The Equilibrium Constant

In 1864, two chemists proposed the **law of mass action**, which expresses the relative concentrations of reactants and products at equilibrium in terms of a quantity called the **equilibrium constant**.

Consider a reaction described by the general equation

$$aA + bB \Leftrightarrow cC + dD$$

In this equation, a, b, c, and d are the coefficients for substances A, B, C, and D. The **equilibrium expression** for this reaction is

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

where K_{eq} is the equilibrium constant.

When the concentrations of the reactants and products are measured at equilibrium and inserted into the equilibrium expression, the result is a constant (at a given temperature). Every reversible reaction obeys this relationship and has a specific equilibrium constant. This observation is called the **law of chemical equilibrium**.

Consider the reaction below

$$2NO_2(g) \Leftrightarrow N_2O_4(g)$$

The equilibrium expression for this reaction is

$$K_{eq} = \frac{[N_2O_4]}{[NO_2]^2}$$

The equilibrium constant must be determined experimentally. To do so, add known concentrations of the reactants and products to a sealed container and wait for it to reach equilibrium. After the reaction has reached equilibrium, the final concentration of each substance is determined.

The table below lists the data for a particular experiment.

Trial	**Initial [NO_2] (M)**	**Initial [N_2O_4] (M)**	**Equilibrium [NO_2] (M)**	**Equilibrium [N_2O_4] (M)**	K_{eq}
1	0.0200	0.0	0.0172	0.00140	4.73
2	0.0300	0.0	0.0243	0.00280	4.74
3	0.0	0.0200	0.0310	0.00452	4.70

K_{eq} is found by inserting the equilibrium concentrations (not the initial concentrations) into the equilibrium expression. For example, for the first set of data

$$K_{eq} = \frac{0.00140}{(0.0172)^2}$$
$$= 4.73$$

You can see from the table that the value of the equilibrium constant does not depend on the initial concentrations of the reactants and products. Regardless of the initial concentrations, each reaction will establish equilibrium, and that equilibrium can be described by the same equilibrium constant.

You can also see that the equilibrium state can be obtained by starting with either nitrogen dioxide, as in the first trial, or with dinitrogen tetroxide, as in the third trial. Thus, the equilibrium state can be reached from either direction (the forward or the reverse reaction).

Each set of equilibrium concentrations is called an **equilibrium position**. The data table above shows three different equilibrium positions for this reaction. There are an infinite number of equilibrium positions, but only one equilibrium constant for each reaction.

Example 1
What is the equilibrium expression for this reaction?

$$2CO(g) + O_2(g) \Leftrightarrow 2CO_2(g)$$

While the equilibrium constant does not tell us anything about the time it takes to reach equilibrium, it does provide important information about the mixture of reactants and products at equilibrium.

The equilibrium constant is a measure of the extent to which a reaction proceeds to completion.

- If $K_{eq} > 1$ there will be more products than reactants at equilibrium. In this case, we say that equilibrium "lies to the right," toward the product side.
- If $K_{eq} < 1$ there will be more reactants than products at equilibrium. In this case, we say that equilibrium "lies to the left," toward the reactant side.
- If $K_{eq} \approx 1$ there will be approximately equal amounts of reactants and products at equilibrium.

The larger the value of the equilibrium constant, the more the reaction proceeds to completion.

Homogeneous and Heterogeneous Equilibria

Equilibrium conditions for reactions in which all the reactants and products are in the same state are called **homogeneous equilibria**. Equilibrium conditions for reactions that involve substances in more than one state are called **heterogeneous equilibria**.

The reaction shown below is an example of a heterogeneous equilibrium.

$$NH_4Cl(s) \Leftrightarrow NH_3(g) + HCl(g)$$

Determining the equilibrium constant for this reaction presents a bit of a problem. The concentration of a pure substance (liquid or solid) does not change during a reaction. Because of this fact, the concentrations of solids and liquids are not included in equilibrium expressions. Thus, the equilibrium expression for this reaction would be

$$K_{eq} = [NH_3][HCl]$$

Example 2
What is the equilibrium expression for this reaction?

$$C(s) + H_2O(g) \Leftrightarrow CO(g) + H_2(g)$$

The Reaction Quotient

When the reactants and products of a chemical reaction are mixed, it is not always obvious if the mixture has or has not reached equilibrium. And, if the mixture is not at equilibrium, it is useful to know the direction in which the system will shift to reach equilibrium.

The **reaction quotient** (*Q*) is used to determine if a reaction is at equilibrium. The reaction quotient is calculated much like the equilibrium constant except that the concentrations that exist at the time the measurement is taken, not the equilibrium concentrations, are used in the equilibrium expression.

Consider the reaction below.

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

The equilibrium constant for this reaction at this temperature is 0.105. Suppose you are running this reaction and want to determine if it is at equilibrium. You measure the concentrations and find that $[NH_3] = 0.15\ M$, $[N_2] = 0.0020\ M$, and $[H_2] = 0.10\ M$.

The reaction quotient is calculated by substituting these concentrations into the equilibrium expression.

$$\begin{aligned} Q &= \frac{[NH_3]^2}{[N_2][H_2]^3} \\ &= \frac{(0.15)^2}{(0.0020)(0.10)^3} \\ &= 11250 \end{aligned}$$

The reaction is not at equilibrium because Q does not equal K_{eq}.

The question now is, if the system is not at equilibrium, in which direction will it proceed to reach equilibrium? The answer depends on the relationship between Q and K_{eq}:

- If $Q < K_{eq}$, there is too much of the reactants and too little of the products at the time of measurement. The reaction will consume reactants and form products to reach equilibrium. Thus, the reaction will proceed to the right (in the direction of the products).

- If $Q > K_{eq}$, there is too much of the products and too little of the reactants at the time of measurement. The reaction will form reactants and consume products to reach equilibrium. Thus, the reaction will proceed to the left (in the direction of the reactants).

- If $Q = K_{eq}$, the system is at equilibrium and no shift will occur.

Example 3
Consider this reaction

$$COCl_2(g) \Leftrightarrow CO(g) + Cl_2(g) \qquad K_{eq} = 170$$

If the concentrations of CO and Cl_2 are each $0.15\,M$ and the concentration of $COCl_2$ is $0.0011\,M$, is the reaction at equilibrium? If not, in which direction will it proceed?

Worksheet

1. Write the equilibrium expression for each of the following reactions:

   a) $2SO_2(g) + O_2(g) \Leftrightarrow 2SO_3(g)$

   b) $CO(g) + 3H_2(g) \Leftrightarrow CH_4(g) + H_2O(g)$

   c) $H_2O(g) + CO(g) \Leftrightarrow H_2(g) + CO_2(g)$

   d) $2H_2(g) + O_2(g) \Leftrightarrow 2H_2O(g)$

   e) $2NO(g) + Br_2(g) \Leftrightarrow 2NOBr(g)$

   f) $NH_4NO_3(s) \Leftrightarrow N_2O(g) + 2H_2O(g)$

   g) $ZnCO_3(s) \Leftrightarrow ZnO(s) + CO_2(g)$

   h) $C(s) + 2S(g) \Leftrightarrow CS_2(g)$

   i) $SnO_2(s) + 2CO(g) \Leftrightarrow Sn(s) + 2CO_2(g)$

   j) $C(s) + CO_2(g) \Leftrightarrow 2CO(g)$

2. A vial contains $0.150\ M\ NO_2$ and $0.300\ M\ N_2O_4$. Calculate Q for the reaction $2NO_2(g) \Leftrightarrow N_2O_4(g)$.

3. At $448°C$, $K_{eq} = 50.5$ for the reaction $H_2(g) + I_2(g) \Leftrightarrow 2HI(g)$. Find Q and predict how the reaction proceeds if $[H_2] = 0.150\ M$, $[I_2] = 0.175\ M$, and $[HI] = 0.950\ M$.

4. At $740°C$, $K_{eq} = 0.0060$ for the decomposition of calcium carbonate ($CaCO_3$), which is described by the equation $CaCO_3(s) \Leftrightarrow CaO(s) + CO_2(g)$. Find Q and predict how the reaction will proceed if $[CO_2] = 0.0004\ M$.

5. For the reaction $CO(g) + H_2O(g) \Leftrightarrow H_2(g) + CO_2(g)$, $K_{eq} = 5.10$ at $527°C$. If $[CO] = 0.15\ M$, $[H_2O] = 0.25\ M$, $[H_2] = 0.42\ M$, and $[CO_2] = 0.37\ M$, calculate Q and determine how the reaction will proceed.