Value of K
Concentration		
Increase [reactant]	Toward formation of product	None
Decrease [reactant]	Toward formation of reactant	None
Increase [product]	Toward formation of reactant	None
Decrease [product]	Toward formation of product	None
Pressure		
Increase 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 $\Delta H_{\text{rxn}}^{\circ} > 0$ Decreases if $\Delta H_{\text{rxn}}^{\circ} < 0$
Decrease T	Toward release of heat	Increases if $\Delta H_{\text{rxn}}^{\circ} < 0$ Decreases if $\Delta H_{\text{rxn}}^{\circ} > 0$
Catalyst added	None; forward and reverse equilibrium attained sooner; rates increase equally	None

SAMPLE PROBLEM 17.12 Determining Equilibrium Parameters from Molecular Scenes

Problem For the reaction,



the following molecular scenes depict different reaction mixtures (X = green, Y = purple):



(a) If $K_c = 2$ 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 reactants or toward products to reach equilibrium?

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

Plan (a) We are given the balanced equation and the value of K_c and must choose the scene representing the mixture at equilibrium. We write the expression for Q_c , and for each scene, count particles and plug in the numbers to solve for the value of Q_c . Whichever scene gives a Q_c equal to K_c represents the mixture at equilibrium. (b) To determine the direction each reaction proceeds in the other two scenes, we compare the value of Q_c with the given K_c . If $Q_c > K_c$, the numerator (product side) is too high, so the reaction proceeds toward reactants; if $Q_c < K_c$, the reaction proceeds toward products. (c) We are given the sign of ΔH and must see whether a rise in T (corresponding to supplying heat) will increase or decrease the amount of the reactant Y_2 . We treat heat as a reactant or product and see whether adding heat shifts the reaction right or left.

Solution (a) For the reaction, we have

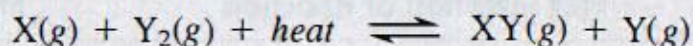
$$Q_c = \frac{[XY][Y]}{[X][Y_2]}$$

$$\text{scene 1: } Q_c = \frac{5 \times 3}{1 \times 1} = 15 \quad \text{scene 2: } Q_c = \frac{4 \times 2}{2 \times 2} = 2 \quad \text{scene 3: } Q_c = \frac{3 \times 1}{3 \times 3} = \frac{1}{3}$$

For scene 2, $Q_c = K_c$, so it represents the mixture at equilibrium.

(b) For scene 1, $Q_c (15) > K_c (2)$, so the reaction proceeds toward reactants. For scene 3, $Q_c (\frac{1}{3}) < K_c (2)$, so the reaction proceeds toward products.

(c) The reaction is endothermic, so heat acts as a reactant:



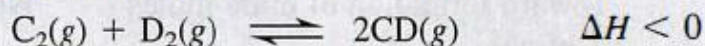
Therefore, adding heat to the left shifts the reaction to the right, so $[Y_2]$ decreases.

Check (a) Remember that quantities in the numerator (or denominator) of Q_c are multiplied, not added. For example, the denominator for scene 1 is $1 \times 1 = 1$, not $1 + 1 = 2$.

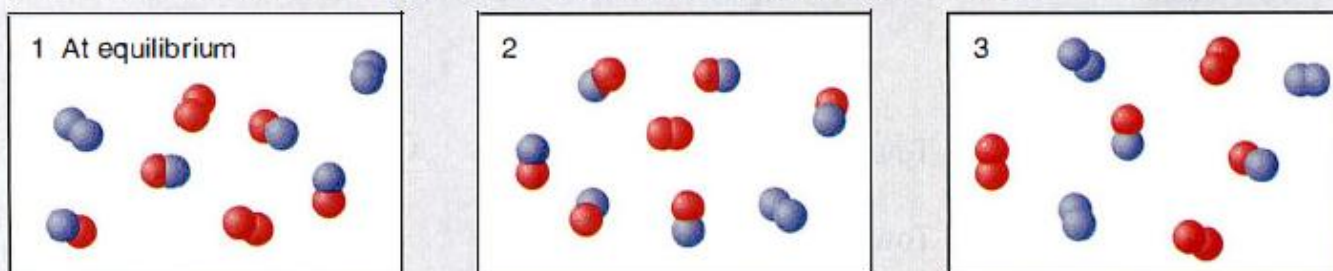
(c) A good check is to imagine that $\Delta H < 0$ and see if you get the opposite result:



If $\Delta H < 0$, adding heat would shift the reaction to the left and increase $[Y_2]$.

FOLLOW-UP PROBLEM 17.12 For the reaction

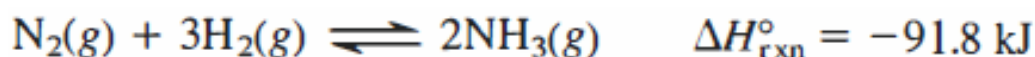
these molecular scenes depict different reaction mixtures (C = red, D = blue):



(a) Calculate the value of K_p . (b) In which direction will the reaction proceed for the mixtures *not* at equilibrium? (c) For the mixture at equilibrium, what effect will a rise in T have on the total moles of gas (increase, decrease, no effect)? Explain.

The Industrial Production of Ammonia

Haber process is industrially for the synthesis of ammonia:



By inspecting the balanced equation and applying equilibrium principles, we can see three ways to maximize the yield of ammonia:

1. Decrease concentration of ammonia. NH_3 is the product, so removing it will shift the equilibrium position toward producing more.
2. Decrease volume (increase pressure). Because four moles of gas react to form two moles of gas, decreasing the volume will shift the equilibrium position toward fewer moles of gas, that is, toward forming more NH_3 .
3. Decrease temperature. Because the formation of ammonia is exothermic, decreasing the temperature (removing heat) will shift the equilibrium position toward formation of product, thereby increasing K_c .

STUDY THE DETAILS GIVEN IN THE TEXT BOOK