Chapter 10: Equilibrium

Equilibrium is a condition that occurs when a chemical reaction is reversible, and the forward and reverse reactions occur simultaneously, at the same rate.

Chemical reactions can be classified into one of two broad categories: those reactions that "go to completion" and those reactions that establish "equilibrium". Burning methane in oxygen to form carbon dioxide and water is a "goes to completion" reaction, and is indicated using a single-headed reaction arrow:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

Equilibrium reactions do not go to completion; instead, the two reactions (arbitrarily labeled "forward" and "reverse") occur simultaneously. The forward and reverse reactions are opposite; the reverse reaction is the forward reaction written backwards. For example, nitrogen gas and hydrogen gas react to form ammonia:

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

This reaction requires pressures between 2100 and 3600 psi and temperatures between 300 and 550 ^{o}C. At these pressures and temperatures ammonia spontaneously decomposes into nitrogen and hydrogen gas:

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

Eventually, these two reactions occur at the same rate. When this happens, the concentrations of nitrogen, hydrogen, and ammonia become constant, and the system is said to be "at equilibrium". Typically, we represent chemical equilibrium using a double-headed reaction arrow:

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

The ***equilibrium constant***, $\boldsymbol{K_{eq}}$, is the ratio of the product concentration to the reactant concentration when equilibrium is achieved. The exact mathematical form of the equilibrium expression, relating K_{eq} to the various reactants and products, depends on the specific chemical equilibrium considered. For the ammonia system, the equilibrium expression is:

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

The use of square brackets [ ] indicates that concentrations of reactants and products are equilibrium concentrations and are molar concentrations (units of moles/liter). The exponents, 2 for ammonia and 3 for hydrogen, are the coefficients from the balanced chemical equation.

For gas phase equilibria, $\boldsymbol{K_p}$ is sometimes used in place of K_{eq}. K_p is the equilibrium constant based on the partial pressure of the gases at equilibrium.

Le Châtlier's Principle

Arguably, the single most important rule governing chemical equilibrium is Le Châtlier's Principle, promulgated by French chemist Henry Louis Le Châtlier (1850 – 1936):

> ***"If a chemical system at equilibrium experiences a change in concentration, temperature or total pressure, the equilibrium will shift in order to minimize that change.***"

Consider the following equilibrium:

$$N_2(g) + 3H_2(g) \Leftrightarrow 2NH_3(g) + \text{Heat}$$

Any change in concentration, temperature, or total pressure can affect this equilibrium by increasing or decreasing the relative amounts of "reactants" and "products". When the equilibrium is disturbed, it re-establishes a new equilibrium. The simplest way of predicting the equilibrium change is based on ***pushes*** and ***pulls***.

Imagine that you have an office chair sitting in front of you. If you push the chair, it moves away from you – the act of pushing moves the chair away from the disturbance (the pushing force, you). If you pull the chair, it moves towards you – the act of pulling moves the chair towards the disturbance (the pulling force). This is a common, everyday situation we have all experienced at one time or another.

We can apply the ideas of pushes and pulls to equilibrium by making the following associations: if I increase the amount of chemical substances or heat (temperature) then I am pushing the reaction. The reaction responds to this push by moving away from the push.

Increasing the amount of nitrogen or hydrogen in our reaction pushes the reaction toward the ammonia side. The concentration of ammonia and the amount of heat produced will both increase. Conversely, increasing the amount of ammonia or increasing the temperature (heating the container) pushes the reaction towards the nitrogen and hydrogen side. Any increase causes the equilibrium to shift left or shift right, away from the side that has been increased.

Any decrease in nitrogen or hydrogen pulls the reaction towards the left side, while any decrease in ammonia or temperature (cooling the container) pulls the reaction towards the right side.

If you understand pushing and pulling physical objects, then you should be able to apply the same idea to pushing and pulling on an equilibrium system.

When the equilibrium changes, the concentrations of all substances involved in the equilibrium must also change. For our equilibrium reaction:

$$N_2(g) + 3H_2(g) \Leftrightarrow 2NH_3(g) + \text{Heat}$$

Let's suppose that we increase the concentration of nitrogen gas.

⇒ We know that the equilibrium will shift to the right, since increasing the concentration of nitrogen gas pushes the reaction right.

⇒ Increasing nitrogen gas causes more ammonia to be produced, so the concentration of ammonia must increase.

⇒ Nitrogen reacts with hydrogen to form more ammonia, so increasing the amount of nitrogen must necessarily reduce the concentration of hydrogen.

⇒ There must also be a general increase in the heat released.

Changing one substance involved in a chemical equilibrium must change all other substances involved in the equilibrium. A new equilibrium is eventually achieved.

General equilibria.

For the general equilibrium reaction:

$$wA + xB \Leftrightarrow yC + zD$$

where A, B, C, and D represent different chemical compounds, and w, x, y, and z represent the numerical coefficients in the balanced chemical equation, we can write a general equilibrium expression:

$$K_{eq} = \frac{[C]^y[D]^z}{[A]^w[B]^x}$$

Two important equilibrium constants encountered in solution chemistry are the ***solubility product constant***, called $\boldsymbol{K_{sp}}$, and the ***weak acid ionization constant, K_a.***

Solubility product equilibria.

Consider an aqueous solution of a very slightly soluble salt, silver chloride (AgCl). In water, most of the silver chloride remains as a solid, but a very small amount dissociates into aqueous silver and chloride ions by the following equilibrium reaction:

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

The equilibrium expression describing this reaction does NOT include the concentration of solid silver chloride, but is instead written as:

$$K_{sp} = \left[\mathrm{Ag}^+\right]\left[\mathrm{Cl}^-\right]$$

For any solubility product equilibrium, the "concentration" of the solid material is ***never*** included in the equilibrium expression.

Reversing the chemical reaction.

In a chemical equilibrium, both of the chemical reactions occur simultaneously. What happens if we write the equilibrium "backwards"?

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

Our new equilibrium expression takes the form:

$$K_{eq} = \frac{1}{\left[\mathrm{Ag}^+\right]\left[\mathrm{Cl}^-\right]}$$

In this case, our equilibrium constant is NOT the same as the K_{sp} for silver chloride; K_{sp} describes the dissociation of a solid material into its component ions. Instead, our new equilibrium constant describes the combination of ions to form a solid material. There is no generally accepted name for this equilibrium constant, and most chemists don't see the need to bother with it when they can write a K_{sp} reaction. If you want, you can call it the precipitation equilibrium constant, and call it K_{ppt}.

Acid ionization constants.

The ionization of a ***weak acid*** (or a weak base) is another example of an equilibrium system. Weak acids ionize << 100%, therefore a substantial amount of the weak acid dissolved in water remains in its molecular, unionized form. For convenience sake, I will only consider monoprotic acids (acids that produce only 1 hydrogen ion per molecule of acid), and I will abbreviate these monoprotic acids as HA.

For the dissociation of a weak acid:

$$HA(aq) \Leftrightarrow H^+(aq) + A^-(aq)$$

We can write an equilibrium expression having the form:

$$K_{eq} = \frac{[H^+][A^-]}{[HA]}$$

The equilibrium constant for weak acid ionizations is normally given the symbol K_a, and is the weak acid ionization constant. With weak acids, it is especially important to remember that the concentrations shown in the equilibrium expression are equilibrium concentrations. Some small amount of the original weak acid, HA, will break-up into H^+ and A^-.

Conjugate acid – base pairs.

For the monoprotic acid HA, the anion A^- is called the ***conjugate base***. The conjugate base of a weak acid is a weak base, and we typically talk about conjugate acid – base pairs. Weak acids always produce weak conjugate bases, and weak bases always produce weak conjugate acids. The A^- reacts with water to reform the weak acid, HA, and hydroxide ion following the reaction:

$$A^-(aq) + H_2O \Leftrightarrow HA(aq) + OH^-(aq)$$

The equilibrium expression for this reaction is:

$$K_b = \frac{[HA][OH^-]}{[A^-]}$$

Notice: the concentration of water does not appear in the equilibrium expression. Concentrations of solvents (in this case water) are omitted from equilibrium expressions.

<u>Other factors affecting equilibrium.</u>

Some equilibrium reactions produce energy or consume energy during the course of the reaction. We can represent these types of reactions as:

$$A + B \Leftrightarrow C + D + \text{heat}$$

or

$$A + B + \text{heat} \Leftrightarrow C + D$$

In either case, heat is treated as if it were a chemical substance for purposes of Le Châtelier's principle. In the first reaction, increasing the temperature (increasing heat) shifts the reaction left, while decreasing temperature shifts the reaction right. In the second reaction, increasing temperature shifts the reaction right, while decreasing the temperature shifts the reaction left.

Note: this temperature effect applies specifically to equilibrium systems, and not to systems that "go to completion".

For equilibria involving gases, changing pressure can affect the equilibrium's position. Consider our ammonia example:

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

Increasing pressure shifts the equilibrium towards the side with fewer total molecules as shown in the balanced chemical equation. In this example, increasing pressure would shift the equilibrium towards ammonia (2 molecules), while decreasing pressure shifts the equilibrium towards nitrogen and hydrogen (4 total molecules, one of nitrogen and three of hydrogen).

If a catalyst is part of the equilibrium, both the forward and reverse reactions occur faster. However, the ratio of forward/reverse reaction remains the same. No net shift in equilibrium position occurs due to a catalyst.

Chapter 10 Homework:

Vocabulary. The following terms are defined and explained in the text. Make sure that you are familiar with the meanings of the terms as used in chemistry. Understand that you may have been given incomplete or mistaken meanings for these terms in earlier courses. The meanings given in the text are correct and proper.

Equilibrium	**Equilibrium constant K_{eq}**	**Le Châtlier's principle**
K_p	**Weak acid**	**pH**
Conjugate acid-base pair	**Conjugate acid**	**Conjugate base**
Weak acid ionization constant K_a		**Solubility product constant K_{sp}**

Writing equilibrium expressions.

1. For the reaction:

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

   write the appropriate equilibrium expression.

2. For the reaction:

   $BrO_3^-(aq) + 2Cr^{+3}(aq) + 4H_2O \Leftrightarrow Br^-(aq) + Cr_2O_7^{-2}(aq) + 8H^+(aq)$,

   write the proper equilibrium expression.

3. Solid calcium fluoride (CaF_2) dissociates into calcium ions and fluoride. Write the appropriate equilibrium expression.

4. Solid calcium hydroxide ($Ca(OH)_2$) dissociates into calcium ions and hydroxide. Write the appropriate equilibrium expression.

5. Ammonia reacts in water solution to produce ammonium and hydroxide ions. Write the appropriate equilibrium expression.

6. Formic acid is a weak monoprotic acid with the formula HCO_2**H** (the H in bold is the acidic hydrogen). Write the proper equilibrium expression for the ionization of formic acid in water.

7. Fluoride (F^-) reacts in water solution to produce hydrogen fluoride and hydroxide. Write the proper equilibrium expression for this reaction.

Le Châtlier's Principle

1. For the reaction:

   Heat + $CaCO_3(s) \Leftrightarrow CaO(s) + CO_2(g)$

   Which direction will the equilibrium shift under the following conditions?

   a. Temperature increases.

   b. Carbon dioxide concentration decreases.

   c. Calcium carbonate mass is doubled.

   d. Calcium oxide mass is halved.

   e. Temperature decreases and carbon dioxide pressure increases.

2. For the reaction:

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

   Which direction will the equilibrium shift under the following conditions?

   a. Container pressure is doubled.

   b. Dinitrogen tetroxide concentration decreases.

   c. Nitrogen dioxide concentration increases.

3. Consider the following reaction, which occurs in hexane solvent (not water):

   CH_3CO_2H + $C_2H_5OH \Leftrightarrow$ $CH_3CO_2C_2H_5$ + H_2O

   Acetic acid   ethanol   ethyl acetate

   Which direction will the reaction shift under the following conditions?

   a. acetic acid increases and water decreases.

   b. ethyl acetate and water increase.

c. ethanol decreases.

4. Consider the following equilibrium reaction:

   $BaCl_2(aq) + Na_2SO_4(aq) \Leftrightarrow BaSO_4(aq) + 2NaCl(aq)$

   Indicate what will happen to the concentration of BaSO4 (increases, decreases, no effect, or not enough information given) in each of the scenarios given below.

   a. Pressure is increased.

   b. temperature increases.

   c. sodium chloride concentration decreases

   d. barium chloride concentration decreases.

   e. sodium sulfate concentration increases.

5. Consider the following equilibrium:

   $3Cu(s) + 6H^{+}(aq) + 2HNO_3(aq) \Leftrightarrow 3Cu^{+2}(aq) + 2NO(g) + 4H_2O + Heat$

   Indicate what will happen to the concentration of nitric acid (increases, decreases, no effect, or not enough information given) in each of the scenarios given below.

   a. pressure is increased.

   b. temperature decreases

   c. copper ion concentration increases

   d. nitrogen oxide concentration decreases.

   e. pH increases

Answers:

Writing equilibrium expressions.

1. $K_{eq} = \dfrac{[CO_2][H_2]}{[CO][H_2O]}$

2. $K_{eq} = \dfrac{[Br^-][Cr_2O_7^{-2}][H^+]^8}{[BrO_3^-][Cr^{+3}]^2}$

3. $CaF_2 \Leftrightarrow Ca^{+2} + 2F^-$

   $K_{sp} = [Ca^{+2}][F^-]^2$

4. $Ca(OH)_2 \Leftrightarrow Ca^{+2} + 2OH^-$

   $K_{sp} = [Ca^{+2}][OH^-]^2$

5. $NH_3 + H_2O \Leftrightarrow NH_4^+ + OH^-$

   $K_b = \dfrac{[NH_4^+][OH^-]}{[NH_3]}$

6. $HCO_2H \Leftrightarrow H^+ + HCO_2^-$

   $Ka = \dfrac{[H^+][HCO_2^-]}{[HCO_2H]}$

7. F- + H2O $\Leftrightarrow$ HF + OH-

   $K_b = \dfrac{[HF][OH^-]}{[F^-]}$

Le Châtlier's Principle

1. Heat + $CaCO_3(s) \Leftrightarrow CaO(s) + CO_2(g)$

a. Shifts right.

b. Shifts right.

c. No effect.

d. No effect.

e. Shifts left.

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

Which direction will the equilibrium shift under the following conditions?

a. Shifts right

b. Shifts right.

c. Shifts right.

3. CH_3CO_2H + $C_2H_5OH \Leftrightarrow$ $CH_3CO_2C_2H_5$ + H_2O

Acetic acid ethanol ethyl acetate

a. Shifts right.

b. Shifts left.

c. Shifts left.

4. $BaCl_2(aq) + Na_2SO_4(aq) \Leftrightarrow BaSO_4(aq) + 2NaCl(aq)$

a. No effect.

b. Not enough information given.

c. Shifts right

d. Shifts left.

e. Shifts right.

5. $3Cu(s) + 6H^{+}(aq) + 2HNO_3(aq) \Leftrightarrow 3Cu^{+2}(aq) + 2NO(g) + 4H_2O$ + Heat

Indicate what will happen to the concentration of nitric acid (increases, decreases, no effect, or not enough information given) in each of the scenarios given below.

a. increases.

b. decreases

c. increases

d. decreases.

e. increases