

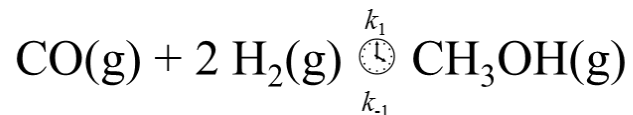
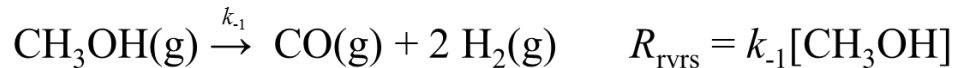
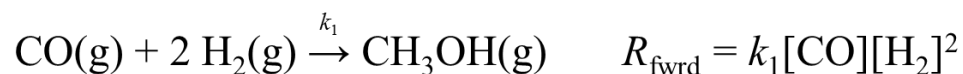
Principles of Chemical Equilibrium



The Concept of Equilibrium and the Equilibrium Constant

Few chemical reactions proceed in only one direction. Most are reversible, at least to some extent. At the start of a reversible process, the reaction proceeds toward the formation of products. As soon as some product molecules are formed, the reverse process begins to take place and reactant molecules are formed from product molecules.

Chemical equilibrium is achieved when the rates of the forward and reverse reactions are equal and the concentrations of the reactants and products remain constant.

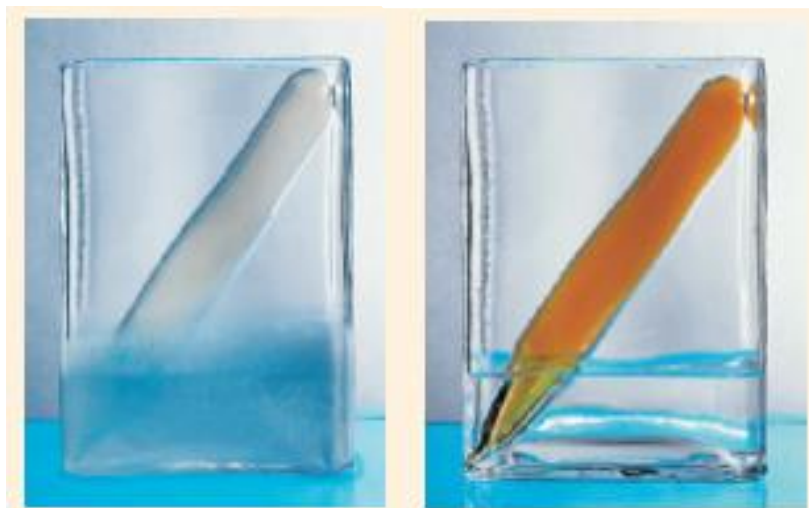


$$R_{\text{fwrd}} = R_{\text{rvrs}}$$

The study of physical equilibrium yields useful information, such as the equilibrium vapor pressure (see Section 11.8). However, chemists are particularly interested in chemical equilibrium processes, such as the reversible reaction involving nitrogen dioxide (NO_2) and dinitrogen tetroxide (N_2O_4) (Figure 14.1). The progress of the reaction



can be monitored easily because N_2O_4 is a colorless gas, whereas NO_2 has a dark-brown color that makes it sometimes visible in polluted air. Suppose that N_2O_4 is injected into an evacuated flask. Some brown color appears immediately, indicating the formation of NO_2 molecules. The color intensifies as the dissociation of N_2O_4 continues until eventually equilibrium is reached. Beyond that point, no further change in color is evident because the concentrations of both N_2O_4 and NO_2 remain constant. We can also bring about an equilibrium state by starting with pure NO_2 . As some of the NO_2 molecules combine to form N_2O_4 , the color fades. Yet another way to create an equilibrium state is to start with a mixture of NO_2 and N_2O_4 and monitor the system until the color stops changing.



These studies demonstrate that the preceding reaction is indeed reversible, because a pure component (N_2O_4 or NO_2) reacts to give the other gas. The important thing to keep in mind is that at equilibrium, the conversions of N_2O_4 to NO_2 and of NO_2 to N_2O_4 are still going on. We do not see a color change because the two rates are equal—the removal of NO_2 molecules takes place as fast as the production of NO_2 molecules, and N_2O_4 molecules are formed as quickly as they dissociate. Figure 14.2 summarizes these three situations.

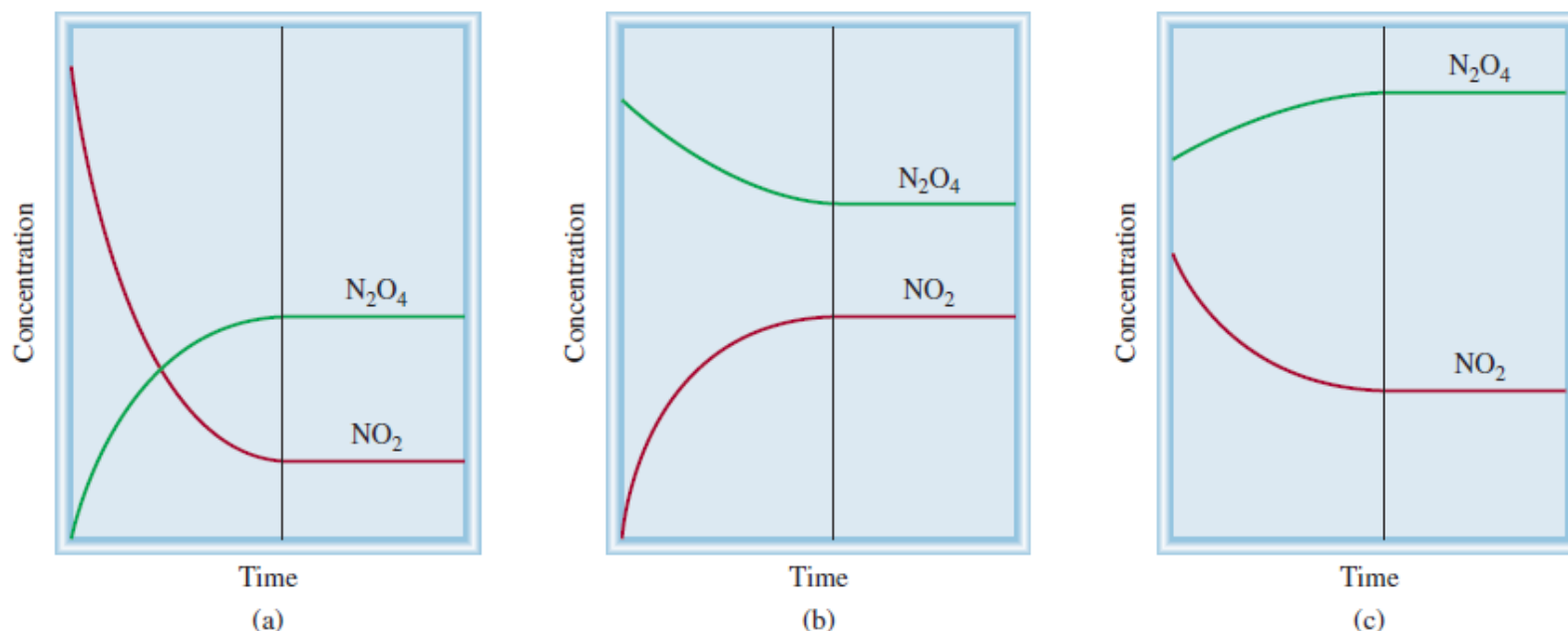


Figure 14.2 Change in the concentrations of NO_2 and N_2O_4 with time, in three situations. (a) Initially only NO_2 is present. (b) Initially only N_2O_4 is present. (c) Initially a mixture of NO_2 and N_2O_4 is present. In each case, equilibrium is established to the right of the vertical line.

The Equilibrium Constant

Table 14.1 shows some experimental data for the reaction just described at 25°C. The gas concentrations are expressed in molarity, which can be calculated from the number of moles of gases present initially and at equilibrium and the volume of the flask in liters. Note that the equilibrium concentrations of NO₂ and N₂O₄ vary, depending on the starting concentrations. We can look for relationships between [NO₂] and [N₂O₄] present at equilibrium by comparing the ratio of their concentrations. The simplest ratio, that is, [NO₂]/[N₂O₄], gives scattered values. But if we examine other possible mathematical relationships, we find that the ratio $\frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}$ at equilibrium gives a nearly constant value that averages 4.63×10^{-3} , regardless of the initial concentrations present:

$$K = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = 4.63 \times 10^{-3} \quad (14.1)$$

where K is a constant. Note that the exponent 2 for [NO₂] in this expression is the same as the stoichiometric coefficient for NO₂ in the reversible reaction.

TABLE 14.1 The NO₂–N₂O₄ System at 25°C

Initial Concentrations (M)		Equilibrium Concentrations (M)		Ratio of Concentrations at Equilibrium	
[NO ₂]	[N ₂ O ₄]	[NO ₂]	[N ₂ O ₄]	$\frac{[\text{NO}_2]}{[\text{N}_2\text{O}_4]}$	$\frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}$
0.000	0.670	0.0547	0.643	0.0851	4.65×10^{-3}
0.0500	0.446	0.0457	0.448	0.102	4.66×10^{-3}
0.0300	0.500	0.0475	0.491	0.0967	4.60×10^{-3}
0.0400	0.600	0.0523	0.594	0.0880	4.60×10^{-3}
0.200	0.000	0.0204	0.0898	0.227	4.63×10^{-3}

We can generalize this phenomenon with the following reaction at equilibrium:



where a , b , c , and d are the stoichiometric coefficients for the reacting species A, B, C, and D. For the reaction at a particular temperature

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b} \quad (14.2)$$

where K is the *equilibrium constant*. Equation (14.2) was formulated by two Norwegian chemists, Cato Guldberg[†] and Peter Waage,[‡] in 1864. It is the mathematical expression of their *law of mass action*, which holds that *for a reversible reaction at equilibrium and a constant temperature, a certain ratio of reactant and product concentrations has a constant value, K (the equilibrium constant)*. Note that although the concentrations may vary, as long as a given reaction is at equilibrium and the temperature does not change, according to the law of mass action, the value of K remains constant. The validity of Equation (14.2) and the law of mass action has been established by studying many reversible reactions.

The equilibrium constant, then, is defined by a *quotient*, the numerator of which is obtained by multiplying together the equilibrium concentrations of the *products*, each raised to a power equal to its stoichiometric coefficient in the balanced equation. Applying the same procedure to the equilibrium concentrations of *reactants* gives the denominator. The magnitude of the equilibrium constant tells us whether an equilibrium reaction favors the products or reactants. If K is much greater than 1 (that is, $K \gg 1$), the equilibrium will lie to the right and favors the products. Conversely, if the equilibrium constant is much smaller than 1 (that is, $K \ll 1$), the equilibrium will lie to the left and favor the reactants (Figure 14.3). In this context, any number greater than 10 is considered to be much greater than 1, and any number less than 0.1 is much less than 1.

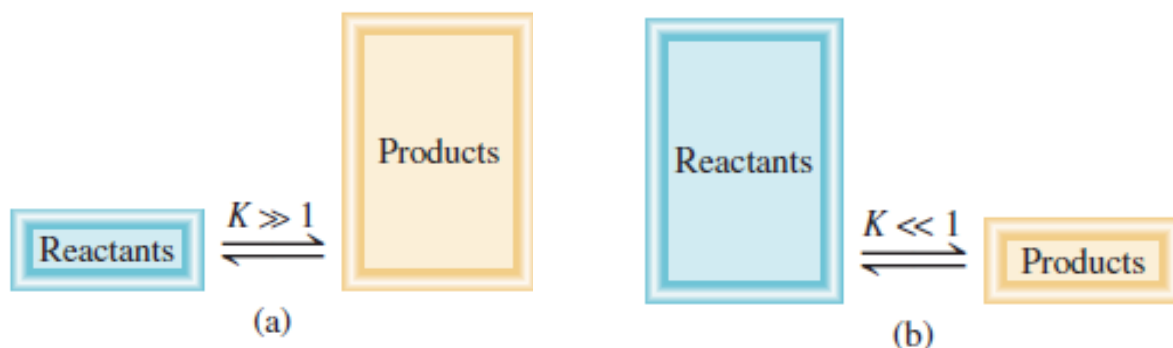


Figure 14.3 (a) At equilibrium, there are more products than reactants, and the equilibrium is said to lie to the right. (b) In the opposite situation, when there are more reactants than products, the equilibrium is said to lie to the left.

Writing Equilibrium Constant Expressions

The concept of equilibrium constants is extremely important in chemistry. As you will soon see, equilibrium constants are the key to solving a wide variety of stoichiometry problems involving equilibrium systems.

To use equilibrium constants, we must express them in terms of the reactant and product concentrations. Our only guide is the law of mass action [Equation (14.2)], which is the general formula for finding equilibrium concentrations. However, because the concentrations of the reactants and products can be expressed in different units and because the reacting species are not always in the same phase, there may be more than one way to express the equilibrium constant for the *same reaction*.

Homogeneous Equilibria

The term **homogeneous equilibrium** applies to reactions in which all reacting species are in the same phase. An example of homogeneous gas-phase equilibrium is the dissociation of N_2O_4 . The equilibrium constant, as given in Equation (14.1), is



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

Note that the subscript in K_c indicates that the concentrations of the reacting species are expressed in molarity or moles per liter. The concentrations of reactants and products in gaseous reactions can also be expressed in terms of their partial pressures.

we see that at constant temperature, the pressure P of a gas is directly related to the concentration in mol/L of the gas; that is, $P=(n/V)RT$. Thus, for the equilibrium process



we can write

$$K_P = \frac{P_{\text{NO}_2}^2}{P_{\text{N}_2\text{O}_4}} \quad (14.3)$$

where P_{NO_2} and $P_{\text{N}_2\text{O}_4}$ are the equilibrium partial pressures (in atm) of NO_2 and N_2O_4 , respectively. The subscript in K_P tells us that equilibrium concentrations are expressed in terms of pressure.

In general, K_c is not equal to K_p , because the partial pressures of reactants and products are not equal to their concentrations expressed in moles per liter. A simple relationship between K_p and K_c can be derived as follows. Let us consider the following equilibrium in the gas phase:



where a and b are stoichiometric coefficients. The equilibrium constant K_c is given by

$$K_c = \frac{[B]^b}{[A]^a}$$

and the expression for K_p is

$$K_p = \frac{P_B^b}{P_A^a}$$

where P_A and P_B are the partial pressures of A and B. Assuming ideal gas behavior,

$$P_A V = n_A RT$$
$$P_A = \frac{n_A RT}{V}$$

where V is the volume of the container in liters. Also

$$P_B V = n_B RT$$
$$P_B = \frac{n_B RT}{V}$$

Substituting these relations into the expression for K_p , we obtain

$$K_p = \frac{\left(\frac{n_B RT}{V}\right)^b}{\left(\frac{n_A RT}{V}\right)^a} = \frac{\left(\frac{n_B}{V}\right)^b}{\left(\frac{n_A}{V}\right)^a} (RT)^{b-a}$$

Now both n_A/V and n_B/V have units of mol/L and can be replaced by [A] and [B], so that

$$K_p = \frac{[B]^b}{[A]^a} (RT)^{\Delta n}$$
$$= K_c (RT)^{\Delta n} \quad (14.4)$$

where

$$\Delta n = b - a$$

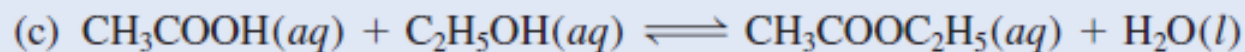
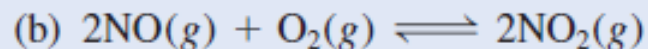
= moles of gaseous products – moles of gaseous reactants

Because pressures are usually expressed in atm, the gas constant R is given by 0.0821 L · atm/K · mol, and we can write the relationship between K_p and K_c as

$$K_p = K_c (0.0821T)^{\Delta n} \quad (14.5)$$

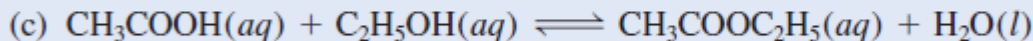
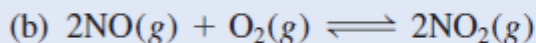
EXAMPLE 14.1

Write expressions for K_c , and K_p if applicable, for the following reversible reactions at equilibrium:



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Write expressions for K_c , and K_p if applicable, for the following reversible reactions at equilibrium:



Strategy Keep in mind the following facts: (1) the K_p expression applies only to gaseous reactions and (2) the concentration of solvent (usually water) does not appear in the equilibrium constant expression.

Solution (a) Because there are no gases present, K_p does not apply and we have only K_c .

$$K_c = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}][\text{H}_2\text{O}]}$$

HF is a weak acid, so that the amount of water consumed in acid ionizations is negligible compared with the total amount of water present as solvent. Thus, we can rewrite the equilibrium constant as

$$K_c = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}]}$$

(b)

$$K_c = \frac{[\text{NO}_2]^2}{[\text{NO}]^2[\text{O}_2]}$$

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

Solution (a) Because there are no gases present, K_p does not apply and we have only K_c .

$$K'_c = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}][\text{H}_2\text{O}]}$$

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

(c) The equilibrium constant K'_c is given by

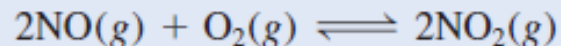
$$K'_c = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}][\text{C}_2\text{H}_5\text{OH}]}$$

Because the water produced in the reaction is negligible compared with the water solvent, the concentration of water does not change. Thus, we can write the new equilibrium constant as

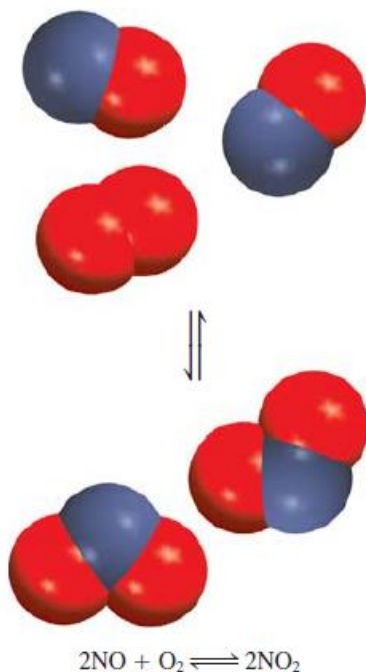
$$K_c = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5]}{[\text{CH}_3\text{COOH}][\text{C}_2\text{H}_5\text{OH}]}$$

EXAMPLE 14.2

The following equilibrium process has been studied at 230°C:

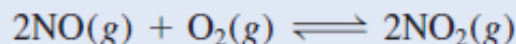


In one experiment, the concentrations of the reacting species at equilibrium are found to be $[\text{NO}] = 0.0542 \text{ M}$, $[\text{O}_2] = 0.127 \text{ M}$, and $[\text{NO}_2] = 15.5 \text{ M}$. Calculate the equilibrium constant (K_c) of the reaction at this temperature.



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Strategy The concentrations given are equilibrium concentrations. They have units of mol/L, so we can calculate the equilibrium constant (K_c) using the law of mass action [Equation (14.2)].

Solution The equilibrium constant is given by

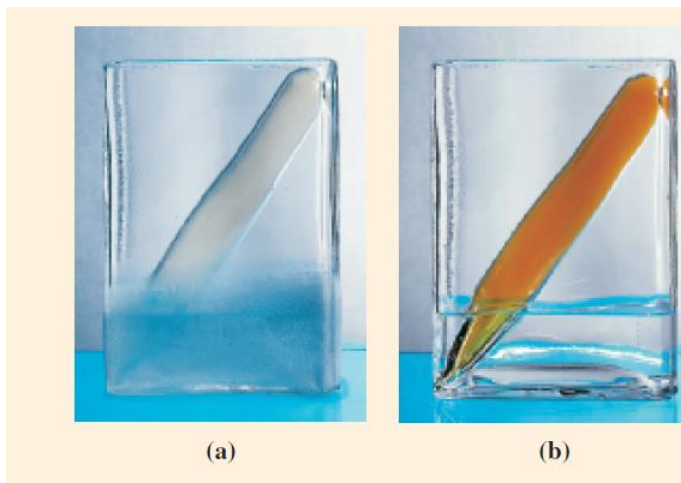
$$K_c = \frac{[\text{NO}_2]^2}{[\text{NO}]^2[\text{O}_2]}$$

Substituting the concentrations, we find that

$$K_c = \frac{(15.5)^2}{(0.0542)^2(0.127)} = 6.44 \times 10^5$$

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

Dinitrogen tetroxide, $\text{N}_2\text{O}_4(\text{l})$, is an important component of rocket fuels—for example, as an oxidizer of liquid hydrazine in the Titan rocket. At 25°C , N_2O_4 is a colorless gas that partially dissociates into NO_2 , a red-brown gas. The color of an equilibrium mixture of these two gases depends on their relative proportions, which in turn depends on the temperature (Fig. 15-7).



▲ FIGURE 15-7
The equilibrium $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2 \text{NO}_2(\text{g})$
(a) At dry ice temperatures, N_2O_4 exists as a solid. The gas in equilibrium with the solid is mostly colorless N_2O_4 , with only a trace of brown NO_2 .
(b) When warmed to room temperature and above, the N_2O_4 melts and vaporizes. The proportion of $\text{NO}_2(\text{g})$ at equilibrium increases over that at low temperatures, and the equilibrium mixture of $\text{N}_2\text{O}_4(\text{g})$ and $\text{NO}_2(\text{g})$ has a red-brown color.

Equilibrium is established in the reaction $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2 \text{NO}_2(\text{g})$ at 25°C . The quantities of the two gases present in a 3.00 L vessel are 7.64 g N_2O_4 and 1.56 g NO_2 . What is the value of K_c for this reaction?



Analyze

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

Solve

Convert the mass of N_2O_4 to moles.

$$\text{mol N}_2\text{O}_4 = 7.64 \text{ g N}_2\text{O}_4 \times \frac{1 \text{ mol N}_2\text{O}_4}{92.01 \text{ g N}_2\text{O}_4} = 8.303 \times 10^{-2} \text{ mol}$$

Convert moles of N_2O_4 to mol/L.

$$[\text{N}_2\text{O}_4] = \frac{8.303 \times 10^{-2} \text{ mol}}{3.00 \text{ L}} = 0.0277 \text{ M}$$

Convert the mass of NO_2 to moles.

$$\text{mol NO}_2 = 1.56 \text{ g NO}_2 \times \frac{1 \text{ mol NO}_2}{46.01 \text{ g NO}_2} = 3.391 \times 10^{-2} \text{ mol}$$

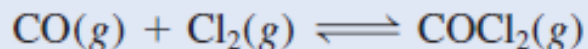
Convert moles of NO_2 to mol/L.

$$[\text{NO}_2] = \frac{3.391 \times 10^{-2}}{3.00 \text{ L}} = 0.0113 \text{ M}$$

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

$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = \frac{(0.0113)^2}{(0.0277)} = 4.61 \times 10^{-3}$$

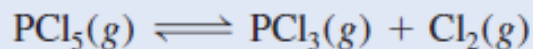
Practice Exercise Carbonyl chloride (COCl_2), also called phosgene, was used in World War I as a poisonous gas. The equilibrium concentrations for the reaction between carbon monoxide and molecular chlorine to form carbonyl chloride



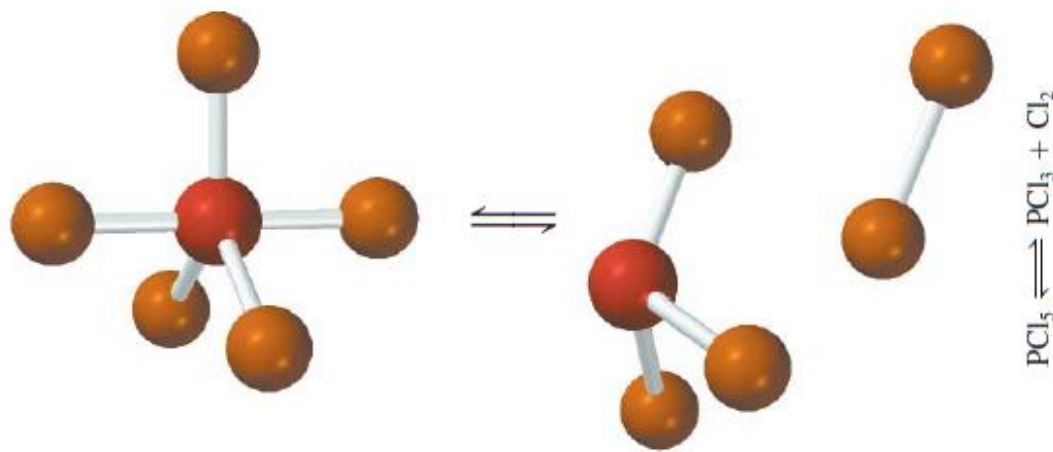
at 74°C are $[\text{CO}] = 1.2 \times 10^{-2} \text{ M}$, $[\text{Cl}_2] = 0.054 \text{ M}$, and $[\text{COCl}_2] = 0.14 \text{ M}$. Calculate the equilibrium constant (K_c).

EXAMPLE 14.3

The equilibrium constant K_p for the decomposition of phosphorus pentachloride to phosphorus trichloride and molecular chlorine

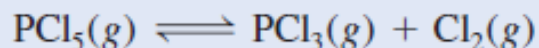


is found to be 1.05 at 250°C. If the equilibrium partial pressures of PCl_5 and PCl_3 are 0.875 atm and 0.463 atm, respectively, what is the equilibrium partial pressure of Cl_2 at 250°C?



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Strategy The concentrations of the reacting gases are given in atm, so we can express the equilibrium constant in K_p . From the known K_p value and the equilibrium pressures of PCl_3 and PCl_5 , we can solve for P_{Cl_2} .

Solution First, we write K_p in terms of the partial pressures of the reacting species

$$K_p = \frac{P_{\text{PCl}_3} P_{\text{Cl}_2}}{P_{\text{PCl}_5}}$$

Knowing the partial pressures, we write

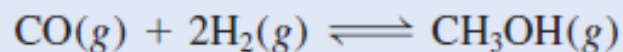
$$1.05 = \frac{(0.463)(P_{\text{Cl}_2})}{(0.875)}$$

or

$$P_{\text{Cl}_2} = \frac{(1.05)(0.875)}{(0.463)} = 1.98 \text{ atm}$$

EXAMPLE 14.4

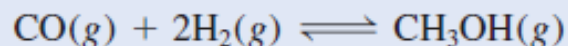
Methanol (CH_3OH) is manufactured industrially by the reaction



The equilibrium constant (K_c) for the reaction is 10.5 at 220°C . What is the value of K_p at this temperature?

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Methanol (CH_3OH) is manufactured industrially by the reaction



The equilibrium constant (K_c) for the reaction is 10.5 at 220°C . What is the value of K_p at this temperature?

Strategy The relationship between K_c and K_p is given by Equation (14.5). What is the change in the number of moles of gases from reactants to product? Recall that

$$\Delta n = \text{moles of gaseous products} - \text{moles of gaseous reactants}$$

What unit of temperature should we use?

Solution The relationship between K_c and K_p is

$$K_p = K_c(0.0821T)^{\Delta n}$$

Because $T = 273 + 220 = 493 \text{ K}$ and $\Delta n = 1 - 3 = -2$, we have

$$\begin{aligned} K_p &= (10.5)(0.0821 \times 493)^{-2} \\ &= 6.41 \times 10^{-3} \end{aligned}$$

Heterogeneous Equilibria

As you might expect, a **heterogeneous equilibrium results from a reversible reaction** involving reactants and products that are in different phases. For example, when calcium carbonate is heated in a closed vessel, the following equilibrium is attained:



The two solids and one gas constitute three separate phases. At equilibrium, we might write the equilibrium constant as

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

The “concentration” of a solid, like its density, is an intensive property and does not depend on how much of the substance is present.

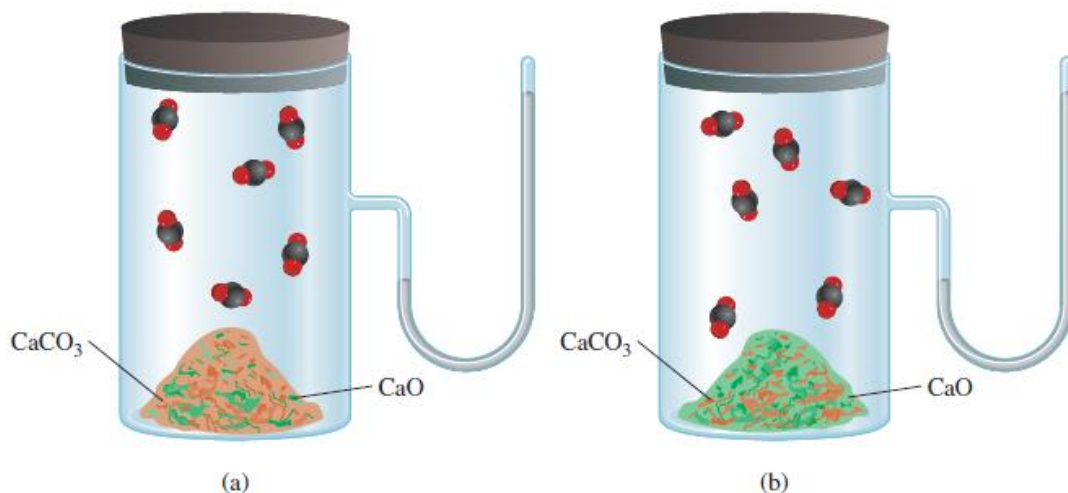


Figure 14.4 In (a) and (b) the equilibrium pressure of CO_2 is the same at the same temperature, despite the presence of different amounts of CaCO_3 and CaO .

For this reason, the terms $[\text{CaCO}_3]$ and $[\text{CaO}]$ are themselves constants and can be combined with the equilibrium constant. We can simplify Equation (14.6) by writing

$$\frac{[\text{CaCO}_3]}{[\text{CaO}]} K'_c = K_c = [\text{CO}_2] \quad (14.7)$$

where K_c , the “new” equilibrium constant, is conveniently expressed in terms of a single concentration, that of CO_2 . Note that the value of K_c does not depend on how much CaCO_3 and CaO are present, as long as some of each is present at equilibrium

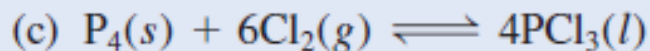
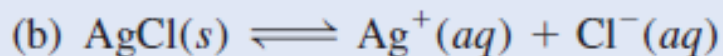
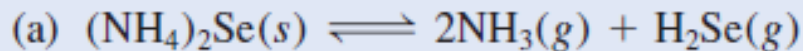
Alternatively, we can express the equilibrium constant as

$$K_P = P_{\text{CO}_2} \quad (14.8)$$

The equilibrium constant in this case is numerically equal to the pressure of CO₂ gas, an easily measurable quantity.

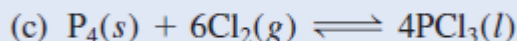
EXAMPLE 14.5

Write the equilibrium constant expression K_c , and K_p if applicable, for each of the following heterogeneous systems:



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Write the equilibrium constant expression K_c , and K_p if applicable, for each of the following heterogeneous systems:



Strategy We omit any pure solids or pure liquids in the equilibrium constant expression because their activities are unity.

Solution (a) Because $(\text{NH}_4)_2\text{Se}$ is a solid, the equilibrium constant K_c is given by

$$K_c = [\text{NH}_3]^2[\text{H}_2\text{Se}]$$

Alternatively, we can express the equilibrium constant K_p in terms of the partial pressures of NH_3 and H_2Se :

$$K_p = P_{\text{NH}_3}^2 P_{\text{H}_2\text{Se}}$$

(b) Here AgCl is a solid so the equilibrium constant is given by

$$K_c = [\text{Ag}^+][\text{Cl}^-]$$

Because no gases are present, there is no K_p expression.

(c) We note that P_4 is a solid and PCl_3 is a liquid, so they do not appear in the equilibrium constant expression. Thus, K_c is given by

$$K_c = \frac{1}{[\text{Cl}_2]^6}$$

$$K_p = \frac{1}{P_{\text{Cl}_2}^6}$$

EXAMPLE 14.6

Consider the following heterogeneous equilibrium:



At 800°C, the pressure of CO_2 is 0.236 atm. Calculate (a) K_p and (b) K_c for the reaction at this temperature.

EXAMPLE 14.6

Consider the following heterogeneous equilibrium:



At 800°C, the pressure of CO_2 is 0.236 atm. Calculate (a) K_p and (b) K_c for the reaction at this temperature.

Strategy Remember that pure solids do not appear in the equilibrium constant expression. The relationship between K_p and K_c is given by Equation (14.5).

Solution (a) Using Equation (14.8) we write

$$\begin{aligned} K_p &= P_{\text{CO}_2} \\ &= 0.236 \end{aligned}$$

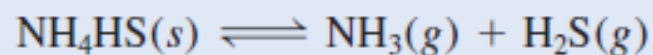
(b) From Equation (14.5), we know

$$K_p = K_c(0.0821T)^{\Delta n}$$

In this case, $T = 800 + 273 = 1073$ K and $\Delta n = 1$, so we substitute these values in the equation and obtain

$$\begin{aligned} 0.236 &= K_c(0.0821 \times 1073) \\ K_c &= 2.68 \times 10^{-3} \end{aligned}$$

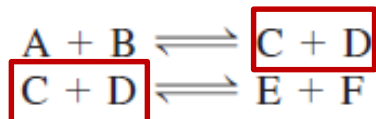
Practice Exercise Consider the following equilibrium at 395 K:



The partial pressure of each gas is 0.265 atm. Calculate K_p and K_c for the reaction.

Multiple Equilibria

The reactions we have considered so far are all relatively simple. A more complicated situation is one in which the product molecules in one equilibrium system are involved in a second equilibrium process:



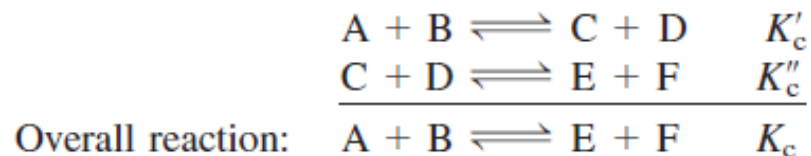
The products formed in the first reaction, C and D, react further to form products E and F. At equilibrium we can write two separate equilibrium constants:

$$K'_c = \frac{[\text{C}][\text{D}]}{[\text{A}][\text{B}]}$$

and

$$K''_c = \frac{[\text{E}][\text{F}]}{[\text{C}][\text{D}]}$$

The overall reaction is given by the sum of the two reactions



and the equilibrium constant K_c for the overall reaction is

$$K_c = \frac{[E][F]}{[A][B]}$$

We obtain the same expression if we take the product of the expressions for K'_c and K''_c :

$$K'_c K''_c = \frac{[C][D]}{[A][B]} \times \frac{[E][F]}{[C][D]} = \frac{[E][F]}{[A][B]}$$

Therefore,

$$K_c = K'_c K''_c \quad (14.9)$$

Relationship of K to the Balanced Chemical Equation

The equilibrium constant expression and the value of K both depend on how we write the equation for a reaction. Here are some general rules to keep in mind.

- When we *reverse* an equation, we *invert* the value of K .
- When we *multiply* the coefficients in a balanced equation by a common factor (2, 3, ...), we raise the equilibrium constant to the *corresponding power* (2, 3, ...).
- When we *divide* the coefficients in a balanced equation by a common factor (2, 3, ...), we take the *corresponding root* of the equilibrium constant (square root, cube root, ...).

To illustrate these points, let us consider the synthesis of methanol (methyl alcohol) from a carbon monoxide–hydrogen mixture called synthesis gas. This reaction is likely to become increasingly important as methanol and its mixtures with gasoline find greater use as motor fuels. The balanced reaction is



Suppose that in discussing the synthesis of CH_3OH from CO and H_2 , we had written the reverse reaction, that is,



Now, according to the generalized equilibrium constant expression (15.7), we should write

$$K' = \frac{a_{\text{CO(g)}} a_{\text{H}_2\text{(g)}}^2}{a_{\text{CH}_3\text{OH(g)}}} = \frac{1}{\frac{a_{\text{CH}_3\text{OH(g)}}}{a_{\text{CO(g)}} a_{\text{H}_2\text{(g)}}^2}} = \frac{1}{K} = \frac{1}{9.23 \times 10^{-3}} = 1.08 \times 10^2$$

In the preceding expression, the equilibrium constant expression and K value for the reaction, as originally written, are printed in blue. We see that $K' = 1/K$.

Suppose that for a certain application we want an equation based on synthesizing *two* moles of $\text{CH}_3\text{OH}(\text{g})$.



Here, $K'' = K^2$. That is,

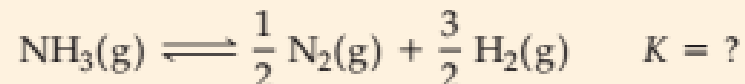
$$K'' = \frac{a_{\text{CH}_3\text{OH}(\text{g})}^2}{a_{\text{CO}(\text{g})}^2 a_{\text{H}_2(\text{g})}^4} = \left(\frac{a_{\text{CH}_3\text{OH}(\text{g})}}{a_{\text{CO}(\text{g})} a_{\text{H}_2(\text{g})}^2} \right)^2 = (K)^2 = (9.23 \times 10^{-3})^2 = 8.52 \times 10^{-5}$$

EXAMPLE 15-3 Relating K to the Balanced Chemical Equation

The following K value is given at 298 K for the synthesis of $\text{NH}_3(\text{g})$ from its elements.

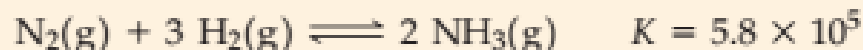


What is the value of K at 298 K for the following reaction?

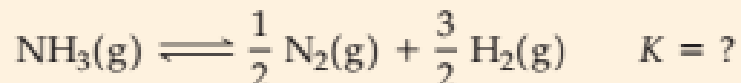


EXAMPLE 15-3 Relating K to the Balanced Chemical Equation

The following K value is given at 298 K for the synthesis of $\text{NH}_3(\text{g})$ from its elements.



What is the value of K at 298 K for the following reaction?



Analyze

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

Solve

First, reverse the given equation. This puts $\text{NH}_3(\text{g})$ on the left side of the equation, where we need it.



The equilibrium constant K' becomes

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

Then, to base the equation on 1 mol $\text{NH}_3(\text{g})$, divide all coefficients by 2.



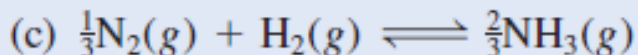
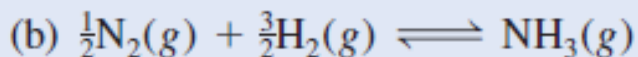
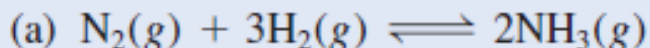
This requires the square root of K' .

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

PRACTICE EXAMPLE B: For the reaction $\text{NO}(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightleftharpoons \text{NO}_2(\text{g})$ at $184\text{ }^\circ\text{C}$, $K = 1.2 \times 10^2$. What is the value of K at $184\text{ }^\circ\text{C}$ for the reaction $2 \text{NO}_2(\text{g}) \rightleftharpoons 2 \text{NO}(\text{g}) + \text{O}_2(\text{g})$?

EXAMPLE 14.7

The reaction for the production of ammonia can be written in a number of ways:

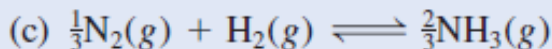
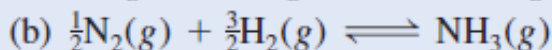
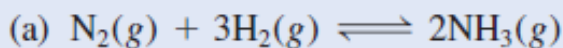


Write the equilibrium constant expression for each formulation. (Express the concentrations of the reacting species in mol/L.)

(d) How are the equilibrium constants related to one another?

EXAMPLE 14.7

The reaction for the production of ammonia can be written in a number of ways:



Write the equilibrium constant expression for each formulation. (Express the concentrations of the reacting species in mol/L.)

(d) How are the equilibrium constants related to one another?

Strategy We are given three different expressions for the same reacting system. Remember that the equilibrium constant expression depends on how the equation is balanced, that is, on the stoichiometric coefficients used in the equation.

Solution

(a)
$$K_a = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$$

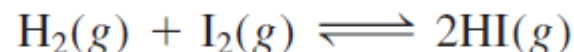
(b)
$$K_b = \frac{[\text{NH}_3]}{[\text{N}_2]^{\frac{1}{2}}[\text{H}_2]^{\frac{3}{2}}}$$

(c)
$$K_c = \frac{[\text{NH}_3]^{\frac{2}{3}}}{[\text{N}_2]^{\frac{1}{3}}[\text{H}_2]}$$

(d)
$$\begin{aligned} K_a &= K_b^2 \\ K_a &= K_c^3 \\ K_b^2 &= K_c^3 \quad \text{or} \quad K_b = K_c^{\frac{3}{2}} \end{aligned}$$

Predicting the Direction of a Reaction

The equilibrium constant K_c for the formation of hydrogen iodide from molecular hydrogen and molecular iodine in the gas phase



is 54.3 at 430°C. Suppose that in a certain experiment we place 0.243 mole of H_2 , 0.146 mole of I_2 , and 1.98 moles of HI all in a 1.00-L container at 430°C. Will there be a net reaction to form more H_2 and I_2 or more HI ? Inserting the starting concentrations in the equilibrium constant expression, we write

$$\frac{[\text{HI}]_0^2}{[\text{H}_2]_0[\text{I}_2]_0} = \frac{(1.98)^2}{(0.243)(0.146)} = 111$$

where the subscript 0 indicates initial concentrations (before equilibrium is reached). Because the quotient $[\text{HI}]_0^2/[\text{H}_2]_0[\text{I}_2]_0$ is greater than K_c , this system is not at equilibrium.

For reactions that have not reached equilibrium, such as the formation of HI considered above, we obtain the *reaction quotient* (Q_c), instead of the equilibrium constant *by substituting the initial concentrations into the equilibrium constant expression*. To determine the direction in which the net reaction will proceed to achieve equilibrium, we compare the values of Q_c and K_c . The three possible cases are as follows:

- $Q_c < K_c$ The ratio of initial concentrations of products to reactants is too small. To reach equilibrium, reactants must be converted to products. The system proceeds from left to right (consuming reactants, forming products) to reach equilibrium.
- $Q_c = K_c$ The initial concentrations are equilibrium concentrations. The system is at equilibrium.
- $Q_c > K_c$ The ratio of initial concentrations of products to reactants is too large. To reach equilibrium, products must be converted to reactants. The system proceeds from right to left (consuming products, forming reactants) to reach equilibrium.

Condition	Direction of Net Chemical Change
$Q < K$	To the right (\longrightarrow)
$Q > K$	To the left (\longleftarrow)
$Q = K$	Equilibrium; no net change (\rightleftharpoons)

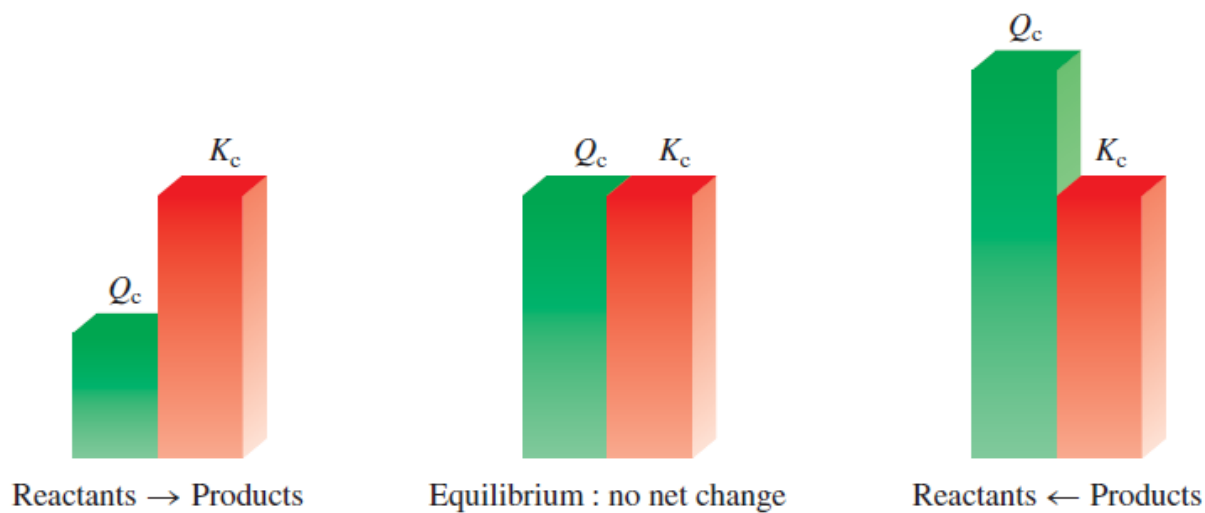
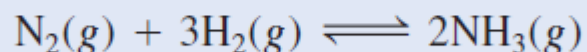


Figure 14.5 The direction of a reversible reaction to reach equilibrium depends on the relative magnitudes of Q_c and K_c . Note that K_c is a constant at a given temperature, but Q_c varies according to the relative amounts of reactants and products present.

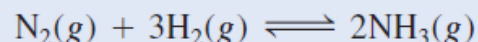
EXAMPLE 14.8

At the start of a reaction, there are 0.249 mol N_2 , 3.21×10^{-2} mol H_2 , and 6.42×10^{-4} mol NH_3 in a 3.50-L reaction vessel at 375°C . If the equilibrium constant (K_c) for the reaction



is 1.2 at this temperature, decide whether the system is at equilibrium. If it is not, predict which way the net reaction will proceed.

At the start of a reaction, there are 0.249 mol N_2 , 3.21×10^{-2} mol H_2 , and 6.42×10^{-4} mol NH_3 in a 3.50-L reaction vessel at 375°C . If the equilibrium constant (K_c) for the reaction



is 1.2 at this temperature, decide whether the system is at equilibrium. If it is not, predict which way the net reaction will proceed.

Strategy We are given the initial amounts of the gases (in moles) in a vessel of known volume (in liters), so we can calculate their molar concentrations and hence the reaction quotient (Q_c). How does a comparison of Q_c with K_c enable us to determine if the system is at equilibrium or, if not, in which direction will the net reaction proceed to reach equilibrium?

Solution The initial concentrations of the reacting species are

$$[\text{N}_2]_0 = \frac{0.249 \text{ mol}}{3.50 \text{ L}} = 0.0711 \text{ M}$$

$$[\text{H}_2]_0 = \frac{3.21 \times 10^{-2} \text{ mol}}{3.50 \text{ L}} = 9.17 \times 10^{-3} \text{ M}$$

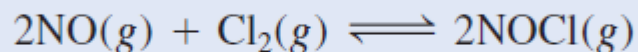
$$[\text{NH}_3]_0 = \frac{6.42 \times 10^{-4} \text{ mol}}{3.50 \text{ L}} = 1.83 \times 10^{-4} \text{ M}$$

Next we write

$$Q_c = \frac{[\text{NH}_3]_0^2}{[\text{N}_2]_0[\text{H}_2]_0^3} = \frac{(1.83 \times 10^{-4})^2}{(0.0711)(9.17 \times 10^{-3})^3} = 0.611$$

Because Q_c is smaller than K_c (1.2), the system is not at equilibrium. The net result will be an increase in the concentration of NH_3 and a decrease in the concentrations of N_2 and H_2 . That is, the net reaction will proceed from left to right until equilibrium is reached.

Practice Exercise The equilibrium constant (K_c) for the formation of nitrosyl chloride, an orange-yellow compound, from nitric oxide and molecular chlorine



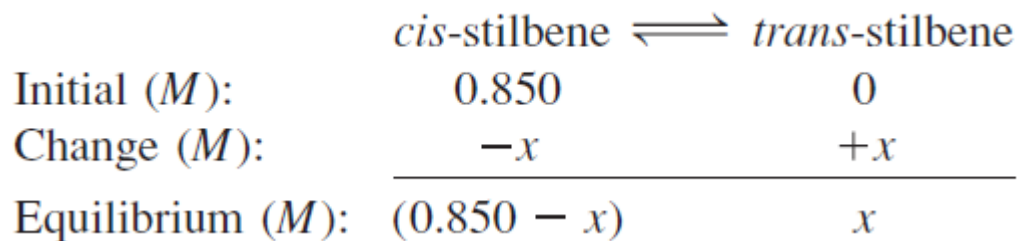
is 6.5×10^4 at 35°C . In a certain experiment, 2.0×10^{-2} mole of NO, 8.3×10^{-3} mole of Cl_2 , and 6.8 moles of NOCl are mixed in a 2.0-L flask. In which direction will the system proceed to reach equilibrium?

Calculating Equilibrium Concentrations

If we know the equilibrium constant for a particular reaction, we can calculate the concentrations in the equilibrium mixture from the initial concentrations. Commonly, only the initial reactant concentrations are given. Let us consider the following system involving two organic compounds, *cis*-stilbene and *trans*-stilbene, in a nonpolar hydrocarbon solvent (Figure 14.6):



The equilibrium constant (K_c) for this system is 24.0 at 200°C. Suppose that initially only *cis*-stilbene is present at a concentration of 0.850 mol/L. How do we calculate the concentrations of *cis*- and *trans*-stilbene at equilibrium? From the



A positive (+) change represents an increase and a negative (−) change a decrease in concentration at equilibrium. Next, we set up the equilibrium constant expression

$$K_c = \frac{[trans\text{-stilbene}]}{[cis\text{-stilbene}]}$$

$$24.0 = \frac{x}{0.850 - x}$$

$$x = 0.816 M$$

Having solved for x , we calculate the equilibrium concentrations of *cis*-stilbene and *trans*-stilbene as follows:

$$[cis\text{-stilbene}] = (0.850 - 0.816) M = 0.034 M$$

$$[trans\text{-stilbene}] = 0.816 M$$

To check the results we could use the equilibrium concentrations to calculate K_c .

We summarize our approach to solving equilibrium constant problems as follows:

1. Express the equilibrium concentrations of all species in terms of the initial concentrations and a single unknown x , which represents the change in concentration.
2. Write the equilibrium constant expression in terms of the equilibrium concentrations. Knowing the value of the equilibrium constant, solve for x .
3. Having solved for x , calculate the equilibrium concentrations of all species.

EXAMPLE 14.9

A mixture of 0.500 mol H_2 and 0.500 mol I_2 was placed in a 1.00-L stainless-steel flask at 430°C . The equilibrium constant K_c for the reaction $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$ is 54.3 at this temperature. Calculate the concentrations of H_2 , I_2 , and HI at equilibrium.

EXAMPLE 14.9

A mixture of 0.500 mol H_2 and 0.500 mol I_2 was placed in a 1.00-L stainless-steel flask at 430°C . The equilibrium constant K_c for the reaction $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$ is 54.3 at this temperature. Calculate the concentrations of H_2 , I_2 , and HI at equilibrium.

Strategy We are given the initial amounts of the gases (in moles) in a vessel of known volume (in liters), so we can calculate their molar concentrations. Because initially no HI was present, the system could not be at equilibrium. Therefore, some H_2 would react with the same amount of I_2 (why?) to form HI until equilibrium was established.

Solution We follow the preceding procedure to calculate the equilibrium concentrations.

Step 1: The stoichiometry of the reaction is 1 mol H_2 reacting with 1 mol I_2 to yield 2 mol HI . Let x be the depletion in concentration (mol/L) of H_2 and I_2 at equilibrium. It follows that the equilibrium concentration of HI must be $2x$. We summarize the changes in concentrations as follows:

	H_2	+	I_2	\rightleftharpoons	2HI
Initial (M):	0.500		0.500		0.000
Change (M):	$-x$		$-x$		$+2x$
Equilibrium (M):	$(0.500 - x)$		$(0.500 - x)$		$2x$

Step 2: The equilibrium constant is given by

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

Substituting, we get

$$54.3 = \frac{(2x)^2}{(0.500 - x)(0.500 - x)}$$

Taking the square root of both sides, we get

$$7.37 = \frac{2x}{0.500 - x}$$
$$x = 0.393 \text{ M}$$

Step 3: At equilibrium, the concentrations are

$$[\text{H}_2] = (0.500 - 0.393) \text{ M} = 0.107 \text{ M}$$

$$[\text{I}_2] = (0.500 - 0.393) \text{ M} = 0.107 \text{ M}$$

$$[\text{HI}] = 2 \times 0.393 \text{ M} = 0.786 \text{ M}$$

Factors That Affect Chemical Equilibrium

Chemical equilibrium represents a balance between forward and reverse reactions. In most cases, this balance is quite delicate. Changes in experimental conditions may disturb the balance and shift the equilibrium position so that more or less of the desired product is formed.

When we say that an equilibrium position shifts to the right, for example, we mean that the net reaction is now from left to right. Variables that can be controlled experimentally are concentration, pressure, volume, and temperature.

Le Châtelier's Principle

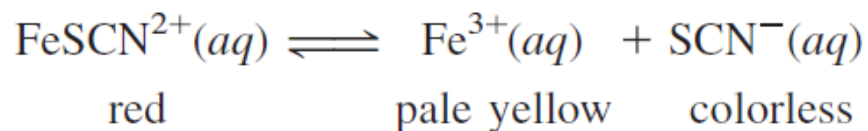
There is a general rule that helps us to predict the direction in which an equilibrium reaction will move when a change in concentration, pressure, volume, or temperature occurs.

The rule, known as **Le Châtelier's† principle**, states that if an external stress is applied to a system at equilibrium, the system adjusts in such a way that the stress is partially offset as the system reaches a new equilibrium position.

The word “stress” here means a change in concentration, pressure, volume, or temperature that removes the system from the equilibrium state. We will use Le Châtelier's principle to assess the effects of such changes.

Changes in Concentration

Iron(III) thiocyanate [$\text{Fe}(\text{SCN})_3$] dissolves readily in water to give a red solution. The red color is due to the presence of hydrated FeSCN^{2+} ion. The equilibrium between undissociated FeSCN^{2+} and the Fe^{3+} and SCN^- ions is given by

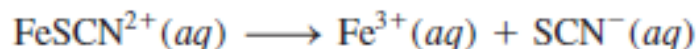


What happens if we add some sodium thiocyanate (NaSCN) to this solution? In this case, the stress applied to the equilibrium system is an increase in the concentration of SCN^- (from the dissociation of NaSCN). To offset this stress, some Fe^{3+} ions react with the added SCN^- ions, and the equilibrium shifts from right to left:



Consequently, the red color of the solution deepens (Figure 14.7). Similarly, if we added iron(III) nitrate [$\text{Fe}(\text{NO}_3)_3$] to the original solution, the red color would also deepen because the additional Fe^{3+} ions [from $\text{Fe}(\text{NO}_3)_3$] would shift the equilibrium from right to left.

Now suppose we add some oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) to the original solution. Oxalic acid ionizes in water to form the oxalate ion, $\text{C}_2\text{O}_4^{2-}$, which binds strongly to the Fe^{3+} ions. The formation of the stable yellow ion $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$ removes free Fe^{3+} ions in solution. Consequently, more FeSCN^{2+} units dissociate and the equilibrium shifts from left to right:



The red solution will turn yellow due to the formation of $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$ ions.

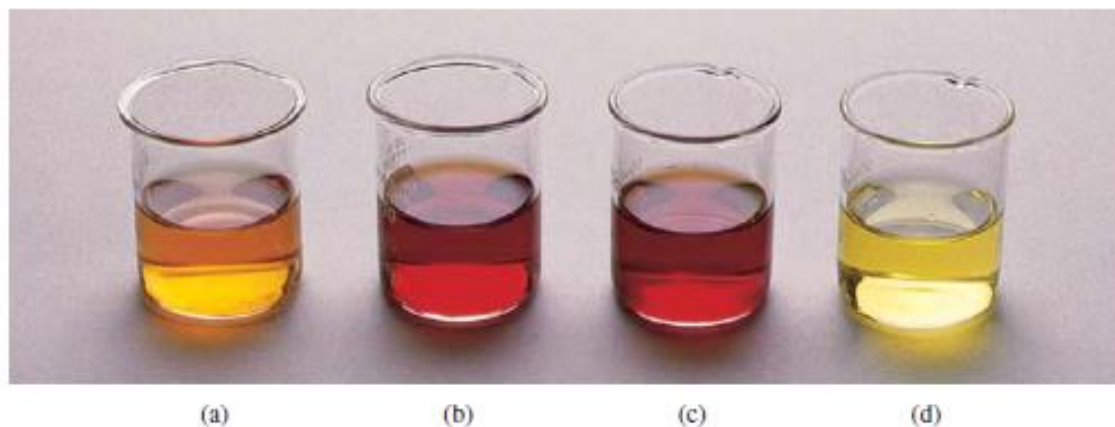
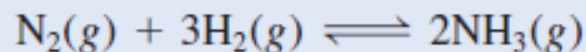


Figure 14.7 Effect of concentration change on the position of equilibrium. (a) An aqueous $\text{Fe}(\text{SCN})_3$ solution. The color of the solution is due to both the red FeSCN^{2+} and the yellow Fe^{3+} ions. (b) After the addition of some NaSCN to the solution in (a), the equilibrium shifts to the left. (c) After the addition of some $\text{Fe}(\text{NO}_3)_3$ to the solution in (a), the equilibrium shifts to the left. (d) After the addition of some $\text{H}_2\text{C}_2\text{O}_4$ to the solution in (a), the equilibrium shifts to the right. The yellow color is due to the $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$ ions.

This experiment demonstrates that all reactants and products are present in the reacting system at equilibrium. Second, increasing the concentrations of the products (Fe^{3+} or SCN^{-}) shifts the equilibrium to the left, and decreasing the concentration of the product Fe^{3+} shifts the equilibrium to the right. These results are just as predicted by Le Châtelier's principle.

EXAMPLE 14.11

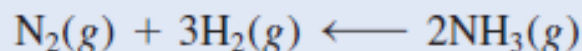
At 720°C, the equilibrium constant K_c for the reaction



is 2.37×10^{-3} . In a certain experiment, the equilibrium concentrations are $[\text{N}_2] = 0.683 \text{ M}$, $[\text{H}_2] = 8.80 \text{ M}$, and $[\text{NH}_3] = 1.05 \text{ M}$. Suppose some NH_3 is added to the mixture so that its concentration is increased to 3.65 M . (a) Use Le Châtelier's principle to predict the shift in direction of the net reaction to reach a new equilibrium. (b) Confirm your prediction by calculating the reaction quotient Q_c and comparing its value with K_c .

Strategy (a) What is the stress applied to the system? How does the system adjust to offset the stress? (b) At the instant when some NH_3 is added, the system is no longer at equilibrium. How do we calculate the Q_c for the reaction at this point? How does a comparison of Q_c with K_c tell us the direction of the net reaction to reach equilibrium.

Solution (a) The stress applied to the system is the addition of NH_3 . To offset this stress, some NH_3 reacts to produce N_2 and H_2 until a new equilibrium is established. The net reaction therefore shifts from right to left; that is,



(b) At the instant when some of the NH_3 is added, the system is no longer at equilibrium. The reaction quotient is given by

$$\begin{aligned} Q_c &= \frac{[\text{NH}_3]_0^2}{[\text{N}_2]_0[\text{H}_2]_0^3} \\ &= \frac{(3.65)^2}{(0.683)(8.80)^3} \\ &= 2.86 \times 10^{-2} \end{aligned}$$

Because this value is greater than 2.37×10^{-3} , the net reaction shifts from right to left until Q_c equals K_c .

Effect of Temperature on Equilibrium

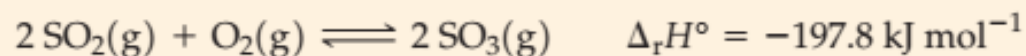
We can think of changing the temperature of an equilibrium mixture in terms of adding heat (raising the temperature) or removing heat (lowering the temperature). According to Le Châtelier's principle, adding heat favors the reaction in which heat is absorbed (*endothermic* reaction). Removing heat favors the reaction in which heat is evolved (*exothermic* reaction). Stated in terms of changing temperature,

Raising the temperature of an equilibrium mixture shifts the equilibrium condition in the direction of the *endothermic* reaction. *Lowering the temperature* causes a shift in the direction of the *exothermic* reaction.

For *endothermic* reactions, K increases as temperature increases. For *exothermic* reactions, K decreases as temperature increases.

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

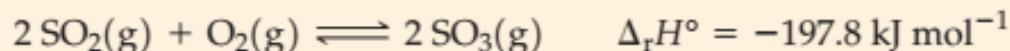
Consider the reaction



Will the amount of $\text{SO}_3(\text{g})$ formed from given amounts of $\text{SO}_2(\text{g})$ and $\text{O}_2(\text{g})$ be greater at high or low temperatures?

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Analyze

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

Solve

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

Changes in Volume and Pressure

Changes in pressure ordinarily do not affect the concentrations of reacting species in condensed phases (say, in an aqueous solution) because liquids and solids are virtually incompressible. On the other hand, concentrations of gases are greatly affected by changes in pressure.

Effect of Changes in Pressure or Volume on Equilibrium

There are three ways to change the pressure of a constant-temperature equilibrium mixture.

- 1. Add or remove a gaseous reactant or product.** The effect of these actions on the equilibrium condition is simply that caused by adding or removing a reaction component, as described previously.
- 2. Add an inert gas to the constant-volume reaction mixture.** This has the effect of increasing the *total* pressure, but the partial pressures of the reacting species are all unchanged. An inert gas added to a constant-volume equilibrium mixture has no effect on the equilibrium condition.
- 3. Change the pressure by changing the volume of the system.** Decreasing the volume of the system increases the pressure, and increasing the system volume decreases the pressure. Thus, the effect of this type of pressure change is simply that of a volume change.

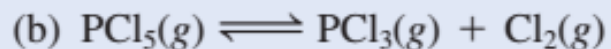
In general, an increase in pressure (decrease in volume) favors the net reaction that decreases the total number of moles of gases (the reverse reaction, in this case), and a decrease in pressure (increase in volume) favors the net reaction that increases the total number of moles of gases (here, the forward reaction).

For reactions in which there is no change in the number of moles of gases, a pressure (or volume) change has no effect on the position of equilibrium.

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

EXAMPLE 14.12

Consider the following equilibrium systems:



Predict the direction of the net reaction in each case as a result of increasing the pressure (decreasing the volume) on the system at constant temperature.



Strategy A change in pressure can affect only the volume of a gas, but not that of a solid because solids (and liquids) are much less compressible. The stress applied is an increase in pressure. According to Le Châtelier's principle, the system will adjust to partially offset this stress. In other words, the system will adjust to decrease the pressure. This can be achieved by shifting to the side of the equation that has fewer moles of gas. Recall that pressure is directly proportional to moles of gas: $PV = nRT$ so $P \propto n$.

Solution (a) Consider only the gaseous molecules. In the balanced equation, there are 3 moles of gaseous reactants and 2 moles of gaseous products. Therefore, the net reaction will shift toward the products (to the right) when the pressure is increased.

(b) The number of moles of products is 2 and that of reactants is 1; therefore, the net reaction will shift to the left, toward the reactant.

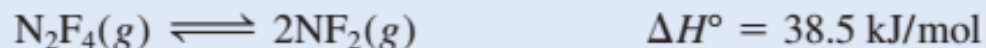
(c) The number of moles of products is equal to the number of moles of reactants, so a change in pressure has no effect on the equilibrium.

Effect of a Catalyst on Equilibrium

A catalyst is a substance that, when added to a reaction mixture, speeds up both the forward and reverse reactions. Equilibrium is achieved more rapidly, but the equilibrium amounts are unchanged by the catalyst.

EXAMPLE 14.13

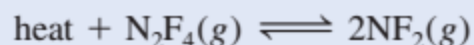
Consider the following equilibrium process between dinitrogen tetrafluoride (N_2F_4) and nitrogen difluoride (NF_2):



Predict the changes in the equilibrium if (a) the reacting mixture is heated at constant volume; (b) some N_2F_4 gas is removed from the reacting mixture at constant temperature and volume; (c) the pressure on the reacting mixture is decreased at constant temperature;

Strategy (a) What does the sign of ΔH° indicate about the heat change (endothermic or exothermic) for the forward reaction? (b) Would the removal of some N_2F_4 increase or decrease the Q_c of the reaction? (c) How would the decrease in pressure change the volume of the system? (d) What is the function of a catalyst? How does it affect a reacting system not at equilibrium? at equilibrium?

Solution (a) The stress applied is the heat added to the system. Note that the $\text{N}_2\text{F}_4 \longrightarrow 2\text{NF}_2$ reaction is an endothermic process ($\Delta H^\circ > 0$), which absorbs heat from the surroundings. Therefore, we can think of heat as a reactant



The system will adjust to remove some of the added heat by undergoing a decomposition reaction (from left to right). The equilibrium constant

$$K_c = \frac{[\text{NF}_2]^2}{[\text{N}_2\text{F}_4]}$$

will therefore increase with increasing temperature because the concentration of NF_2 has increased and that of N_2F_4 has decreased. Recall that the equilibrium constant is a constant only at a particular temperature. If the temperature is changed, then the equilibrium constant will also change.

(b) The stress here is the removal of N_2F_4 gas. The system will shift to replace some of the N_2F_4 removed. Therefore, the system shifts from right to left until equilibrium is reestablished. As a result, some NF_2 combines to form N_2F_4 .

- (c) The stress applied is a decrease in pressure (which is accompanied by an increase in gas volume). The system will adjust to remove the stress by increasing the pressure. Recall that pressure is directly proportional to the number of moles of a gas. In the balanced equation we see that the formation of NF_2 from N_2F_4 will increase the total number of moles of gases and hence the pressure. Therefore, the system will shift from left to right to reestablish equilibrium. The equilibrium constant will remain unchanged because temperature is held constant.
- (d) The function of a catalyst is to increase the rate of a reaction. If a catalyst is added to a reacting system not at equilibrium, the system will reach equilibrium faster than if left undisturbed. If a system is already at equilibrium, as in this case, the addition of a catalyst will not affect either the concentrations of NF_2 and N_2F_4 or the equilibrium constant.