

## 14.2: The Empirical Law of Mass Action

### Learning Objectives

- To know the relationship between the equilibrium constant and the rate constants for the forward and reverse reactions.
- To write an equilibrium constant expression for any reaction.
- To understand how different phases affect equilibria.

Because an equilibrium state is achieved when the forward reaction rate equals the reverse reaction rate, under a given set of conditions there must be a relationship between the composition of the system at equilibrium and the kinetics of a reaction (represented by rate constants). We can show this relationship using the decomposition reaction of  $N_2O_4$  to  $NO_2$ . Both the forward and reverse reactions for this system consist of a single elementary reaction, so the reaction rates are as follows:

$$\text{forward rate} = k_f[N_2O_4] \quad (14.2.1)$$

and

$$\text{reverse rate} = k_r[NO_2]^2 \quad (14.2.2)$$

At equilibrium, the forward rate equals the reverse rate (definition of equilibrium):

$$k_f[N_2O_4] = k_r[NO_2]^2 \quad (14.2.3)$$

so

$$\frac{k_f}{k_r} = \frac{[NO_2]^2}{[N_2O_4]} \quad (14.2.4)$$

The ratio of the rate constants gives us a new constant, the **equilibrium constant** ( $K$ ), which is defined as follows:

$$K = \frac{k_f}{k_r} \quad (14.2.5)$$

Hence there is a fundamental relationship between chemical kinetics and chemical equilibrium: under a given set of conditions, the composition of the equilibrium mixture is determined by the magnitudes of the rate constants for the forward and the reverse reactions.

The equilibrium constant is equal to the rate constant for the forward reaction divided by the rate constant for the reverse reaction.

Table 14.2.1 lists the initial and equilibrium concentrations from five different experiments using the reaction system described by Equation 14.2.1. At equilibrium the magnitude of the quantity  $[NO_2]^2/[N_2O_4]$  is essentially the same for all five experiments. In fact, no matter what the initial concentrations of  $NO_2$  and  $N_2O_4$  are, at equilibrium the quantity  $[NO_2]^2/[N_2O_4]$  will always be  $6.53 \pm 0.03 \times 10^{-3}$  at  $25^\circ\text{C}$ , which corresponds to the ratio of the rate constants for the forward and reverse reactions (Equation 14.2.5). That is, at a given temperature, the equilibrium constant for a reaction always has the same value, even though the specific concentrations of the reactants and products vary depending on their initial concentrations.

Table 14.2.1: Initial and Equilibrium Concentrations for  $NO_2 : N_2O_4$  Mixtures at  $25^\circ\text{C}$

Experiment	Initial Concentrations		Concentrations at Equilibrium		$K = [NO_2]^2/[N_2O_4]$
	$[N_2O_4]$ (M)	$[NO_2]$ (M)	$[N_2O_4]$ (M)	$[NO_2]$ (M)	
1	0.0500	0.0000	0.0417	0.0165	$6.54 \times 10^{-3}$
2	0.0000	0.1000	0.0417	0.0165	$6.54 \times 10^{-3}$
3	0.0750	0.0000	0.0647	0.0206	$6.56 \times 10^{-3}$
4	0.0000	0.0750	0.0304	0.0141	$6.54 \times 10^{-3}$

Experiment	Initial Concentrations		Concentrations at Equilibrium		$K = [NO_2]^2/[N_2O_4]$
	$[N_2O_4]$ (M)	$[NO_2]$ (M)	$[N_2O_4]$ (M)	$[NO_2]$ (M)	
5	0.0250	0.0750	0.0532	0.0186	$6.50 \times 10^{-3}$

## Developing an Equilibrium Constant Expression

In 1864, the Norwegian chemists Cato Guldberg (1836–1902) and Peter Waage (1833–1900) carefully measured the compositions of many reaction systems at equilibrium. They discovered that for any reversible reaction of the general form



where  $A$  and  $B$  are reactants,  $C$  and  $D$  are products, and  $a$ ,  $b$ ,  $c$ , and  $d$  are the stoichiometric coefficients in the balanced chemical equation for the reaction, the ratio of the product of the equilibrium concentrations of the products (raised to their coefficients in the balanced chemical equation) to the product of the equilibrium concentrations of the reactants (raised to their coefficients in the balanced chemical equation) is always a constant under a given set of conditions. This relationship is known as the [law of mass action](#) and can be stated as follows:

$$K = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad (14.2.7)$$

where  $K$  is the equilibrium constant for the reaction. Equation 14.2.6 is called the equilibrium equation, and the right side of Equation 14.2.7 is called the equilibrium constant expression. The relationship shown in Equation 14.2.7 is true for any pair of opposing reactions regardless of the mechanism of the reaction or the number of steps in the mechanism.

The equilibrium constant can vary over a wide range of values. The values of  $K$  shown in Table 14.2.2 for example, vary by 60 orders of magnitude. Because products are in the numerator of the equilibrium constant expression and reactants are in the denominator, values of  $K$  greater than  $10^3$  indicate a strong tendency for reactants to form products. In this case, chemists say that equilibrium lies to the right as written, favoring the formation of products. An example is the reaction between  $H_2$  and  $Cl_2$  to produce  $HCl$ , which has an equilibrium constant of  $1.6 \times 10^{33}$  at 300 K. Because  $H_2$  is a good reductant and  $Cl_2$  is a good oxidant, the reaction proceeds essentially to completion. In contrast, values of  $K$  less than  $10^{-3}$  indicate that the ratio of products to reactants at equilibrium is very small. That is, reactants do not tend to form products readily, and the equilibrium lies to the left as written, favoring the formation of reactants.

Table 14.2.2: Equilibrium Constants for Selected Reactions\*

Reaction	Temperature (K)	Equilibrium Constant (K)
$S(s) + O_2(g) \rightleftharpoons SO_2(g)$	300	$4.4 \times 10^{53}$
$2H_2(g) + O_2(g) \rightleftharpoons 2H_2O(g)$	500	$2.4 \times 10^{47}$
$H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$	300	$1.6 \times 10^{33}$
$H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$	300	$4.1 \times 10^{18}$
$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$	300	$4.2 \times 10^{13}$
$3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$	300	$2.7 \times 10^8$
$H_2(g) + D_2(g) \rightleftharpoons 2HD(g)$	100	1.92
$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$	300	$2.9 \times 10^{-1}$
$I_2(g) \rightleftharpoons 2I(g)$	800	$4.6 \times 10^{-7}$
$Br_2(g) \rightleftharpoons 2Br(g)$	1000	$4.0 \times 10^{-7}$
$Cl_2(g) \rightleftharpoons 2Cl(g)$	1000	$1.8 \times 10^{-9}$
$F_2(g) \rightleftharpoons 2F(g)$	500	$7.4 \times 10^{-13}$

\*Equilibrium constants vary with temperature. The  $K$  values shown are for systems at the indicated temperatures.

You will also notice in Table 14.2.2 that equilibrium constants have no units, even though Equation 14.2.7 suggests that the units of concentration might not always cancel because the exponents may vary. **In fact, equilibrium constants are calculated using “effective concentrations,” or activities, of reactants and products, which are the ratios of the measured concentrations to a standard state of 1 M.** As shown in Equation 14.2.8, the units of concentration cancel, which makes  $K$  unitless as well:

$$\frac{[A]_{\text{measured}}}{[A]_{\text{standard state}}} = \frac{\cancel{M}}{\cancel{M}} = \frac{\frac{\text{mol}}{L}}{\frac{\text{mol}}{L}} \quad (14.2.8)$$

Many reactions have equilibrium constants between 1000 and 0.001 ( $10^3 \geq K \geq 10^{-3}$ ), neither very large nor very small. At equilibrium, these systems tend to contain significant amounts of both products and reactants, indicating that there is not a strong tendency to form either products from reactants or reactants from products. An example of this type of system is the reaction of gaseous hydrogen and deuterium, a component of high-stability fiber-optic light sources used in ocean studies, to form HD:



The equilibrium constant expression for this reaction is

$$K = \frac{[\text{HD}]^2}{[\text{H}_2][\text{D}_2]} \quad (14.2.10)$$

with  $K$  varying between 1.9 and 4 over a wide temperature range (100–1000 K). Thus an equilibrium mixture of  $\text{H}_2$ ,  $\text{D}_2$ , and HD contains significant concentrations of both product and reactants.

Figure 14.2.1 summarizes the relationship between the magnitude of  $K$  and the relative concentrations of reactants and products at equilibrium for a general reaction, written as reactants  $\rightleftharpoons$  products. Because there is a direct relationship between the kinetics of a reaction and the equilibrium concentrations of products and reactants (Equations 14.2.8 and 14.2.7), when  $k_f \gg k_r$ ,  $K$  is a **large** number, and the concentration of products at equilibrium predominate. This corresponds to an essentially irreversible reaction. Conversely, when  $k_f \ll k_r$ ,  $K$  is a very **small** number, and the reaction produces almost no products as written. Systems for which  $k_f \approx k_r$  have significant concentrations of both reactants and products at equilibrium.

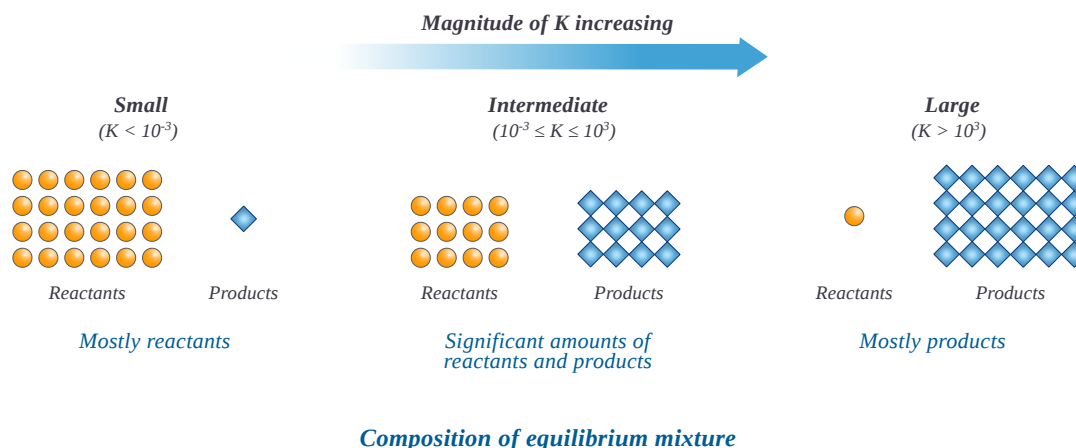


Figure 14.2.1: The Relationship between the Composition of the Mixture at Equilibrium and the Magnitude of the Equilibrium Constant. The larger the  $K$ , the farther the reaction proceeds to the right before equilibrium is reached, and the greater the ratio of products to reactants at equilibrium. (CC BY-NC; Ümit Kaya)

A large value of the equilibrium constant  $K$  means that products predominate at equilibrium; a small value means that reactants predominate at equilibrium.

### ✓ Example 14.2.1

Write the equilibrium constant expression for each reaction.

- $N_2(g) + 3 H_2(g) \rightleftharpoons 2 NH_3(g)$
- $CO(g) + \frac{1}{2} O_2(g) \rightleftharpoons CO_2(g)$
- $2 CO_2(g) \rightleftharpoons 2 CO(g) + O_2(g)$

**Given:** balanced chemical equations

**Asked for:** equilibrium constant expressions

**Strategy:**

Refer to Equation 14.2.7. Place the arithmetic product of the concentrations of the products (raised to their stoichiometric coefficients) in the numerator and the product of the concentrations of the reactants (raised to their stoichiometric coefficients) in the denominator.

**Solution:**

The only product is ammonia, which has a coefficient of 2. For the reactants,  $N_2$  has a coefficient of 1 and  $H_2$  has a coefficient of 3. The equilibrium constant expression is as follows:

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

The only product is carbon dioxide, which has a coefficient of 1. The reactants are  $CO$ , with a coefficient of 1, and  $O_2$ , with a coefficient of  $\frac{1}{2}$ . Thus the equilibrium constant expression is as follows:

$$K = \frac{[CO_2]}{[CO][O_2]^{1/2}}$$

This reaction is the reverse of the reaction in part b, with all coefficients multiplied by 2 to remove the fractional coefficient for  $O_2$ . The equilibrium constant expression is therefore the inverse of the expression in part b, with all exponents multiplied by 2:

$$K = \frac{[CO]^2[O_2]}{[CO_2]^2}$$

### ? Exercise 14.2.1

Write the equilibrium constant expression for each reaction.

- $N_2O(g) \rightleftharpoons N_2(g) + \frac{1}{2} O_2(g)$
- $2 C_8H_{18}(g) + 25 O_2(g) \rightleftharpoons 16 CO_2(g) + 18 H_2O(g)$
- $H_2(g) + I_2(g) \rightleftharpoons 2 HI(g)$

**Answer a**

$$K = \frac{[N_2][O_2]^{1/2}}{[N_2O]}$$

**Answer b**

$$K = \frac{[CO_2]^{16}[H_2O]^{18}}{[C_8H_{18}]^2[O_2]^{25}}$$

**Answer c**

$$K = \frac{[HI]^2}{[H_2][I_2]}$$

### ✓ Example 14.2.2

Predict which systems at equilibrium will (a) contain essentially only products, (b) contain essentially only reactants, and (c) contain appreciable amounts of both products and reactants.

1.  $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$   $K_{(700K)} = 54$
2.  $2CO_{2(g)} \rightleftharpoons 2CO_{(g)} + O_{2(g)}$   $K_{(1200K)} = 3.1 \times 10^{-18}$
3.  $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$   $K_{(613K)} = 97$
4.  $2O_{3(g)} \rightleftharpoons 3O_{2(g)}$   $K_{(298K)} = 5.9 \times 10^{55}$

**Given:** systems and values of  $K$

**Asked for:** composition of systems at equilibrium

**Strategy:**

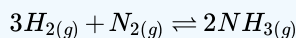
Use the value of the equilibrium constant to determine whether the equilibrium mixture will contain essentially only products, essentially only reactants, or significant amounts of both.

**Solution:**

- a. Only system 4 has  $K \gg 10^3$ , so at equilibrium it will consist of essentially only products.
- b. System 2 has  $K \ll 10^{-3}$ , so the reactants have little tendency to form products under the conditions specified; thus, at equilibrium the system will contain essentially only reactants.
- c. Both systems 1 and 3 have equilibrium constants in the range  $10^3 \geq K \geq 10^{-3}$ , indicating that the equilibrium mixtures will contain appreciable amounts of both products and reactants.

### ? Exercise 14.2.2

Hydrogen and nitrogen react to form ammonia according to the following balanced chemical equation:



Values of the equilibrium constant at various temperatures were reported as

- $K_{25^\circ C} = 3.3 \times 10^8$ ,
  - $K_{177^\circ C} = 2.6 \times 10^3$ , and
  - $K_{327^\circ C} = 4.1$ .
- a. At which temperature would you expect to find the highest proportion of  $H_2$  and  $N_2$  in the equilibrium mixture?
  - b. Assuming that the reaction rates are fast enough so that equilibrium is reached quickly, at what temperature would you design a commercial reactor to operate to maximize the yield of ammonia?

**Answer a**

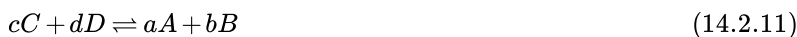
327°C, where  $K$  is smallest

**Answer b**

25°C

## Variations in the Form of the Equilibrium Constant Expression

Because equilibrium can be approached from either direction in a chemical reaction, the equilibrium constant expression and thus the magnitude of the equilibrium constant depend on the form in which the chemical reaction is written. For example, if we write the reaction described in Equation 14.2.6 in reverse, we obtain the following:



The corresponding equilibrium constant  $K'$  is as follows:

$$K' = \frac{[A]^a[B]^b}{[C]^c[D]^d} \quad (14.2.12)$$

This expression is the inverse of the expression for the original equilibrium constant, so  $K' = 1/K$ . That is, when we write a reaction in the reverse direction, the equilibrium constant expression is inverted. For instance, the equilibrium constant for the reaction  $N_2O_4 \rightleftharpoons 2NO_2$  is as follows:

$$K = \frac{[NO_2]^2}{[N_2O_4]} \quad (14.2.13)$$

but for the opposite reaction,  $2NO_2 \rightleftharpoons N_2O_4$ , the equilibrium constant  $K'$  is given by the inverse expression:

$$K' = \frac{[N_2O_4]}{[NO_2]^2} \quad (14.2.14)$$

Consider another example, the formation of water:  $2H_{2(g)} + O_{2(g)} \rightleftharpoons 2H_2O_{(g)}$ . Because  $H_2$  is a good reductant and  $O_2$  is a good oxidant, this reaction has a very large equilibrium constant ( $K = 2.4 \times 10^{47}$  at 500 K). Consequently, the equilibrium constant for the reverse reaction, the decomposition of water to form  $O_2$  and  $H_2$ , is very small:  $K' = 1/K = 1/(2.4 \times 10^{47}) = 4.2 \times 10^{-48}$ . As suggested by the very small equilibrium constant, and fortunately for life as we know it, a substantial amount of energy is indeed needed to dissociate water into  $H_2$  and  $O_2$ .

The equilibrium constant for a reaction written in reverse is the *inverse* of the equilibrium constant for the reaction as written originally.

Writing an equation in different but chemically equivalent forms also causes both the equilibrium constant expression and the magnitude of the equilibrium constant to be different. For example, we could write the equation for the reaction



as



with the equilibrium constant  $K''$  is as follows:

$$K'' = \frac{[N_2O_4]^{1/2}}{[NO_2]} \quad (14.2.17)$$

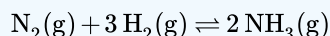
The values for  $K'$  (Equation 14.2.14) and  $K''$  are related as follows:

$$K'' = (K')^{1/2} = \sqrt{K'} \quad (14.2.18)$$

In general, if all the coefficients in a balanced chemical equation were subsequently multiplied by  $n$ , then the new equilibrium constant is the original equilibrium constant raised to the  $n^{\text{th}}$  power.

✓ Example 14.2.3: The Haber Process

At 745 K,  $K$  is 0.118 for the following reaction:



What is the equilibrium constant for each related reaction at 745 K?

- $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$
- $\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightleftharpoons NH_3(g)$

**Given:** balanced equilibrium equation,  $K$  at a given temperature, and equations of related reactions

**Asked for:** values of  $K$  for related reactions

**Strategy:**

Write the equilibrium constant expression for the given reaction and for each related reaction. From these expressions, calculate  $K$  for each reaction.

### Solution:

The equilibrium constant expression for the given reaction of  $N_2(g)$  with  $H_2(g)$  to produce  $NH_3(g)$  at 745 K is as follows:

$$K = \frac{[NH_3]^2}{[N_2][H_2]^3} = 0.118$$

This reaction is the reverse of the one given, so its equilibrium constant expression is as follows:

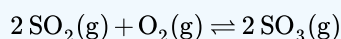
$$K' = \frac{1}{K} = \frac{[N_2][H_2]^3}{[NH_3]^2} = \frac{1}{0.118} = 8.47$$

In this reaction, the stoichiometric coefficients of the given reaction are divided by 2, so the equilibrium constant is calculated as follows:

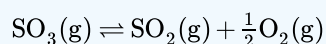
$$K'' = \frac{[NH_3]}{[N_2]^{1/2}[H_2]^{3/2}} = K^{1/2} = \sqrt{K} = \sqrt{0.118} = 0.344$$

### ? Exercise

At 527°C, the equilibrium constant for the reaction



is  $7.9 \times 10^4$ . Calculate the equilibrium constant for the following reaction at the same temperature:

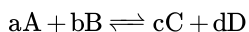


### Answer

$$3.6 \times 10^{-3}$$

## Law of Mass Action for Gas-Phase Reactions

For reactions that involve species in solution, the concentrations used in equilibrium calculations are usually expressed in moles/liter. For gases, however, the concentrations are usually expressed in terms of partial pressures rather than molarity, where the standard state is 1 atm of pressure. The symbol  $K_p$  is used to denote equilibrium constants calculated from partial pressures. For the general reaction



in which all the components are gases, the equilibrium constant expression can be written as the ratio of the partial pressures of the products and reactants (each raised to its coefficient in the chemical equation):

$$K_p = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b} \quad (14.2.19)$$

Thus  $K_p$  for the decomposition of  $N_2O_4$  (Equation 14.2.1) is as follows:

$$K_p = \frac{(P_{NO_2})^2}{P_{N_2O_4}} \quad (14.2.20)$$

Like  $K$ ,  $K_p$  is a unitless quantity because the quantity that is actually used to calculate it is an “effective pressure,” the ratio of the measured pressure to a standard state of 1 bar (approximately 1 atm), which produces a unitless quantity. The “effective pressure” is called the **fugacity**, just as activity is the effective concentration.

Because partial pressures are usually expressed in atmospheres or mmHg, the molar concentration of a gas and its partial pressure do not have the same numerical value. Consequently, the numerical values of  $K$  and  $K_p$  are usually different. They are, however, related by the ideal gas constant ( $R$ ) and the absolute temperature ( $T$ ):

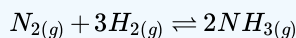
$$K_p = K(RT)^{\Delta n} \quad (14.2.21)$$

where  $K$  is the equilibrium constant expressed in units of concentration and  $\Delta n$  is the difference between the numbers of moles of gaseous products and gaseous reactants ( $n_p - n_r$ ). The temperature is expressed as the absolute temperature in Kelvin. According to Equation 14.2.21,  $K_p = K$  only if the moles of gaseous products and gaseous reactants are the same (i.e.,  $\Delta n = 0$ ). For the decomposition of  $N_2O_4$ , there are 2 mol of gaseous product and 1 mol of gaseous reactant, so  $\Delta n = 1$ . Thus, for this reaction,

$$K_p = K(RT)^1 = KRT \quad (14.2.22)$$

#### ✓ Example 14.2.4: The Haber Process (again)

The equilibrium constant for the reaction of nitrogen and hydrogen to give ammonia is 0.118 at 745 K. The balanced equilibrium equation is as follows:



What is  $K_p$  for this reaction at the same temperature?

**Given:** equilibrium equation, equilibrium constant, and temperature

**Asked for:**  $K_p$

**Strategy:**

Use the coefficients in the balanced chemical equation to calculate  $\Delta n$ . Then use Equation 14.2.21 to calculate  $K$  from  $K_p$ .

**Solution:**

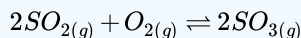
This reaction has 2 mol of gaseous product and 4 mol of gaseous reactants, so  $\Delta n = (2 - 4) = -2$ . We know  $K$ , and  $T = 745 \text{ K}$ . Thus, from Equation 14.2.18 we have the following:

$$K_p = K(RT)^{-2} = \frac{K}{(RT)^2} = \frac{0.118}{\{[0.08206(L \cdot atm)/(mol \cdot K)][745 \text{ K}]\}^2} = 3.16 \times 10^{-5}$$

Because  $K_p$  is a unitless quantity, the answer is  $K_p = 3.16 \times 10^{-5}$ .

#### ? Exercise 14.2.4:

Calculate  $K_p$  for the reaction



at 527°C, if  $K = 7.9 \times 10^4$  at this temperature.

**Answer**

$$K_p = 1.2 \times 10^3$$

### Law of Mass Action for Reactions Involving Pure Substances and Multiple Phases

When the products and reactants of a reaction at equilibrium in a single phase (e.g., liquid, gas or solids of different lattices), the system is a **homogeneous equilibrium**. In such situations, the concentrations of the reactants and products can vary over a wide range. In contrast, a system where the reactants and products are in two or more phase is called a **heterogeneous equilibrium** (e.g., the reaction of a gas with a solid or liquid or two different solid lattices in co-existing).

Because the molar concentrations of pure liquids and solids normally do not vary greatly with temperature, their concentrations are treated as constants, which allows us to simplify equilibrium constant expressions that involve pure solids or liquids. The reference states for pure solids and liquids are those forms stable at 1 bar (approximately 1 atm), which are assigned an activity of 1. (Recall that the density of water, and thus its volume, changes by only a few percentage points between 0 °C and 100 °C.)

Consider the following reaction, which is used in the final firing of some types of pottery to produce brilliant metallic glazes:





The glaze is created when metal oxides are reduced to metals by the product, carbon monoxide. The equilibrium constant expression for this reaction is as follows:

$$K = \frac{[CO]^2}{[CO_2][C]} \quad (14.2.24)$$

Because graphite is a solid, however, its molar concentration, determined from its density and molar mass, is essentially constant and has the following value:

$$[C] = \frac{2.26 \text{ g/cm}^3}{12.01 \text{ g/mol}} \times 1000 \text{ cm}^3/\text{L} = 188 \text{ mol/L} = 188 \text{ M} \quad (14.2.25)$$

We can rearrange Equation 14.2.25 so that the constant terms are on one side:

$$K[C] = K(188) = \frac{[CO]^2}{[CO_2]} \quad (14.2.26)$$

Incorporating the constant value of  $[C]$  into the equilibrium equation for the reaction in Equation 14.2.26

$$K' = \frac{[CO]^2}{[CO_2]} \quad (14.2.27)$$

The equilibrium constant for this reaction can also be written in terms of the partial pressures of the gases:

$$K_p = \frac{(P_{CO})^2}{P_{CO_2}} \quad (14.2.28)$$

Incorporating all the constant values into  $K'$  or  $K_p$  allows us to focus on the substances whose concentrations change during the reaction.

Although the concentrations of pure liquids or solids are not written explicitly in the equilibrium constant expression, these substances must be present in the reaction mixture for chemical equilibrium to occur. Whatever the concentrations of  $CO$  and  $CO_2$ , the system described in Equation 14.2.23 will reach chemical equilibrium only if a stoichiometric amount of solid carbon or excess solid carbon has been added so that some is still present once the system has reached equilibrium. As shown in Figure 14.2.2, it does not matter whether 1 g or 100 g of solid carbon is present; in either case, the composition of the gaseous components of the system will be the same at equilibrium.

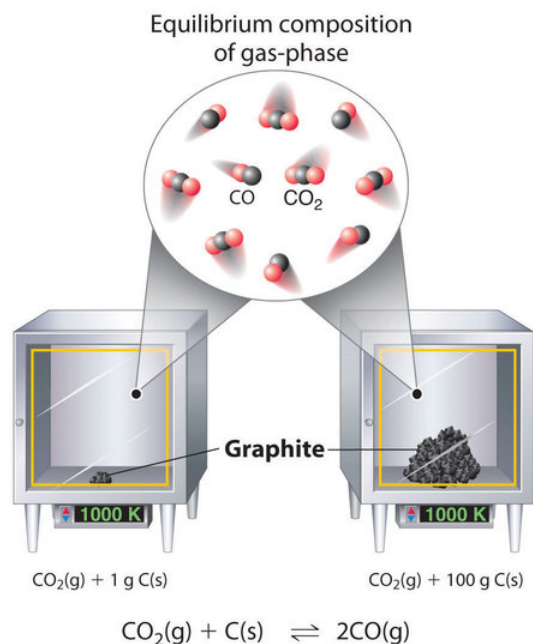


Figure 14.2.2: Effect of the Amount of Solid Present on Equilibrium in a Heterogeneous Solid–Gas System. In the system, the equilibrium composition of the gas phase at a given temperature, 1000 K in this case, is the same whether a small amount of solid carbon (left) or a large amount (right) is present.

### ✓ Example 14.2.1

Write each expression for  $K$ , incorporating all constants, and  $K_p$  for the following equilibrium reactions.

- $\text{PCl}_3(\text{l}) + \text{Cl}_2(\text{g}) \rightleftharpoons \text{PCl}_5(\text{s})$
- $\text{Fe}_3\text{O}_4(\text{s}) + 4\text{H}_2(\text{g}) \rightleftharpoons 3\text{Fe}(\text{s}) + 4\text{H}_2\text{O}(\text{g})$

**Given:** balanced equilibrium equations

**Asked for:** expressions for  $K$  and  $K_p$

**Strategy:**

Find  $K$  by writing each equilibrium constant expression as the ratio of the concentrations of the products and reactants, each raised to its coefficient in the chemical equation. Then express  $K_p$  as the ratio of the partial pressures of the products and reactants, each also raised to its coefficient in the chemical equation.

#### Solution

This reaction contains a pure solid ( $\text{PCl}_5$ ) and a pure liquid ( $\text{PCl}_3$ ). Their concentrations do not appear in the equilibrium constant expression because they do not change significantly. So

$$K = \frac{1}{[\text{Cl}_2]}$$

and

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

This reaction contains two pure solids ( $\text{Fe}_3\text{O}_4$  and  $\text{Fe}$ ), which do not appear in the equilibrium constant expressions. The two gases do, however, appear in the expressions:

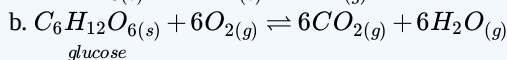
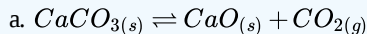
$$K = \frac{[\text{H}_2\text{O}]^4}{[\text{H}_2]^4}$$

and

$$K_p = \frac{(P_{H_2O})^4}{(P_{H_2})^4}$$

### ? Exercise 14.2.1

Write the expressions for  $K$  and  $K_p$  for the following reactions.



**Answer a**

$$K = [CO_2] \text{ and } K_p = P_{CO_2}$$

**Answer b**

$$K = \frac{[CO_2]^6 [H_2O]^6}{[O_2]^6} \text{ and } K_p = \frac{(P_{CO_2})^6 (P_{H_2O})^6}{(P_{O_2})^6}$$

For reactions carried out in solution, the concentration of the solvent is omitted from the equilibrium constant expression even when the solvent appears in the balanced chemical equation for the reaction. The concentration of the solvent is also typically much greater than the concentration of the reactants or products (recall that pure water is about 55.5 M, and pure ethanol is about 17 M). Consequently, the solvent concentration is essentially constant during chemical reactions, and the solvent is therefore treated as a pure liquid. The equilibrium constant expression for a reaction contains only those species whose concentrations could change significantly during the reaction.

The concentrations of pure solids, pure liquids, and solvents are omitted from equilibrium constant expressions because they do not change significantly during reactions when enough is present to reach equilibrium.

### Summary

- The law of mass action describes a system at equilibrium in terms of the concentrations of the products and the reactants.
- For a system involving one or more gases, either the molar concentrations of the gases or their partial pressures can be used.
- Definition of equilibrium constant in terms of forward and reverse rate constants:

$$K = \frac{k_f}{k_r}$$

- Equilibrium constant expression (law of mass action):

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

- Equilibrium constant expression for reactions involving gases using partial pressures:

$$K_p = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b}$$

- Relationship between  $K_p$  and  $K$ :

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

The ratio of the rate constants for the forward and reverse reactions at equilibrium is the equilibrium constant ( $K$ ), a unitless quantity. The composition of the equilibrium mixture is therefore determined by the magnitudes of the forward and reverse rate constants at equilibrium. Under a given set of conditions, a reaction will always have the same  $K$ . For a system at equilibrium, the law of mass action relates  $K$  to the ratio of the equilibrium concentrations of the products to the concentrations of the reactants raised to their respective powers to match the coefficients in the equilibrium equation. The ratio is called the equilibrium constant

expression. When a reaction is written in the reverse direction,  $K$  and the equilibrium constant expression are inverted. For gases, the equilibrium constant expression can be written as the ratio of the partial pressures of the products to the partial pressures of the reactants, each raised to a power matching its coefficient in the chemical equation. An equilibrium constant calculated from partial pressures ( $K_p$ ) is related to  $K$  by the ideal gas constant ( $R$ ), the temperature ( $T$ ), and the change in the number of moles of gas during the reaction. An equilibrated system that contains products and reactants in a single phase is a homogeneous equilibrium; a system whose reactants, products, or both are in more than one phase is a heterogeneous equilibrium.

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