**19.1 The Nature of Equilibrium**

**Lesson Objectives**

* Describe the nature of a reversible reaction.
* Define chemical equilibrium.
* Write chemical equilibrium expressions from balanced chemical equations.
* Calculate the equilibrium constant for a reaction, and perform calculations involving that constant.

**Lesson Vocabulary**

* chemical equilibrium
* equilibrium constant
* reversible reaction

**Check Your Understanding**

**Recalling Prior Knowledge**

* What is the rate of a chemical reaction?
* How is concentration usually measured?

When a reaction takes place in both the forward and reverse directions, it is said to be reversible. Reversible reactions can reach a stable state that is referred to as chemical equilibrium. In this lesson, you will learn about the nature of reversible reactions, chemical equilibrium, and how to calculate and use equilibrium constants.

**Reversible Reactions**

Up until this point, we have written the equations for chemical reactions in a way that would seem to indicate that all reactions proceed until all of the reactants have been converted into products. In reality, a great many chemical reactions do not proceed entirely to completion. A **reversible reaction** *is a reaction in which the conversion of reactants to products and the conversion of products to reactants occur simultaneously*. One example of a reversible reaction is the reaction of hydrogen gas and iodine vapor to form hydrogen iodide. The forward and reverse reactions can be written as follows.

Forward reaction: H2(*g*)+I2(*g*)→2HI(*g*)

Reverse reaction: 2HI(*g*)→H2(*g*)+I2(*g*)

In the forward reaction, hydrogen and iodine combine to form hydrogen iodide. In the reverse reaction, hydrogen iodide decomposes back into hydrogen and iodine. The two reactions can be combined into one equation by the use of a double arrow.

H2(*g*)+I2(*g*)⇌2HI(*g*)

The double arrow indicates that the reaction is reversible.

When hydrogen and iodine gases are mixed in a sealed container, they begin to react and form hydrogen iodide. At first, only the forward reaction occurs because no HI is present. As the forward reaction proceeds, it begins to slow down as the concentrations of H2 and I2 decrease. As soon as some HI has formed, it begins to decompose back into H2 and I2. The rate of the reverse reaction starts out slow because the concentration of HI is low. Gradually, the rate of the forward reaction decreases, while the rate of the reverse reaction increases. Eventually, the rate at which H2 and I2 combine to produce HI becomes equal to the rate at which HI decomposes back into H2 and I2. When the rates of the forward and reverse reactions have become equal to one another, the reaction has achieved a state of balance. **Chemical equilibrium** *is the state of a system in which the rate of the forward reaction is equal to the rate of the reverse reaction*. The **Figure** [below](https://www.ck12.org/book/CK-12-Chemistry-Intermediate/section/19.1/#x-ck12-SW50Q2gtMTktMDEtRm9yd2FyZC1SZXZlcnNlLVJlYWN0aW9ucw..) shows this reaction graphically.



As a reaction begins, only the forward reaction occurs. Over time, the forward reaction rate decreases, while the rate of the reverse reaction increases. After a certain amount of time has passed, the rates of both reactions are equal, and the reaction has reached equilibrium.

Chemical equilibrium can be attained whether the reaction begins with all reactants and no products, all products and no reactants, or some of both. Illustrated in the **Figure** [below](https://www.ck12.org/book/CK-12-Chemistry-Intermediate/section/19.1/#x-ck12-SW50Q2gtMTktMDItU3RhcnRpbmctQ29uZGl0aW9ucw..) are the changes in the concentrations of H2, I2, and HI for two different initial reaction mixtures. In the situation depicted by the graph on the left, the reaction begins with only H2 and I2 present. There is no HI initially. As the reaction proceeds toward equilibrium, the concentrations of H2 and I2 gradually decrease, while the concentration of HI gradually increases. When the curve levels out and the concentrations all become constant, equilibrium has been reached. After a system has reached equilibrium, the concentrations of all substances remain constant. In the reaction depicted by the graph on the right, the reaction begins with only HI and no H2 or I2. In this case, the concentration of HI gradually decreases, while the concentrations of H2 and I2 gradually increase until equilibrium is again reached. Notice that in both cases, the relative position of equilibrium is the same, as shown by the relative concentrations of reactants and products. The concentration of HI at equilibrium is significantly higher than the concentrations of H2 and I2. This is true whether the reaction began with all reactants or all products. The equilibrium position is a property of the particular reversible reaction and does not depend upon the initial concentrations of the reactants and products.



(A) The reaction begins with only reactants (H2 and I2) and reaches equilibrium when the concentrations of reactants and products become constant. (B) The same reaction, beginning with only product (HI). The relative concentrations of the reactants and products are the same in both cases.

**Conditions for Equilibrium and Types of Equilibrium**

It may be tempting to think that once equilibrium has been reached, the reaction stops. However, chemical equilibrium is a dynamic process. The forward and reverse reactions continue to occur even after equilibrium has been reached, but, because the rates of the two reactions are equal, there is no net change in the relative amounts of reactants and products for a reaction that is at equilibrium. The conditions and properties of a system at equilibrium are summarized below.

1. The system must be closed, meaning no substances can enter or leave the system.
2. Equilibrium is a dynamic process. Even though we don’t observe any changes, both the forward and reverse reactions are still taking place.
3. The rates of the forward and reverse reactions must be equal.
4. The amounts of reactants and products do not have to be equal. However, after equilibrium is attained, the amounts of reactants and products will remain constant.

The description of equilibrium in this chapter refers primarily to equilibrium between reactants and products in a chemical reaction. In previous chapters, we introduced the concepts of phase equilibrium and solution equilibrium. A phase equilibrium occurs when a substance is in equilibrium between two states. For example, a stoppered flask of water attains equilibrium when the rate of evaporation is equal to the rate of condensation. A solution equilibrium occurs when a solid substance is in a saturated solution. At this point, the rate of dissolution is equal to the rate of recrystallization. Although these are all different types of transformations, most of the rules regarding equilibrium apply to any situation in which a process occurs reversibly.

**The Equilibrium Constant**

Consider the hypothetical reversible reaction in which reactants A and B react to form products C and D. This equilibrium can be shown below, where the lower case letters represent the coefficients of each substance.

aA+bB⇌cC+dD

As we have established, the rates of the forward and reverse reactions are the same at equilibrium, and so the concentrations of all of the substances are constant. The **equilibrium constant (Keq)** *is the ratio of the mathematical product of the concentrations of the products to the mathematical product of the concentrations of the reactants for a reaction that is at equilibrium*. Each concentration is raised to the power of its coefficient in the balanced chemical equation. For the general reaction above, the equilibrium constant expression is written as follows:

Keq=[C]c[D]d[A]a[B]b

The concentrations of each substance, indicated by the square brackets around the formula, are measured in molarity units (mol/L).

The value of the equilibrium constant for any reaction can be determined by experiment. As detailed in the above section, the equilibrium position for a given reaction does not depend on the starting concentrations, so the equilibrium constant has the same value regardless of the initial amounts of each reaction component. It does, however, depend on the temperature of the reaction. Equilibrium is defined as a condition in which the rates of the forward and reverse reactions are equal. A change in temperature will change the rates of both the forward and reverse reactions, but not to the same extent. As a result, the equilibrium constant is altered. For any reaction in which a Keq is given, the temperature should be specified.

The general value of the equilibrium constant gives us information about whether the reactants or the products are favored at equilibrium. Since the product concentrations are in the numerator of the equilibrium expression, a Keq > 1 means that the products are favored over the reactants. A Keq < 1 means that the reactants are favored over the products.

Though it would often seem that the Keq value would have various units depending on the values of the exponents in the expression, the general rule is that any units are dropped. All Keq values will be reported as having no units.

**Sample Problem 19.1: Calculating an Equilibrium Constant**

Equilibrium occurs when nitrogen monoxide gas reacts with oxygen gas to form nitrogen dioxide gas.

2NO(*g*)+O2(*g*)⇌2NO2(*g*)

At 230°C, the equilibrium concentrations for a certain experiment are measured to be [NO] = 0.0542 M, [O2] = 0.127 M, and [NO2] = 15.5 M. Calculate the equilibrium constant at this temperature.

*Step 1: List the known values and plan the problem.*

Known

* [NO] = 0.0542 M
* [O2] = 0.127 M
* [NO2] = 15.5 M

Unknown

* Keq value

The equilibrium expression is first written according to the general form in the text. The equilibrium values are substituted into the expression, and the value is calculated.

*Step 2: Solve.*

Keq=[NO2]2[NO]2[O2]

Substituting in the concentrations at equilibrium:

Keq=(15.5)2(0.0542)2(0.127)=6.44×105

*Step 3: Think about your result.*

The equilibrium concentration of the product NO2 is significantly higher than the concentrations of the reactants NO and O2. As a result, the Keq value is much larger than 1, an indication that the product is favored at equilibrium.

***Practice Problem***

1. The Haber process for the production of ammonia results in the equilibrium represented by the reaction: N2(*g*)+3H2(*g*)⇌2NH3(*g*). At equilibrium at a certain temperature, a 5.0 L flask contains 1.25 mol N2, 0.75 mol H2, and 0.50 mol NH3. Calculate Keq for the reaction at this temperature.

The equilibrium expression only shows those substances whose concentrations are variable during the reaction. A pure solid or a pure liquid does not have a concentration that will vary during a reaction. Therefore, an equilibrium expression omits pure solids and liquids and only shows the concentrations of gases and aqueous solutions. The decomposition of mercury(II) oxide can be shown by the equation below, followed by its equilibrium expression.

2HgO(*s*)⇌2Hg(*l*)+O2(*g*)    Keq=[O2]

The stoichiometry of an equation can also be used in a calculation of an equilibrium constant. At 40°C, solid ammonium carbamate decomposes to ammonia and carbon dioxide gases.

NH4CO2NH2(*s*)⇌2NH3(*g*)+CO2(*g*)

At equilibrium, [CO2] is found to be 4.71 × 10−3 M. Can the Keq value be calculated from just that information? Because the ammonium carbamate is a solid, it is not present in the equilibrium expression.

Keq=[NH3]2[CO2]

The stoichiometry of the chemical equation indicates that, as the ammonium carbamate decomposes, 2 mol of ammonia gas is produced for every 1 mol of carbon dioxide. If we can assume that all of the ammonia and carbon dioxide present is from the decomposition of ammonium carbamate, the concentration of ammonia at any point will be twice the concentration of carbon dioxide. At equilibrium, [NH3] = 2 × (4.71 × 10−3) = 9.42 × 10−3 M. Substituting these values into the Keq expression:

Keq=(9.42×10−3)2(4.71×10−3)=4.18×10−7

**Using Equilibrium Constants**

The equilibrium constants are known for a great many reactions. Hydrogen and bromine gases combine to form hydrogen bromide gas. The equation and Keq for this reaction when it is run at 730°C are given below.

H2(*g*)+Br2(*g*)⇌2HBr(*g*)    Keq=2.18×106

A certain reaction is begun with only HBr. When the reaction mixture reaches equilibrium at 730°C, the concentration of bromine gas is measured to be 0.00243 M. What is the concentration of the H2 and the HBr at equilibrium?

Since the reaction begins with only HBr, and the mole ratio of H2 to Br2 is 1:1, the concentration of H2 at equilibrium is also 0.00243 M. The equilibrium expression can be rearranged to solve for the concentration of HBr at equilibrium.

Keq[HBr]=[HBr]2[H2][Br2]=Keq[H2][Br2]−−−−−−−−−−√=2.18×106(0.00243)(0.00243)−−−−−−−−−−−−−−−−−−−−−−−√=3.59 M

Since the value of the equilibrium constant is very high, the concentration of HBr is much greater than that of H2 and Br2 at equilibrium.

**Lesson Summary**

* A reversible reaction is one in which products are converted to reactants as well as reactants being converted to products. Equilibrium is achieved when the rate of the forward reaction is equal to the rate of the reverse reaction. Once at equilibrium, the concentrations of all substances remain constant, and no net change occurs in the system.
* An equilibrium constant can be calculated for any reaction. Once a reaction reaches equilibrium, the ratio of the mathematical product of all product concentrations to the mathematical product of all reactant concentrations, each raised to the power of its coefficient, will always be equal to its equilibrium constant at that temperature. Note that solid and liquid reaction components are not included in the calculation of the equilibrium constant, since their concentrations are not dependent on the amount present and thus do not change over the course of the reaction.
* An equilibrium constant greater than 1 indicates that the products of the reaction as written are favored. An equilibrium constant less than 1 indicates that the reactants are favored.

**Lesson Review Questions**

**Reviewing Concepts**

1. How do the amounts of reactants and products change after a reaction has reached equilibrium?
2. How does the position of equilibrium depend upon the starting concentrations of all the reactants and products?
3. What types of substances are not included in equilibrium expressions and why?
4. In general, which reaction is favored (forward, reverse, or neither) if the value of Keq at a specified temperature is
	1. equal to 1?
	2. very small?
	3. very large?

**Problems**

1. Write Keq expressions for each of the following equilibrium reactions.
	1. 3O2(*g*)⇌2O3(*g*)
	2. H3PO4(*aq*)⇌3H+(*aq*)+PO3−4(*aq*)
	3. 2NO2(*g*)+7H2(*g*)⇌2NH3(*g*)+4H2O(*l*)
	4. 2NaHCO3(*s*)⇌Na2CO3(*s*)+CO2(*g*)+H2O(*g*)
2. Oxygen reacts with hydrogen chloride to form chlorine gas and water vapor: 4HCl(*g*)+O2(*g*)⇌2Cl2(*g*)+2H2O(*g*). At a certain temperature, the equilibrium mixture consists of 0.0012 M HCl, 3.8 × 10−4 M O2, 0.058 M Cl2, and 0.058 M H2O. Calculate the value of the equilibrium constant at this temperature.
3. At equilibrium at 2500 K, [HCl] = 0.0625 M and [H2] = [Cl2] = 0.00450 M for the reaction: H2(*g*)+Cl2(*g*)⇌2HCl(*g*).
	1. Calculate the equilibrium constant for the reaction as written above.
	2. Calculate the equilibrium constant for the reaction written instead as:

2HCl(*g*)⇌H2(*g*)+Cl2(*g*). What is the relationship of the Keq values in parts a and b?

1. Consider the following reaction: H2S(*aq*)⇌H+(*aq*)+HS−(*aq*), Keq=9.5 × 10-8 at 25°C. In a certain equilibrium mixture at 25°C, [H+] = [HS−] = 2.7 × 10−4 M. Determine the concentration of H2S in this mixture.
2. Phosphorus pentachloride gas decomposes to phosphorus trichloride and chlorine: PCl5(*g*)⇌PCl3(*g*)+Cl2(*g*). In a certain reaction, 0.500 mol of PCl5 is introduced into a 5.00 L container at 250°C. When the reaction reaches equilibrium, the mixture is analyzed and found to contain 0.194 mol Cl2. Determine the value of Keq at 250°C for this reaction.
3. Nitrogen monoxide combines with chlorine at 400°C to form nitrosyl chloride by the following reaction: 2NO(*g*)+Cl2(*g*)⇌2NOCl(*g*), Keq=28.1 at 400°C. In a certain reaction, a quantity of NOCl is allowed to decompose at 400°C until equilibrium is reached. The [NO] at equilibrium is 9.40 × 10−3 M. Find the concentrations of Cl2 and of NOCl.

**Further Reading / Supplemental Links**

* The Equilibrium Constant and the Mass Action Expression, <http://www.kentchemistry.com/links/Kinetics/EquilibriumConstant.htm>
* Equilibrium Constants: Kc, <http://www.chemguide.co.uk/physical/equilibria/kc.html>

**Points to Consider**

Disruptions to a system at equilibrium can occur in the form of a change in temperature, pressure, or concentrations of one or more of the substances in the equilibrium.

* How does an equilibrium respond to a change in conditions?
* Is the value of the equilibrium constant affected by such changes?