CHAPTER 13

Chemical Equilibrium

Opening Essay

Imagine you are stranded in a rowboat in the middle of the ocean. Suddenly, your boat springs a small leak, and you need to bail out water. You grab a bucket and begin to bail. After a few minutes, your efforts against the leak keep the water to only about half an inch, but any further bailing doesn't change the water level; the leak brings in as much water as you bail out.

You are at *equilibrium*. Two opposing processes have reached the same speed, and there is no more overall change in the process.

Chemical reactions are like that as well. Most of them come to an equilibrium. The actual position of the equilibrium—whether it favors the reactants or the products—is characteristic of a chemical reaction; it is difficult to see just by looking at the balanced chemical equation. But chemistry has tools to help you understand the equilibrium of chemical reactions—the focus of our study in this chapter.

So far in this text, when we present a chemical reaction, we have implicitly assumed that the reaction goes to completion. Indeed, our stoichiometric calculations were based on this; when we asked how much of a product is produced when so much of a reactant reacts, we are assuming that *all* of a reactant reacts. However, this is usually not the case; many reactions do not go to completion, and many chemists have to deal with that. In this chapter, we will study this phenomenon and see ways in which we can affect the extent of chemical reactions.

1. CHEMICAL EQUILIBRIUM

LEARNING OBJECTIVES

1. **Define *chemical equilibrium*.**
2. **Recognize chemical equilibrium as a dynamic process.**

Consider the following reaction occurring in a closed container (so that no material can go in or out):

$$H_2 + I_2 \rightarrow 2HI$$

This is simply the reaction between elemental hydrogen and elemental iodine to make hydrogen iodide. The way the equation is written, we are led to believe that the reaction goes to completion, that all the H_2 and the I_2 react to make HI.

However, this is not the case. The reverse chemical reaction is also taking place:

$$2HI \rightarrow H_2 + I_2$$

It acts to undo what the first reaction does. Eventually, the reverse reaction proceeds so quickly that it matches the speed of the forward reaction. When that happens, any continued overall reaction stops: the reaction has reached **chemical equilibrium** (sometimes just spoken as *equilibrium*; plural *equilibria*), the point at which the forward and reverse processes balance each other's progress.

chemical equilibrium

The point at which forward and reverse chemical reactions balance each other's progress.

Because two opposing processes are occurring at once, it is conventional to represent an equilibrium using a double arrow, like this:

$$H_2 + I_2 \ ?\ 2HI$$

The double arrow implies that the reaction is going in both directions. Note that the reaction must still be balanced.

EXAMPLE 1

Write the equilibrium equation that exists between calcium carbonate as a reactant and calcium oxide and carbon dioxide as products.

Solution

As this is an equilibrium situation, a double arrow is used. The equilibrium equation is written as follows:

$$\mathrm{CaCO_3 \ ? \ CaO + CO_2}$$

Test Yourself

Write the equilibrium equation between elemental hydrogen and elemental oxygen as reactants and water as the product.

Answer

$\mathrm{2H_2 + O_2 \ ? \ 2H_2O}$

One thing to note about equilibrium is that the reactions do not stop; both the forward reaction and the reverse reaction continue to occur. They both occur at the same rate, so any overall change by one reaction is cancelled by the reverse reaction. We say that chemical equilibrium is *dynamic*, rather than static. Also, because both reactions are occurring simultaneously, the equilibrium can be written backward. For example, representing an equilibrium as

$$\mathrm{H_2 + I_2 \ ? \ 2HI}$$

is the same thing as representing the same equilibrium as

$$\mathrm{2HI \ ? \ H_2 + I_2}$$

The reaction must be at equilibrium for this to be the case, however.

KEY TAKEAWAYS

- Chemical reactions eventually reach equilibrium, a point at which forward and reverse reactions balance each other's progress.
- Chemical equilibria are dynamic: the chemical reactions are always occurring; they just cancel each other's progress.

EXERCISES

1. Define *chemical equilibrium*. Give an example.
2. Explain what is meant when it is said that chemical equilibrium is dynamic.
3. Write the equilibrium equation between elemental hydrogen and elemental chlorine as reactants and hydrochloric acid as the product.
4. Write the equilibrium equation between iron(III) sulfate as the reactant and iron(III) oxide and sulfur trioxide as the products.
5. Graphite and diamond are two forms of elemental carbon. Write the equilibrium equation between these two forms in two different ways.
6. At 1,500 K, iodine molecules break apart into iodine atoms. Write the equilibrium equation between these two species in two different ways.

ANSWERS

1. the situation when the forward and reverse chemical reactions occur, leading to no additional net change in the reaction position; $H_2 + I_2$? 2HI (answers will vary)
3. $H_2 + Cl_2$? 2HCl
5. C (gra) ? C (dia); C (dia) ? C (gra)

2. THE EQUILIBRIUM CONSTANT

LEARNING OBJECTIVES

1. **Explain the importance of the equilibrium constant.**
2. **Construct an equilibrium constant expression for a chemical reaction.**

In the mid 1860s, Norwegian scientists C. M. Guldberg and P. Waage noted a peculiar relationship between the amounts of reactants and products in an equilibrium. No matter how many reactants they started with, a certain ratio of reactants and products was achieved at equilibrium. Today, we call this observation the **law of mass action**. It relates the amounts of reactants and products at equilibrium for a chemical reaction. For a general chemical reaction occurring in solution,

law of mass action

The relationship of the amounts of reactants and products at equilibrium.

$$aA + bB \text{ ? } cC + dD$$

the **equilibrium constant**, also known as K_{eq}, is defined by the following expression:

equilibrium constant

A numerical value that relates to the ratio of products and reactants at equilibrium.

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

where [A] is the molar concentration of species A at equilibrium, and so forth. The coefficients *a*, *b*, *c*, and *d* in the chemical equation become exponents in the expression for K_{eq}. The K_{eq} is a characteristic numerical value for a given reaction at a given temperature; that is, each chemical reaction has its own characteristic K_{eq}. The concentration of each reactant and product in a chemical reaction at equilibrium is *related*; the concentrations cannot be random values, but they depend on each other. The numerator of the expression for K_{eq} has the concentrations of every product (however many products there are), while the denominator of the expression for K_{eq} has the concentrations of every reactant, leading to the common *products over reactants* definition for the K_{eq}.

Let us consider a simple example. Suppose we have this equilibrium:

$$A \text{ ? } B$$

There is one reactant, one product, and the coefficients on each are just 1 (assumed, not written). The K_{eq} expression for this equilibrium is

$$K_{eq} = \frac{[B]}{[A]}$$

(Exponents of 1 on each concentration are understood.) Suppose the numerical value of K_{eq} for this chemical reaction is 2.0. If [B] = 4.0 M, then [A] must equal 2.0 M so that the value of the fraction equals 2.0:

$$K_{eq} = \frac{[B]}{[A]} = \frac{4.0}{2.0} = 2.0$$

By convention, the units are understood to be M and are omitted from the K_{eq} expression. Suppose [B] were 6.0 M. For the K_{eq} value to remain constant (it is, after all, called the equilibrium *constant*), then [A] would have to be 3.0 M at equilibrium:

$$K_{eq} = \frac{[B]}{[A]} = \frac{6.0}{3.0} = 2.0$$

If [A] were *not* equal to 3.0 M, the reaction would not be at equilibrium, and a net reaction would occur until that ratio was indeed 2.0. At that point, the reaction is at equilibrium, and any net change would cease. (Recall, however, that the forward and reverse reactions do not stop because chemical equilibrium is dynamic.)

The issue is the same with more complex expressions for the K_{eq}; only the mathematics becomes more complex. Generally speaking, given a value for the K_{eq} and all but one concentration at equilibrium, the missing concentration can be calculated.

EXAMPLE 2

Given the following reaction:

$$H_2 + I_2 \text{ ? } 2HI$$

If the equilibrium [HI] is 0.75 M and the equilibrium [H_2] is 0.20 M, what is the equilibrium [I_2] if the K_{eq} is 0.40?

Solution

We start by writing the K_{eq} expression. Using the *products over reactants* approach, the K_{eq} expression is as follows:

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

Note that [HI] is squared because of the coefficient 2 in the balanced chemical equation. Substituting for the equilibrium [H_2] and [HI] and for the given value of K_{eq}:

$$0.40 = \frac{(0.75)^2}{(0.20)[I_2]}$$

To solve for [I_2], we have to do some algebraic rearrangement: divide the 0.40 into both sides of the equation and multiply both sides of the equation by [I_2]. This brings [I_2] into the numerator of the left side and the 0.40 into the denominator of the right side:

$$[I_2] = \frac{(0.75)^2}{(0.20)(0.40)}$$

Solving,

$$[I_2] = 7.0 \text{ M}$$

The concentration unit is assumed to be molarity. This value for [I_2] can be easily verified by substituting 0.75, 0.20, and 7.0 into the expression for K_{eq} and evaluating: you should get 0.40, the numerical value of K_{eq} (and you do).

Test Yourself

Given the following reaction:

$$H_2 + I_2 \text{ ? } 2HI$$

If the equilibrium [HI] is 0.060 M and the equilibrium [I_2] is 0.90 M, what is the equilibrium [H_2] if the K_{eq} is 0.40?

Answer

0.010 M

In some types of equilibrium problems, square roots, cube roots, or even higher roots need to be analyzed to determine a final answer. Make sure you know how to perform such operations on your calculator; if you do not know, ask your instructor for assistance.

EXAMPLE 3

The following reaction is at equilibrium:

$$N_2 + 3H_2 \text{ ? } 2NH_3$$

The K_{eq} at a particular temperature is 13.7. If the equilibrium $[N_2]$ is 1.88 M and the equilibrium $[NH_3]$ is 6.62 M, what is the equilibrium $[H_2]$?

Solution

We start by writing the K_{eq} expression from the balanced chemical equation:

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

Substituting for the known equilibrium concentrations and the K_{eq}, this becomes

$$13.7 = \frac{(6.62)^2}{(1.88)[H_2]^3}$$

Rearranging algebraically and then evaluating the numerical expression, we get

$$[H_2]^3 = \frac{(6.22)^2}{(1.88)(13.7)} = 1.502112129$$

To solve for $[H_2]$, we need to take the cube root of the equation. Performing this operation, we get

$$[H_2] = 1.15 \text{ M}$$

You should verify that this is correct using your own calculator to confirm that you know how to do a cube root correctly.

Test Yourself

The following reaction is at equilibrium:

$$N_2 + 3H_2 \text{ ? } 2NH_3$$

The K_{eq} at a particular temperature is 13.7. If the equilibrium $[N_2]$ is 0.055 M and the equilibrium $[H_2]$ is 1.62 M, what is the equilibrium $[NH_3]$?

Answer

1.79 M

The K_{eq} was defined earlier in terms of concentrations. For gas-phase reactions, the K_{eq} can also be defined in terms of the partial pressures of the reactants and products, P_i. For the gas-phase reaction

$$aA(g) + bB(g) \text{ ? } cC(g) + dD(g)$$

the pressure-based equilibrium constant, K_P, is defined as follows:

$$K_P = \frac{P_C^c P_D^d}{P_A^a P_B^b}$$

where P_A is the partial pressure of substance A at equilibrium in atmospheres, and so forth. As with the concentration-based equilibrium constant, the units are omitted when substituting into the expression for K_P.

EXAMPLE 4

What is the K_P for this reaction, given the equilibrium partial pressures of 0.664 atm for NO_2 and 1.09 for N_2O_4?

$$2NO_2(g) \text{ ? } N_2O_4(g)$$

Solution

Write the K_P expression for this reaction:

$$K_P = \frac{P_{N_2O_4}}{P^2_{NO_2}}$$

Then substitute the equilibrium partial pressures into the expression and evaluate:

$$K_P = \frac{(1.09)}{(0.664)^2} = 2.47$$

Test Yourself

What is the K_P for this reaction, given the equilibrium partial pressures of 0.44 atm for H_2, 0.22 atm for Cl_2, and 2.98 atm for HCl?

$$H_2 + Cl_2 \text{ ? } 2HCl$$

Answer

91.7

There is a simple relationship between K_{eq} (based on concentration units) and K_P (based on pressure units):

$$K_P = K_{eq} \cdot (RT)^{\Delta n}$$

where R is the ideal gas law constant (in units of L·atm/mol·K), T is the absolute temperature, and Δn is the change in the number of moles of gas in the balanced chemical equation, defined as $n_{gas,prods} - n_{gas,rcts}$. Note that this equation implies that if the number of moles of gas are the same in reactants and products, $K_{eq} = K_P$.

EXAMPLE 5

What is the K_P at 25°C for this reaction if the K_{eq} is 4.2×10^{-2}?

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

Solution

Before we use the relevant equation, we need to do two things: convert the temperature to kelvins and determine Δn. Converting the temperature is easy:

$$T = 25 + 273 = 298 \text{ K}$$

To determine the change in the number of moles of gas, take the number of moles of gaseous products and subtract the number of moles of gaseous reactants. There are 2 mol of gas as product and 4 mol of gas of reactant:

$$\Delta n = 2 - 4 = -2 \text{ mol}$$

Note that Δn is negative. Now we can substitute into our equation, using R = 0.08205 L·atm/mol·K. The units are omitted for clarity:

$$K_P = (4.2 \times 10^{-2})(0.08205)(298)^{-2}$$

Solving,

$$K_P = 7.0 \times 10^{-5}$$

Test Yourself

What is the K_P at 25°C for this reaction if the K_{eq} is 98.3?

$$I_2(g) \ ?\ 2I(g)$$

Answer

2.40×10^3

Finally, we recognize that many chemical reactions involve substances in the solid or liquid phases. For example, a particular chemical reaction is represented as follows:

$$2NaHCO_3(s) \ ?\ Na_2CO_3(s) + CO_2(g) + H_2O(\ell)$$

This chemical equation includes all three phases of matter. This kind of equilibrium is called a **heterogeneous equilibrium** because there is more than one phase present.

The rule for heterogeneous equilibria is as follows: *Do not include the concentrations of pure solids and pure liquids in* K_{eq} *expressions.* Only partial pressures for gas-phase substances or concentrations in solutions are included in the expressions of equilibrium constants. As such, the equilibrium constant expression for this reaction would simply be

heterogeneous equilibrium

An equilibrium in which more than one phase of reactants or products is present.

$$K_P = P_{CO_2}$$

because the two solids and one liquid would not appear in the expression.

KEY TAKEAWAYS

- Every chemical equilibrium can be characterized by an equilibrium constant, known as K_{eq}.
- The K_{eq} and K_P expressions are formulated as amounts of products divided by amounts of reactants; each amount (either a concentration or a pressure) is raised to the power of its coefficient in the balanced chemical equation.
- Solids and liquids do not appear in the expression for the equilibrium constant.

EXERCISES

1. Define the *law of mass action*.
2. What is an equilibrium constant for a chemical reaction? How is it constructed?
3. Write the K_{eq} expression for each reaction.
   a. $H_2 + Cl_2 ? 2HCl$
   b. $NO + NO_2 ? N_2O_3$
4. Write the K_{eq} expression for each reaction.
   a. $C_2H_5OH + NaI ? C_2H_5I + NaOH$
   b. $PCl_3 + Cl_2 ? PCl_5$
5. Write the K_P expression for each reaction.
   a. $2H_2(g) + O_2(g) ? 2H_2O(g)$
   b. $2H_2O_2(g) ? 2H_2O(g) + O_2(g)$
6. Write the K_P expression for each reaction.
   a. $CH_4(g) + 2O_2(g) ? CO_2(g) + 2H_2O(g)$
   b. $CH_4(g) + 4Cl_2(g) ? CCl_4(g) + 4HCl(g)$
7. The following reaction is at equilibrium:

   $PBr_3 + Br_2 ? PBr_5$

   The equilibrium $[Br_2]$ and $[PBr_5]$ are 2.05 M and 0.55 M, respectively. If the K_{eq} is 1.65, what is the equilibrium $[PBr_3]$?
8. The following reaction is at equilibrium:

   $CO + Cl_2 ? CoCl_2$

   The equilibrium [CO] and $[Cl_2]$ are 0.088 M and 0.103 M, respectively. If the K_{eq} is 0.225, what is the equilibrium $[COCl_2]$?
9. The following reaction is at equilibrium:

   $CH_4 + 2Cl_2 ? CH_2Cl_2 + 2HCl$

   If $[CH_4]$ is 0.250 M, $[Cl_2]$ is 0.150 M, and $[CH_2Cl_2]$ is 0.175 M at equilibrium, what is [HCl] at equilibrium if the K_{eq} is 2.30?
10. The following reaction is at equilibrium:

    $4HBr + O_2 ? 2H_2O + 2Br_2$

    If [HBr] is 0.100 M, $[O_2]$ is 0.250 M, and $[H_2O]$ is 0.0500 M at equilibrium, what is $[Br_2]$ at equilibrium if the K_{eq} is 0.770?
11. Write the K_P expression for the following gas-phase reaction:

    $4NO_2(g) + O_2(g) ? 2N_2O_5(g)$
12. Write the K_P expression for the following gas-phase reaction:

    $ClO(g) + O_3(g) ? ClO_2(g) + O_2(g)$
13. What is the equilibrium partial pressure of $COBr_2$ if the equilibrium partial pressures of CO and Br_2 are 0.666 atm and 0.235 atm and the K_P for this equilibrium is 4.08?

    $CO(g) + Br_2(g) ? COBr_2(g)$
14. What is the equilibrium partial pressure of O_3 if the equilibrium partial pressure of O_2 is 0.0044 atm and K_P for this equilibrium is 0.00755?

    $3O_2(g) ? 2O_3(g)$
15. Calculate the K_P for this reaction at 298 K if the $K_{eq} = 1.76 \times 10^{-3}$.

    $3O_2(g) ? 2O_3(g)$
16. Calculate the K_P for this reaction at 310 K if the $K_{eq} = 6.22 \times 10^{3}$.

    $4NO_2(g) + O_2(g) ? 2N_2O_5(g)$
17. Calculate the K_{eq} for this reaction if the $K_P = 5.205 \times 10^{-3}$ at 660°C.

    $CO(g)+ F_2(g) ? COF_2(g)$
18. Calculate the K_{eq} for this reaction if the $K_P = 78.3$ at 100°C.

    $4HCl(g) + O_2(g) ? 2H_2O(g) + 2Cl_2(g)$
19. Write the correct K_{eq} expression for this reaction.

    $NaOH(aq) + HCl(aq) ? NaCl(aq) + H_2O(\ell)$
20. Write the correct K_{eq} expression for this reaction.

    $AgNO_3(aq) + NaCl(aq) ? AgCl(s) + NaNO_3(aq)$
21. Write the correct K_P expression for this reaction.

    $CaCO_3(s) ? CaO(s) + CO_2(g)$
22. Write the correct K_P expression for this reaction.

    $C_2H_2(g) + 2I_2(s) ? C_2H_2I_4(g)$

ANSWERS

1. the relationship between the concentrations of reactants and products of a chemical reaction at equilibrium
3. a. $K_{eq} = \frac{[HCl]^2}{[H_2][Cl_2]}$

   b. $K_{eq} = \frac{[N_2O_3]}{[NO][NO_2]}$
5. a. $K_P = \frac{P^2_{H_2O}}{P^2_{H_2}P_{O_2}}$

   b. $K_P = \frac{P^2_{H_2O}P_{O_2}}{P^2_{H_2O_2}}$
7. 0.163 M
9. 0.272 M
11. $K_P = \frac{P^2_{N_2O_5}}{P^4_{NO_2}P_{O_2}}$
13. 0.639 atm
15. 7.20×10^{-5}
17. $K_{eq} = 3.98 \times 10^{-1}$
19. $K_{eq} = \frac{[NaCl]}{[NaOH][HCl]}$
21. $K_P = P_{CO_2}$

3. SHIFTING EQUILIBRIA: LE CHATELIER'S PRINCIPLE

LEARNING OBJECTIVES

1. **Define *Le Chatelier's principle*.**
2. **Predict the direction of shift for an equilibrium under stress.**

Once equilibrium is established, the reaction is over, right? Not exactly. An experimenter has some ability to affect the equilibrium.

Chemical equilibria can be shifted by changing the conditions that the system experiences. We say that we "stress" the equilibrium. When we stress the equilibrium, the chemical reaction is no longer at equilibrium, and the reaction starts to move back toward equilibrium in such a way as to decrease the stress. The formal statement is called **Le Chatelier's principle**: If an equilibrium is stressed, then the reaction shifts to reduce the stress.

Le Chatelier's principle

If an equilibrium is stressed, then the reaction shifts to reduce the stress.

There are several ways to stress an equilibrium. One way is to add or remove a product or a reactant in a chemical reaction at equilibrium. When additional reactant is added, the equilibrium shifts to reduce this stress: it makes more product. When additional product is added, the equilibrium shifts to reactants to reduce the stress. If reactant or product is removed, the equilibrium shifts to make more reactant or product, respectively, to make up for the loss.

EXAMPLE 6

Given this reaction at equilibrium:

$$N_2 + 3H_2 \ ? \ 2NH_3$$

In which direction—toward reactants or toward products—does the reaction shift if the equilibrium is stressed by each change?

1. H_2 is added.
2. NH_3 is added.
3. NH_3 is removed.

Solution

1. If H_2 is added, there is now more reactant, so the reaction will shift toward products to reduce the added H_2.
2. If NH_3 is added, there is now more product, so the reaction will shift toward reactants to reduce the added NH_3.
3. If NH_3 is removed, there is now less product, so the reaction will shift toward products to replace the product removed.

Test Yourself

Given this reaction at equilibrium:

$$CO(g) + Br_2(g) \ ? \ COBr_2(g)$$

In which direction—toward reactants or toward products—does the reaction shift if the equilibrium is stressed by each change?

1. Br_2 is removed.
2. $COBr_2$ is added.

Answers

1. toward reactants
2. toward reactants

It is worth noting that when reactants or products are added or removed, *the value of the* K_{eq} *does not change*. The chemical reaction simply shifts, in a predictable fashion, to reestablish concentrations so that the K_{eq} expression reverts to the correct value.

How does an equilibrium react to a change in pressure? Pressure changes do not markedly affect the solid or liquid phases. However, pressure strongly impacts the gas phase. Le Chatelier's principle implies that a pressure increase shifts an equilibrium to the side of the reaction with the fewer number of moles of gas, while a pressure decrease shifts an equilibrium to the side of the reaction with the greater number of moles of gas. If the number of moles of gas is the same on both sides of the reaction, pressure has no effect.

EXAMPLE 7

What is the effect on this equilibrium if pressure is increased?

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

Solution

According to Le Chatelier's principle, if pressure is increased, then the equilibrium shifts to the side with the fewer number of moles of gas. This particular reaction shows a total of 4 mol of gas as reactants and 2 mol of gas as products, so the reaction shifts toward the products side.

Test Yourself

What is the effect on this equilibrium if pressure is decreased?

$$3O_2(g) \rightleftharpoons 2O_3(g)$$

Answer

Reaction shifts toward reactants.

What is the effect of temperature changes on an equilibrium? It depends on whether the reaction is endothermic or exothermic. Recall that *endothermic* means that energy is absorbed by a chemical reaction, while *exothermic* means that energy is given off by the reaction. As such, energy can be thought of as a reactant or a product, respectively, of a reaction:

$$\text{endothermic: energy} + \text{reactants} \rightarrow \text{products}$$

$$\text{exothermic: reactants} \rightarrow \text{products} + \text{energy}$$

Because temperature is a measure of the energy of the system, increasing temperature can be thought of as adding energy. The reaction will react as if a reactant or a product is being added and will act accordingly by shifting to the other side. For example, if the temperature is increased for an endothermic reaction, essentially a reactant is being added, so the equilibrium shifts toward products. Decreasing the temperature is equivalent to decreasing a reactant (for endothermic reactions) or a product (for exothermic reactions), and the equilibrium shifts accordingly.

EXAMPLE 8

Predict the effect of increasing the temperature on this equilibrium.

$$PCl_3 + Cl_2 \rightleftharpoons PCl_5 + 60\ \text{kJ}$$

Solution

Because energy is listed as a product, it is being produced, so the reaction is exothermic. If the temperature is increasing, a product is being added to the equilibrium, so the equilibrium shifts to minimize the addition of extra product: it shifts back toward reactants.

Test Yourself

Predict the effect of decreasing the temperature on this equilibrium.

$$N_2O_4 + 57\ \text{kJ} \rightleftharpoons 2NO_2$$

Answer

Equilibrium shifts toward reactants.

In the case of temperature, the value of the equilibrium has changed because the K_{eq} is dependent on temperature. That is why equilibria shift with changes in temperature.

A **catalyst** is a substance that increases the speed of a reaction. Overall, a catalyst is not a reactant and is not used up, but it still affects how fast a reaction proceeds. However, a catalyst does not affect the extent or position of a reaction at equilibrium. It helps a reaction achieve equilibrium faster.

catalyst

A substance that increases the speed of a reaction.

Chemistry Is Everywhere: Equilibria in the Garden

Hydrangeas are common flowering plants around the world. Although many hydrangeas are white, there is one common species (*Hydrangea macrophylla*) whose flowers can be either red or blue, as shown in the accompanying figure. How is it that a plant can have different colored flowers like this?

Garden Equilibria

This species of hydrangea has flowers that can be either red or blue. Why the color difference?

© *Thinkstock*

Interestingly, the color of the flowers is due to the acidity of the soil that the hydrangea is planted in. An astute gardener can adjust the pH of the soil and actually change the color of the flowers. However, it is not the H^+ or OH^- ions that affect the color of the flowers. Rather, it is the presence of aluminum that causes the color change.

The solubility of aluminum in soil—and thus the ability of plants to absorb it—is dependent on the acidity of the soil. If the soil is relatively acidic, the aluminum is more soluble, and plants can absorb it more easily. Under these conditions, hydrangea flowers are blue as Al ions interact with anthocyanin pigments in the plant. In more basic soils, aluminum is less soluble, and under these conditions the hydrangea flowers are red. Gardeners who change the pH of their soils to change the color of their hydrangea flowers are therefore employing Le Chatelier's principle: the amount of acid in the soil changes the equilibrium of aluminum solubility, which in turn affects the color of the flowers.

KEY TAKEAWAYS

- Le Chatelier's principle addresses how an equilibrium shifts when the conditions of an equilibrium are changed.
- The direction of shift can be predicted for changes in concentrations, temperature, or pressure.
- Catalysts do not affect the position of an equilibrium; they help reactions achieve equilibrium faster.

EXERCISES

1. Define *Le Chatelier's principle.*
2. What is meant by a stress? What are some of the ways an equilibrium can be stressed?
3. Given this equilibrium, predict the direction of shift for each stress.

$$H_2(g) + I_2(s) + 53\text{ kJ} \ ?\ 2HI(g)$$

   a. decreased temperature
   b. increased pressure
   c. removal of HI

4. Given this equilibrium, predict the direction of shift for each stress.

   $H_2(g) + F_2(g)\ ?\ 2HF(g) + 546\text{ kJ}$

   a. increased temperature
   b. addition of H_2
   c. decreased pressure
5. Given this equilibrium, predict the direction of shift for each stress.

   $2SO_2(g) + O_2(g)\ ?\ 2SO_3(g) + 196\text{ kJ}$

   a. removal of SO_3
   b. addition of O_2
   c. decreased temperature
6. Given this equilibrium, predict the direction of shift for each stress listed.

   $CO_2(g) + C(s) + 171\text{ kJ}\ ?\ 2CO(g)$

   a. addition of CO
   b. increased pressure
   c. addition of a catalyst
7. The synthesis of NH_3 uses this chemical reaction.

   $N_2(g) + 3H_2(g)\ ?\ 2NH_3(g) + 92\text{ kJ}$

   Identify three stresses that can be imposed on the equilibrium to maximize the amount of NH_3.
8. The synthesis of $CaCO_3$ uses this chemical reaction.

   $CaO(s) + CO_2(g)\ ?\ CaCO_3(s) + 180\text{ kJ}$

   Identify three stresses that can be imposed on the equilibrium to maximize the amount of $CaCO_3$.

ANSWERS

1. When an equilibrium is stressed, the equilibrium shifts to minimize that stress.
3. a. toward reactants
   b. toward reactants
   c. toward products
5. a. toward products
   b. toward products
   c. toward products
7. increased pressure, decreased temperature, removal of NH_3

4. CALCULATING EQUILIBRIUM CONSTANT VALUES

LEARNING OBJECTIVE

1. **Calculate equilibrium concentrations from the values of the initial amounts and the K_{eq}.**

There are some circumstances in which, given some initial amounts and the K_{eq}, you will have to determine the concentrations of all species when equilibrium is achieved. Such calculations are not difficult to do, especially if a consistent approach is applied. We will consider such an approach here.

Suppose we have this simple equilibrium. Its associated K_{eq} is 4.0, and the initial concentration of each reactant is 1.0 M:

$$\begin{array}{lclcl} H_2(g) & + & Cl_2(g) & ? & 2HCl(g) \qquad\qquad K_{eq} = 4.0 \\ 1.0\text{ M} & & 1.0\text{ M} & & \end{array}$$

Because we have concentrations for the reactants but not the products, we presume that the reaction will proceed in the forward direction to make products. But by how much will it proceed? We don't know, so let us assign it a variable. Let us assume that x M H_2 reacts as the reaction goes to equilibrium. This means that at equilibrium, we have $(1.0 – x)$ M H_2 left over.

According to the balanced chemical equation, H_2 and Cl_2 react in a 1:1 ratio. How do we know that? The coefficients of these two species in the balanced chemical equation are 1 (unwritten, of course). This means that if x M H_2 reacts, x M Cl_2 reacts as well. If we start with 1.0 M Cl_2 at the beginning and we react x M, we have $(1.0 - x)$ M Cl_2 left at equilibrium.

How much HCl is made? We start with zero, but we also see that 2 mol of HCl are made for every mole of H_2 (or Cl_2) that reacts (from the coefficients in the balanced chemical equation), so if we lose x M H_2, we gain $2x$ M HCl. So now we know the equilibrium concentrations of our species:

$$\begin{array}{ccccccc} H_2(g) & + & Cl_2(g) & ? & 2HCl(g) & & K_{eq} = 4.0 \\ (1.0 - x)\text{ M} & & (1.0 - x)\text{ M} & & 2x\text{ M} & & \end{array}$$

We can substitute these concentrations into the K_{eq} expression for this reaction and combine it with the known value of K_{eq}:

$$K_{eq} = \frac{[HCl]^2}{[H_2][Cl_2]} = \frac{(2x)^2}{(1-x)(1-x)} = 4.0$$

This is an equation in one variable, so we should be able to solve for the unknown value. This expression may look formidable, but first we can simplify the denominator and write it as a perfect square as well:

$$\frac{(2x)^2}{(1-x)^2} = 4.0$$

The fraction is a perfect square, as is the 4.0 on the right. So we can take the square root of both sides:

$$\frac{2x}{1-x} = 2.0$$

Now we rearrange and solve (be sure you can follow each step):

$$2x = 2.0 - 2.0x$$

$$4x = 2.0$$

$$x = 0.50$$

Now we have to remind ourselves what x is—the amount of H_2 and Cl_2 that reacted—and $2x$ is the equilibrium [HCl]. To determine the equilibrium concentrations, we need to go back and evaluate the expressions $1 - x$ and $2x$ to get the equilibrium concentrations of our species:

$$1.0 - x = 1.0 - 0.50 = 0.50\text{ M} = [H_2] = [Cl_2]$$

$$2x = 2(0.50) = 1.0\text{ M} = [HCl]$$

The units are assumed to be molarity. To check, we simply substitute these concentrations and verify that we get the numerical value of the K_{eq}, in this case 4.0:

$$\frac{(1.0)^2}{(0.50)(0.50)} = 4.0$$

We formalize this process by introducing the ICE chart, where ICE stands for initial, change, and equilibrium. The initial values go in the first row of the chart. The change values, usually algebraic expressions because we do not yet know their exact numerical values, go in the next row. However, the change values *must* be in the proper stoichiometric ratio as indicated by the balanced chemical equation. Finally, the equilibrium expressions in the last row are a combination of the initial value and the change value for each species. The expressions in the equilibrium row are substituted into the K_{eq} expression, which yields an algebraic equation that we try to solve.

The ICE chart for the above example would look like this:

	$H_2(g)$	+	$Cl_2(g)$	?	$2HCl(g)$	$K_{eq} = 4.0$
I	1.0		1.0		0	
C	$-x$		$-x$		$+2x$	
E	$1.0 - x$		$1.0 - x$		$+2x$	

Substituting the last row into the expression for the K_{eq} yields

$$K_{eq} = \frac{[HCl]^2}{[H_2][Cl_2]} = \frac{(2x)^2}{(1-x)(1-x)} = 4.0$$

which, of course, is the same expression we have already solved and yields the same answers for the equilibrium concentrations. The ICE chart is a more formalized way to do these types of problems. The + sign is included explicitly in the change row of the ICE chart to avoid any confusion.

Sometimes when an ICE chart is set up and the K_{eq} expression is constructed, a more complex algebraic equation will result. One of the more common equations has an x^2 term in it and is called a *quadratic equation*. There will be two values possible for the unknown x, and for a quadratic equation with the general formula $ax^2 + bx + c = 0$ (where a, b, and c are the *coefficients* of the quadratic equation), the two possible values are as follows:

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

One value of x is the + sign used in the numerator, and the other value of x is the − sign used in the numerator. In this case, one value of x typically makes no sense as an answer and can be discarded as physically impossible, leaving only one possible value and the resulting set of concentrations. Example 9 illustrates this.

EXAMPLE 9

Set up an ICE chart and solve for the equilibrium concentrations in this chemical reaction.

$$\begin{array}{cccccc} COI_2(g) & ? & CO(g) & + & I_2(g) & K_{eq} = 0.00088 \\ 0.55\ M & & 0 & & 0 & \end{array}$$

Solution

The ICE chart is set up like this. First, the initial values:

	COI2(g)	?	CO(g)	+	I2(g)
I	0.55		0		0
C					
E					

Some of the COI_2 will be lost, but how much? We don't know, so we represent it by the variable x. So x M COI_2 will be lost, and for each COI_2 that is lost, x M CO and x M I_2 will be produced. These expressions go into the change row:

	COI2(g)	?	CO(g)	+	I2(g)
I	0.55		0		0
C	$-x$		$+x$		$+x$
E					

At equilibrium, the resulting concentrations will be a combination of the initial amount and the changes:

	COI2(g)	?	CO(g)	+	I2(g)
I	0.55		0		0
C	$-x$		$+x$		$+x$
E	$0.55 - x$		$+x$		$+x$

The expressions in the equilibrium row go into the K_{eq} expression:

$$K_{eq} = \frac{[CO][I_2]}{[COI_2]} = 0.00088 = \frac{(x)(x)}{(0.55 - x)}$$

We rearrange this into a quadratic equation that equals 0:

$$0.000484 - 0.00088x = x^2$$

$$x^2 + 0.00088x - 0.000484 = 0$$

Now we use the quadratic equation to solve for the two possible values of x:

$$x = \frac{-0.00088 \pm \sqrt{(0.00088)^2 - 4(1)(-0.000484)}}{2(1)}$$

Evaluate for both signs in the numerator—first the + sign and then the – sign:

$$x = 0.0216 \text{ or } x = -0.0224$$

Because x is the final concentration of both CO and I_2, it cannot be negative, so we discount the second numerical answer as impossible. Thus $x = 0.0216$.

Going back to determine the final concentrations using the expressions in the E row of our ICE chart, we have

$$[COI_2] = 0.55 - x = 0.55 - 0.0216 = 0.53 \text{ M}$$

$$[CO] = x = 0.0216 \text{ M}$$

$$[I_2] = x = 0.0216 \text{ M}$$

You can verify that these numbers are correct by substituting them into the K_{eq} expression and evaluating and comparing to the known K_{eq} value.

Test Yourself

Set up an ICE chart and solve for the equilibrium concentrations in this chemical reaction.

$$\begin{array}{ccccccc} N_2H_2(g) & ? & N_2(g) & + & H_2(g) & & K_{eq} = 0.052 \\ 0.075\text{ M} & & 0 & & 0 & & \end{array}$$

Answer

The completed ICE chart is as follows:

	$N_2H_2(g)$	?	$N_2(g)$	+	$H_2(g)$
I	0.075		0		0
C	$-x$		$+x$		$+x$
E	$0.075 - x$		$+x$		$+x$

Solving for x gives the equilibrium concentrations as $[N_2H_2] = 0.033$ M; $[N_2] = 0.042$ M; and $[H_2] = 0.042$ M

KEY TAKEAWAY

- An ICE chart is a convenient way to determine equilibrium concentrations from starting amounts.

EXERCISES

1. Describe the three parts of an ICE chart.
2. What is the relationship between the equilibrium row in an ICE chart and the other two rows?
3. Set up (but do not solve) an ICE chart for this reaction, given the initial conditions.

$$\begin{array}{ccc} 3O_2(g) & ? & 2O_3(g) \\ 0.075\text{ M} & & \end{array}$$

4. Set up (but do not solve) an ICE chart for this reaction, given the initial conditions.

$$\begin{array}{ccccccc} CH_4(g) & + & 2O_2(g) & ? & CO_2(g) & + & 2H_2O(g) \\ 0.750\text{ M} & & 0.450\text{ M} & & & & \end{array}$$

5. Given that pure solids and liquids do not appear in K_{eq} expressions, set up the ICE chart for this reaction, given the initial conditions.

$$\begin{array}{ccccccc} CH_4(g) & + & 2O_2(g) & ? & CO_2(g) & + & 2H_2O(\ell) \\ 0.0060\text{ M} & & 0.055\text{ M} & & & & \end{array}$$

6. Given that pure solids and liquids do not appear in K_{eq} expressions, set up the ICE chart for this reaction, given the initial conditions.

$$\begin{array}{ccccccc} N_2H_4(\ell) & + & O_2(g) & ? & N_2(g) & + & 2H_2O(\ell) \\ 2.33\text{ M} & & 1.09\text{ M} & & & & \end{array}$$

7. Determine the equilibrium concentrations for this chemical reaction with the given K_{eq}.

$HCN(g)$? $HNC(g)$ $K_{eq} = 4.50$
2.00 M

8. Determine the equilibrium concentrations for this chemical reaction with the given K_{eq}.

$IF_3(g) + F_2(g)$? $IF_5(g)$ $K_{eq} = 7.59$
1.0 M 0.50 M

9. Determine the equilibrium concentrations for this chemical reaction with the given K_{eq}.

$N_2O_3(g)$? $NO(g) + NO_2(g)$ $K_{eq} = 2.50$
0.0663 M

10. Determine the equilibrium concentrations for this chemical reaction with the given K_{eq}.

$CO(g) + H_2O(g)$? $CO_2(g) + H_2(g)$ $K_{eq} = 16.0$
0.750 M 0.750 M

11. Determine the equilibrium concentrations for this chemical reaction with the given K_{eq}.

$H_2S(g)$? $H_2(g) + S(s)$ $K_{eq} = 0.055$
0.882 M

12. Determine the equilibrium concentrations for this chemical reaction with the given K_{eq}.

$2AgCl(s) + F_2(g)$? $2AgF(s) + Cl_2(g)$ $K_{eq} = 1.2 \times 10^2$
1.99M

ANSWERS

1. I = initial concentrations; C = change in concentrations; E = equilibrium concentrations

3.

	$3O_2$	?	$2O_3$
I	0.075		0
C	$-3x$		$+2x$
E	$0.075 - 3x$		$+2x$

5.

	CH_4	+	$2O_2$	?	CO_2	+	$2H_2O$
I	0.0060		0.055		0		0
C	$-x$		$-2x$		$+x$		—
E	$0.0060 - x$		$0.055 - 2x$		$+x$		—

7. [HCN] = 0.364 M; [HNC] = 1.64 M
9. [N_2O_3] = 0.0017 M; [NO] = [NO_2] = 0.0646 M
11. [H_2S] = 0.836 M; [H_2] = 0.046 M

5. SOME SPECIAL TYPES OF EQUILIBRIA

LEARNING OBJECTIVE

1. **Identify several special chemical equilibria and construct their K_a expressions.**

In one sense, all chemical equilibria are treated the same. However, there are several classes of reactions that are noteworthy because of either the identities of the reactants and products or the form of the K_{eq} expression.

5.1 Weak Acids and Bases

In Chapter 12, we noted how some acids and bases are strong and some are weak. If an acid or base is strong, it is ionized 100% in H_2O. HCl(aq) is an example of a strong acid:

$$\text{HCl(aq)} \xrightarrow{100\%} \text{H}^+\text{(aq)} + \text{Cl}^-\text{(aq)}$$

However, if an acid or base is weak, it may dissolve in H_2O but does not ionize completely. This means that there is an equilibrium between the unionized acid or base and the ionized form. $HC_2H_3O_2$ is an example of a weak acid:

$$\text{HC}_2\text{H}_3\text{O}_2\text{(aq)} \ ?\ \text{H}^+\text{(aq)} + \text{C}_2\text{H}_3\text{O}_2{}^-\text{(aq)}$$

$HC_2H_3O_2$ is soluble in H_2O (in fact, it is the acid in vinegar), so the reactant concentration will appear in the equilibrium constant expression. But not all the molecules separate into ions. This is the case for all weak acids and bases.

An **acid dissociation constant**, K_a, is the equilibrium constant for the dissociation of a weak acid into ions. Note the *a* subscript on the *K*; it implies that the substance is acting as an acid. The larger K_a is, the stronger the acid is. Table 13.1 lists several acid dissociation constants. Keep in mind that they are just equilibrium constants.

acid dissociation constant

The equilibrium constant for the dissociation of a weak acid into ions.

TABLE 13.1 Acid Dissociation Constants for Some Weak Acids

Acid	K_a
$HC_2H_3O_2$	1.8×10^{-5}
$HClO_2$	1.1×10^{-2}
$H_2PO_4^-$	6.2×10^{-8}
HCN	6.2×10^{-10}
HF	6.3×10^{-4}
HNO_2	5.6×10^{-4}
H_3PO_4	7.5×10^{-3}

Note also that the acid dissociation constant refers to *one* H^+ ion coming off the initial reactant. Thus the acid dissociation constant for H_3PO_4 refers to this equilibrium:

$$\text{H}_3\text{PO}_4\text{(aq)} \ ?\ \text{H}^+\text{(aq)} + \text{H}_2\text{PO}_4{}^-\text{(aq)} \quad K_a = 7.5 \times 10^{-3}$$

The $H_2PO_4^-$ ion, called the dihydrogen phosphate ion, is also a weak acid with its own acid dissociation constant:

$$\text{H}_2\text{PO}_4{}^-\text{(aq)} \ ?\ \text{H}^+\text{(aq)} + \text{HPO}_4{}^{2-}\text{(aq)} \quad K_a = 6.2 \times 10^{-8}$$

Thus for so-called *polyprotic* acids, each H^+ ion comes off in sequence, and each H^+ ion that ionizes does so with its own characteristic K_a.

EXAMPLE 10

Write the equilibrium equation and the K_a expression for HSO_4^- acting as a weak acid.

Solution

HSO_4^- acts as a weak acid by separating into an H^+ ion and an SO_4^{2-} ion:

$$HSO_4^-(aq) \ ? \ H^+(aq) + SO_4^{2-}(aq)$$

The K_a is written just like any other equilibrium constant, in terms of the concentrations of products divided by concentrations of reactants:

$$K_a = \frac{[H^+][SO_4^{2-}]}{[HSO_4^-]}$$

Test Yourself

Write the equilibrium equation and the K_a expression for HPO_4^{2-} acting as a weak acid.

Answer

$$HPO_4^{2-}(aq) \ ? \ H^+(aq) + PO_4^{3-}(aq) \qquad K_a = \frac{[H^+][PO_4^{3-}]}{[HPO_4^{2-}]}$$

The K_a is used in equilibrium constant problems just like other equilibrium constants are. However, in some cases, we can simplify the mathematics if the numerical value of the K_a is small, much smaller than the concentration of the acid itself. Example 11 illustrates this.

EXAMPLE 11

What is the pH of a 1.00 M solution of $HC_2H_3O_2$? The K_a of $HC_2H_3O_2$ is 1.8×10^{-5}.

Solution

This is a two-part problem. We need to determine $[H^+]$ and then use the definition of pH to determine the pH of the solution. For the first part, we can use an ICE chart:

	$HC_2H_3O_2(aq)$	?	$H^+(g)$	+	$C_2H_3O_2^-(g)$
I	1.00		0		0
C	$-x$		$+x$		$+x$
E	$1.00 - x$		$+x$		$+x$

We now construct the K_a expression, substituting the concentrations from the equilibrium row in the ICE chart:

$$K_a = \frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} = \frac{(x)(x)}{(1.00 - x)} = 1.8 \times 10^{-5}$$

Here is where a useful approximation comes in: at 1.8×10^{-5}, $HC_2H_3O_2$ will not ionize very much, so we expect that the value of x will be small. It should be so small that in the denominator of the fraction, the term $(1.00 - x)$ will likely be very close to 1.00. As such, we would introduce very little error if we simply neglect the x in that term, making it equal to 1.00:

$$(1.00 - x) \approx 1.00 \text{ for small values of } x$$

This simplifies the mathematical expression we need to solve:

$$\frac{(x)(x)}{1.00} = 1.8 \times 10^{-5}$$

This is much easier to solve than a more complete quadratic equation. The new equation to solve becomes

$$x^2 = 1.8 \times 10^{-5}$$

Taking the square root of both sides,

$$x = 4.2 \times 10^{-3}$$

Because x is the equilibrium concentrations of H^+ and $C_2H_3O_2^-$, we thus have

$$[H^+] = 4.2 \times 10^{-3} \text{ M}$$

Notice that we are justified by neglecting the x in the denominator; it truly is small compared to 1.00. Now we can determine the pH of the solution:

$$\text{pH} = -\log[H^+] = -\log(4.2 \times 10^{-3}) = 2.38$$

Test Yourself

What is the pH of a 0.500 M solution of HCN? The K_a of HCN is 6.2×10^{-10}.

Answer

4.75

Weak bases also have dissociation constants, labeled K_b (the *b* subscript stands for base). However, values of K_b are rarely tabulated because there is a simple relationship between the K_b of a base and the K_a of its conjugate acid:

$$K_a \times K_b = 1.0 \times 10^{-14}$$

Thus it is simple to calculate the K_b of a base from the K_a of its conjugate acid.

EXAMPLE 12

What is the value of K_b for $C_2H_3O_2^-$, which can accept a proton and act as a base?

Solution

To determine the K_b for $C_2H_3O_2^-$, we need to know the K_a of its conjugate acid. The conjugate acid of $C_2H_3O_2^-$ is $HC_2H_3O_2$. The K_a for $HC_2H_3O_2$ is in Table 13.1 and is 1.8×10^{-5}. Using the mathematical relationship between K_a and K_b:

$$(1.8 \times 10^{-5})K_b = 1.0 \times 10^{-14}$$

Solving,

$$K_b = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

Test Yourself

What is the value of K_b for PO_4^{3-}, which can accept a proton and act as a base? The K_a for HPO_4^{2-} is 2.2×10^{-13}.

Answer

4.5×10^{-2}

5.2 Autoionization of Water

In Chapter 12, we introduced the autoionization of water—the idea that water can act as a proton donor and proton acceptor simultaneously. Because water is not a strong acid (Table 12.2), it must be a weak acid, which means that its behavior as an acid must be described as an equilibrium. That equilibrium is as follows:

$$H_2O(\ell) + H_2O(\ell) \;?\; H_3O^+(aq) + OH^-(aq)$$

The equilibrium constant includes $[H_3O^+]$ and $[OH^-]$ but not $[H_2O(\ell)]$ because it is a pure liquid. Hence the expression *does not have any terms in its denominator*:

$$K = [H_3O^+][OH^-] \equiv K_w = 1.0 \times 10^{-14}$$

This is the same K_w that was introduced in Chapter 12 and the same 1.0×10^{-14} that appears in the relationship between the K_a and the K_b of a conjugate acid-base pair. In fact, we can rewrite this relationship as follows:

$$K_a \times K_b = K_w$$

5.3 Insoluble Compounds

In Chapter 4, Section 2, on chemical reactions, the concept of soluble and insoluble compounds was introduced. Solubility rules were presented that allow a person to predict whether certain simple ionic compounds will or will not dissolve.

Describing a substance as soluble or insoluble is a bit misleading because virtually all substances are soluble; they are just soluble to different extents. In particular for ionic compounds, what we typically describe as an *insoluble* compound can actually be ever so slightly soluble; an equilibrium is quickly established between the solid compound and the ions that do form in solution. Thus the hypothetical compound MX does in fact dissolve but only very slightly. That means we can write an equilibrium for it:

$$MX(s) \;?\; M^+(aq) + X^-(aq)$$

The equilibrium constant for a compound normally considered insoluble is called a **solubility product constant** and is labeled K_{sp} (with the subscript *sp*, meaning "solubility product"). Because the reactant is a solid, its concentration does not appear in the K_{sp} expression, so like K_w, expressions for K_{sp} do not have denominators. For example, the chemical equation and the expression for the K_{sp} for AgCl, normally considered insoluble, are as follows:

solubility product constant

The equilibrium constant for a compound normally considered insoluble.

$$\mathrm{AgCl(s)}\ ?\ \mathrm{Ag^+(aq)} + \mathrm{Cl^-(aq)} \quad K_{sp} = [\mathrm{Ag^+}][\mathrm{Cl^-}]$$

Table 13.2 lists some values of the K_{sp} for slightly soluble ionic compounds.

TABLE 13.2 Solubility Product Constants for Slightly Soluble Ionic Compounds

Compound	K_{sp}
$BaSO_4$	1.1×10^{-10}
$Ca(OH)_2$	5.0×10^{-6}
$Ca_3(PO_4)_2$	2.1×10^{-33}
$Mg(OH)_2$	5.6×10^{-12}
HgI_2	2.9×10^{-29}
AgCl	1.8×10^{-10}
AgI	8.5×10^{-17}
Ag_2SO_4	1.5×10^{-5}

EXAMPLE 13

Write the K_{sp} expression for $Ca_3(PO_4)_2$.

Solution

Recall that when an ionic compound dissolves, it separates into its individual ions. For $Ca_3(PO_4)_2$, the ionization reaction is as follows:

$$\mathrm{Ca_3(PO_4)_2(s)}\ ?\ \mathrm{3Ca^{2+}(aq)} + \mathrm{2PO_4{}^{3-}(aq)}$$

Hence the K_{sp} expression is

$$K_{sp} = [\mathrm{Ca^{2+}}]^3[\mathrm{PO_4{}^{3-}}]^2$$

Test Yourself

Write the K_{sp} expression Ag_2SO_4.

Answer

$K_{sp} = [\mathrm{Ag^+}]^2[\mathrm{SO_4{}^{2-}}]$

Equilibrium problems involving the K_{sp} can also be done, and they are usually more straightforward than other equilibrium problems because there is no denominator in the K_{sp} expression. Care must be taken, however, in completing the ICE chart and evaluating exponential expressions.

EXAMPLE 14

What are $[Ag^+]$ and $[Cl^-]$ in a saturated solution of AgCl? The K_{sp} of AgCl is 1.8×10^{-10}.

Solution

The chemical equation for the dissolving of AgCl is

$$AgCl(s) \; ? \; Ag^+(aq) + Cl^-(aq)$$

The K_{sp} expression is as follows:

$$K_{sp} = [Ag^+][Cl^-]$$

So the ICE chart for the equilibrium is as follows:

	AgCl(s)	?	$Ag^+(aq)$	+	$Cl^-(aq)$
I			0		0
C	$-x$		$+x$		$+x$
E			$+x$		$+x$

Notice that we have little in the column under AgCl except the stoichiometry of the change; we do not need to know its initial or equilibrium concentrations because its concentration does not appear in the K_{sp} expression. Substituting the equilibrium values into the expression:

$$(x)(x) = 1.8 \times 10^{-10}$$

Solving,

$$x^2 = 1.8 \times 10^{-10}$$

$$x = 1.3 \times 10^{-5}$$

Thus $[Ag^+]$ and $[Cl^-]$ are both 1.3×10^{-5} M.

Test Yourself

What are $[Ba^{2+}]$ and $[SO_4{}^{2-}]$ in a saturated solution of $BaSO_4$? The K_{sp} of $BaSO_4$ is 1.1×10^{-10}.

Answer

1.0×10^{-5} M

EXAMPLE 15

What are [Ca^{2+}] and [PO_4^{3-}] in a saturated solution of $Ca_3(PO_4)_2$? The K_{sp} of $Ca_3(PO_4)_2$ is 2.1×10^{-33}.

Solution

This is similar to Example 14, but the ICE chart is much different because of the number of ions formed.

	$Ca_3(PO_4)_2(s)$	?	$3Ca^{2+}(aq)$	+	$2PO_4^{3-}(aq)$
I			0		0
C	$-x$		$+3x$		$+2x$
E			$+3x$		$+2x$

For every unit of $Ca_3(PO_4)_2$ that dissolves, three Ca^{2+} ions and two PO_4^{3-} ions are formed. The expression for the K_{sp} is also different:

$$K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2 = 2.1 \times 10^{-33}$$

Now when we substitute the unknown concentrations into the expression, we get

$$(3x)^3(2x)^2 = 2.1 \times 10^{-33}$$

When we raise each expression inside parentheses to the proper power, remember that the power affects everything inside the parentheses, including the number. So

$$(27x^3)(4x^2) = 2.1 \times 10^{-33}$$

Simplifying,

$$108x^5 = 2.1 \times 10^{-33}$$

Dividing both sides of the equation by 108, we get

$$x^5 = 1.9 \times 10^{-35}$$

Now we take the fifth root of both sides of the equation (be sure you know how to do this on your calculator):

$$x = 1.1 \times 10^{-7}$$

We are not done yet. We still need to determine the concentrations of the ions. According to the ICE chart, [Ca^{2+}] is $3x$, not x. So

$$[Ca^{2+}] = 3x = 3 \times 1.1 \times 10^{-7} = 3.3 \times 10^{-7}\ M$$

[PO_4^{3-}] is $2x$, so

$$[PO_4^{3-}] = 2x = 2 \times 1.1 \times 10^{-7} = 2.2 \times 10^{-7}\ M$$

Test Yourself

What are [Mg^{2+}] and [OH^-] in a saturated solution of $Mg(OH)_2$? The K_{sp} of $Mg(OH)_2$ is 5.6×10^{-12}.

Answer

[Mg^{2+}] = 1.1×10^{-4} M; [OH^-] = 2.2×10^{-4} M

Food and Drink App: Solids in Your Wine Bottle

People who drink wine from bottles (as opposed to boxes) will occasionally notice some insoluble materials in the wine, either crusting the bottle, stuck to the cork, or suspended in the liquid wine itself. The accompanying figure shows a cork encrusted with colored crystals. What are these crystals?

The red crystals on the top of the wine cork are from insoluble compounds that are not soluble in the wine.

Source: *Photo courtesy of Paul A. Hernandez, http://www.flickr.com/photos/paul_a_hernandez/2940862302/.*

One of the acids in wine is tartaric acid ($H_2C_4H_4O_6$). Like the other acids in wine (citric and malic acids, among others), tartaric acid imparts a slight tartness to the wine. Tartaric acid is rather soluble in H_2O, dissolving over 130 g of the acid in only 100 g of H_2O. However, the potassium salt of singly ionized tartaric acid, potassium hydrogen tartrate ($KHC_4H_4O_6$; also known as potassium bitartrate and better known in the kitchen as cream of tartar), has a solubility of only 6 g per 100 g of H_2O. Thus, over time, wine stored at cool temperatures will slowly precipitate potassium hydrogen tartrate. The crystals precipitate in the wine or grow on the insides of the wine bottle and, if the bottle is stored on its side, on the bottom of the cork. The color of the crystals comes from pigments in the wine; pure potassium hydrogen tartrate is clear in its crystalline form, but in powder form it is white.

The crystals are harmless to ingest; indeed, cream of tartar is used as an ingredient in cooking. However, most wine drinkers don't like to chew their wine, so if tartrate crystals are present in a wine, the wine is usually filtered or decanted to remove the crystals. Tartrate crystals are almost exclusively in red wines; white and rose wines do not have as much tartaric acid in them.

KEY TAKEAWAY

- Equilibrium constants exist for certain groups of equilibria, such as weak acids, weak bases, the autoionization of water, and slightly soluble salts.

EXERCISES

1. Explain the difference between the K_{eq} and the K_{sp}.
2. Explain the difference between the K_a and the K_b.
3. Write the balanced chemical equation that represents the equilibrium between HF(aq) as reactants and H^+(aq) and F^-(aq) as products.
4. Write the balanced chemical equation that represents the equilibrium between CaF_2(s) as reactants and Ca^{2+}(aq) and F^-(aq) as products.
5. Assuming that all species are dissolved in solution, write the K_{eq} expression for the chemical equation in Exercise 3.
6. Noting the phase labels, write the K_{sp} expression for the chemical equation in Exercise 4.
7. Determine the concentrations of all species in the ionization of 0.100 M $HClO_2$ in H_2O. The K_a for $HClO_2$ is 1.1×10^{-2}.
8. Determine the concentrations of all species in the ionization of 0.0800 M HCN in H_2O. The K_a for HCN is 6.2×10^{-10}.
9. Determine the pH of a 1.00 M solution of HNO_2. The K_a for HNO_2 is 5.6×10^{-4}.
10. Determine the pH of a 3.35 M solution of $HC_2H_3O_2$. The K_a for $HC_2H_3O_2$ is 1.8×10^{-5}.
11. Write the chemical equations and K_a expressions for the stepwise dissociation of H_3PO_4.
12. Write the chemical equations and K_a expressions for the stepwise dissociation of $H_3C_6H_5O_7$.
13. If the K_a for HNO_2 is 5.6×10^{-4}, what is the K_b for NO_2^-(aq)?
14. If the K_a for HCN is 6.2×10^{-10}, what is the K_b for CN^-(aq)?

15. What is $[OH^-]$ in a solution whose $[H^+]$ is 3.23×10^{-6} M?
16. What is $[OH^-]$ in a solution whose $[H^+]$ is 9.44×10^{-11} M?
17. What is $[H^+]$ in a solution whose $[OH^-]$ is 2.09×10^{-2} M?
18. What is $[H^+]$ in a solution whose $[OH^-]$ is 4.07×10^{-7} M?
19. Write the balanced chemical equation and the K_{sp} expression for the slight solubility of $Mg(OH)_2(s)$.
20. Write the balanced chemical equation and the K_{sp} expression for the slight solubility of $Fe_2(SO_4)_3(s)$.
21. What are $[Sr^{2+}]$ and $[SO_4{}^{2-}]$ in a saturated solution of $SrSO_4(s)$? The K_{sp} of $SrSO_4(s)$ is 3.8×10^{-4}.
22. What are $[Ba^{2+}]$ and $[F^-]$ in a saturated solution of $BaF_2(s)$? The K_{sp} of $BaF_2(s)$ is 1.8×10^{-7}.
23. What are $[Ca^{2+}]$ and $[OH^-]$ in a saturated solution of $Ca(OH)_2(s)$? The K_{sp} of $Ca(OH)_2(s)$ is 5.0×10^{-6}.
24. What are $[Pb^{2+}]$ and $[I^-]$ in a saturated solution of PbI_2? The K_{sp} for PbI_2 is 9.8×10^{-9}.

ANSWERS

1. The K_{sp} is a special type of the K_{eq} and applies to compounds that are only slightly soluble.
3. $HF(aq) \ ? \ H^+(aq) + F^-(aq)$
5. $K_{eq} = \frac{[H^+][F^-]}{[HF]}$
7. $[HClO_2] = 0.0719$ M; $[H^+] = [ClO_2{}^-] = 0.0281$ M
9. 1.63
11. $H_3PO_4(aq) \ ? \ H^+(aq) + H_2PO_4{}^-(aq);\ K_a = \frac{[H^+][H_2PO_4{}^-]}{[H_3PO_4]}$

    $H_2PO_4{}^-(aq) \ ? \ H^+(aq) + HPO_4{}^{2-}(aq);\ K_a = \frac{[H^+][HPO_4{}^{2-}]}{[H_2PO_4{}^-]}$

    $HPO_4{}^{2-}(aq) \ ? \ H^+(aq) + PO_4{}^{3-}(aq);\ K_a = \frac{[H^+][PO_4{}^{3-}]}{[HPO_4{}^{2-}]}$
13. 1.8×10^{-11}
15. 3.10×10^{-9} M
17. 4.78×10^{-13} M
19. $MgOH_2(s) \ ? \ Mg^{2+}(aq) + 2OH^-(aq);\ K_{sp} = [Mg^{2+}][OH^-]^2$
21. $[Sr^{2+}] = [SO_4{}^{2-}] = 1.9 \times 10^{-2}$ M
23. $[Ca^{2+}] = 0.011$ M; $[OH^-] = 0.022$ M

6. END-OF-CHAPTER MATERIAL

ADDITIONAL EXERCISES

1. What is the relationship between the K_{sp} expressions for a chemical reaction and its reverse chemical reaction?
2. What is the relationship between the K_W value for H_2O and its reverse chemical reaction?
3. For the equilibrium

   $PCl_3(g) + Cl_2(g) \ ? \ PCl_5(g) + 60\text{ kJ}$

   list four stresses that serve to increase the amount of PCl_5.
4. For the equilibrium

   $N_2O_4 + 57\text{ kJ} \ ? \ 2NO_2$

   list four stresses that serve to increase the amount of NO_2.

5. Does a very large K_{eq} favor the reactants or the products? Explain your answer.
6. Is the K_{eq} for reactions that favor reactants large or small? Explain your answer.
7. Show that $K_a \times K_b = K_w$ by determining the expressions for these two reactions and multiplying them together.

   $HX(aq)$? $H^+(aq) + X^-(aq)$

   $X^-(aq) + H_2O(\ell)$? $HX(aq) + OH^-(aq)$

8. Is the conjugate base of a strong acid weak or strong? Explain your answer.
9. What is the solubility in moles per liter of AgCl? Use data from Table 13.2.
10. What is the solubility in moles per liter of $Ca(OH)_2$? Use data from Table 13.2.
11. Under what conditions is $K_{eq} = K_P$?
12. Under what conditions is $K_{eq} > K_P$ when the temperature is 298 K?
13. What is the pH of a saturated solution of $Mg(OH)_2$? Use data from Table 13.2.
14. What are the pH and the pOH of a saturated solution of $Fe(OH)_3$? The K_{sp} of $Fe(OH)_3$ is 2.8×10^{-39}.
15. For a salt that has the general formula MX, an ICE chart shows that the K_{sp} is equal to x^2, where x is the concentration of the cation. What is the appropriate formula for the K_{sp} of a salt that has a general formula of MX_2?
16. Referring to Exercise 15, what is the appropriate formula for the K_{sp} of a salt that has a general formula of M_2X_3 if the concentration of the cation is defined as $2x$, rather than x?
17. Consider a saturated solution of $PbBr_2(s)$. If $[Pb^{2+}]$ is 1.33×10^{-5} M, find each of the following.
    a. $[Br^-]$
    b. the K_{sp} of $PbBr_2(s)$
18. Consider a saturated solution of $Pb_3(PO_4)_2(s)$. If $[Pb^{2+}]$ is 7.34×10^{-14} M, find each of the following.
    a. $[PO_4{}^{3-}]$
    b. the K_{sp} of $Pb_3(PO_4)_2(s)$

ANSWERS

1. They are reciprocals of each other.
3. increase the pressure; decrease the temperature; add PCl_3; add Cl_2; remove PCl_5
5. favor products because the numerator of the ratio for the K_{eq} is larger than the denominator
7. $K_a \times K_b = \frac{[H^+]\cancel{[X^-]}}{\cancel{[HX]}} \times \frac{\cancel{[HX]}[OH^-]}{\cancel{[X^-]}} = [H^+][OH^-] = K_w$
9. 1.3×10^{-5} mol/L
11. $K_{eq} = K_P$ when the number of moles of gas on both sides of the reaction is the same.
13. 10.35
15. $4x^3$
17. a. 2.66×10^{-5} M
    b. 9.41×10^{-15}