UNIT II

Chemical Foundations of Biological Systems

Foundational Concept: The principles that govern chemical interactions and reactions form the basis for a broader understanding of the molecular dynamics of living systems.

The Unique Nature of Water and Its Solutions

Read This Chapter to Learn About

➤ Acid–Base Reactions

➤ Ions in Solutions

➤ Solubility

➤ Acid–Base Titrations

ACID–BASE REACTIONS

An acid reacts with a base to form an ionic compound, often called a **salt**, plus water.

Brønsted–Lowry Definition of Acids and Bases

ACIDS

An **acid** is a compound that produces H^+ **(hydronium ion)** in water solution. There are strong acids and weak acids. A **strong acid** is defined as an acid that dissociates fully into two ions in water solution.

The six strong acids are HCl, HBr, HI, HNO_3, H_2SO_4, and $HClO_4$.

All other acids are **weak acids**, defined as an acid that dissociates only to a very small extent in water solution. Some examples are HF, HCN, H_2CO_3, H_3PO_4, acetic acid, and oxalic acid.

BASES

A **base** is a compound that produces **OH⁻ (hydroxide ion)** in water solution. There are strong bases and weak bases. A **strong base** fully dissociates into its ions in water solution. Among the strong bases are hydroxides of groups IA and IIA that are fully soluble in water. They are LiOH, NaOH, KOH, and $Ba(OH)_2$.
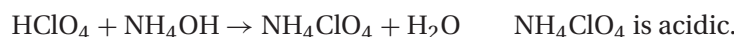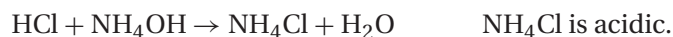
There are many **weak bases**, but most of them are organic analogs of ammonia, NH_3. Ammonia dissolves in water, but only a very small percentage of NH_3 molecules produce NH_4OH, which then dissociates into NH_4^+ and OH^-.

TYPES OF ACID–BASE REACTIONS

When a strong acid reacts with a strong base, the ionic compound that forms is **neutral** in water solution. The ionic compound is formed by taking the cation from the base and the anion from the acid.

$$HCl + KOH \rightarrow KCl + H_2O \qquad \text{KCl is neutral.}$$
$$H_2SO_4 + NaOH \rightarrow NaHSO_4 + H_2O \qquad \text{NaHSO}_4 \text{ is neutral.}$$

When a strong acid reacts with a weak base, the ionic compound that forms is **acidic** in water solution.

$$HCl + NH_4OH \rightarrow NH_4Cl + H_2O \qquad \text{NH}_4\text{Cl is acidic.}$$
$$HClO_4 + NH_4OH \rightarrow NH_4ClO_4 + H_2O \qquad \text{NH}_4\text{ClO}_4 \text{ is acidic.}$$

When a weak acid reacts with a strong base, the ionic compound that forms is **basic** in water solution.

$$HF + NaOH \rightarrow NaF + H_2O \qquad \text{NaF is basic.}$$
$$HCN + KOH \rightarrow KCN + H_2O \qquad \text{KCN is basic.}$$

Compounds, such as water, that can serve as an acid (donates a proton) or base (accepts a proton) are referred to as **amphiprotic compounds**.

Ionization of Water

Acidity is a measure of the concentration of H^+ in a dilute water solution. It is measured using the **pH scale**, which is based on a process that water undergoes called **autoionization**:

$$H_2O \ (l) \rightleftarrows H^+(aq) + OH^- \ (aq) \qquad K_w = 1 \times 10^{-14}$$

This is an **equilibrium process** that lies very far to the left. The K for this, in other words, is very small. It is called K_w (for water) and $K_w = 1 \times 10^{-14}$ at 25 °C. This means that approximately 1 out of every 10^{14} molecules dissociates into ions in this manner.

An acid produces H^+ in water solution. A base produces OH^- (hydroxide) in water solution. When an acid reacts with a base, a salt is formed. This chapter discusses these compounds and their interactions.

The pH Scale

The pH scale is from 0 to 14. It is a logarithmic scale (powers of 10). Each pH is 10-fold less acidic than the next lower pH value.

At pH 7, a solution is neutral.

$$[H^+] = [OH^-]$$

Writing the K expression,

$$K_w = [H^+][OH^-] = 1 \times 10^{-14}$$

At pH 7,

$$[H^+] = [OH^-] = 1 \times 10^{-7} \text{ M}$$

From this, you can see that the $pH = -\log[H^+]$ and that $pOH = -\log[OH^-]$. When the pH is 7, the pOH is 7 as well.

$$pH + pOH = 14$$

When $[H^+] = 1 \times 10^{-3}$ M, the pH = 3; and when $[OH^-] = 1 \times 10^{-11}$ M, the pOH = 11.

EXAMPLE: Calculate the pH if $[H^+]$ is 3.5×10^{-5} M.

SOLUTION:

➤ Because the exponent is −5, the pH is near 5.
➤ $pH = -\log(3.5 \times 10^{-5}) = 4.5$

EXAMPLE: Calculate $[H^+]$ when pH = 8.4.

SOLUTION:

➤ $8.4 = -\log[H^+]$
➤ $[H^+] = 10^{-8.4} = 4 \times 10^{-9}$ M

EXAMPLE: Calculate $[OH^-]$ when pH = 10.6.

SOLUTION:

➤ $pOH = 14 - 10.6 = 3.4$
➤ $[OH^-] = 10^{-3.4} = 4 \times 10^{-4}$ M

Conjugate Acids and Bases

A Brønsted–Lowry acid, which is a **proton donor**, can be represented in general as **HX** and a Brønsted–Lowry base, which is a **proton acceptor**, can be represented as **X⁻**. The general reaction of an acid placed in water would be described in the following form:

$$HX + H_2O \rightarrow X^- + H_3O^+$$

$$\text{acid} + \text{base} \rightarrow \text{base} + \text{acid}$$
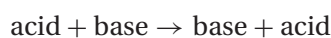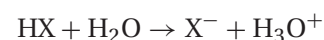
where the acid (HX) donates a proton to water (which acts as a base) to yield H_3O^+, which is a hydronium ion (a water molecule that has accepted a donated proton). HX and X^- are often referred to as a **conjugate acid–base pair** defined as a pair of compounds that differ in structure by one proton. HX is a conjugate acid while X^- is the conjugate base. The acid, which has the proton to donate, is the conjugate acid, while the base, which is ready to accept the proton, is the conjugate base.

An example of a reaction involving an acid is:

$$HCl + H_2O \rightarrow Cl^- + H_3O^+$$
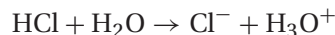
(hydrochloric acid) + (water) → (chloride ion) + (hydronium ion)

acid + base → base + acid

The same process applies when a base is placed in water, which yields the general reaction:

$$X^- + H_2O \rightarrow HX + OH^-$$

base + acid → acid + base

where the base (X^-) accepts a proton from water (which acts as an acid) to yield the conjugate acid of the base and OH^- (hydroxide ion). An example of a reaction involving a base is:

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$$
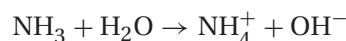
(ammonia) + (water) → (ammonium ion) + (hydroxide ion)
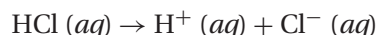
base + acid → acid + base

Strong Acids and Bases

STRONG ACIDS

A strong acid is an acid where every molecule dissociates into H^+ and the counter ion (the conjugate base). There are six strong acids––HCl, HBr, HI, HNO_3, H_2SO_4, and $HClO_4$.

The equation for the dissociation of HCl is written:

$$HCl\ (aq) \rightarrow H^+\ (aq) + Cl^-\ (aq)$$

Because there is no reverse reaction taking place, strong acids do not involve any equilibrium process. Simple stoichiometry suffices. The concentration of the proton and the concentration of the conjugate base Cl^- are equal to the initial concentration of the acid.

If 1,000 HCl molecules are dissolved in water, they dissociate into 1,000 H^+ and 1,000 Cl^- ions.

STRONG BASES

If the base is a strong base, every molecule dissociates into ions in water solution. The most common strong bases are LiOH, NaOH, KOH, and $Ba(OH)_2$.

$$KOH\ (aq) \rightarrow K^+\ (aq) + OH^-\ (aq)$$

$$Ba(OH)_2\ (aq) \rightarrow Ba^{2+}\ (aq) + 2\ OH^-\ (aq)$$
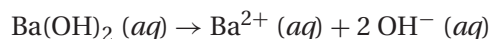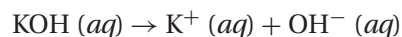
There is no equilibrium here; stoichiometry suffices to determine $[OH^-]$ and, thus, pH. For LiOH, KOH, and NaOH, the base concentration equals the hydroxide concentration.

$$[KOH] = [OH^-]$$

For $Ba(OH)_2$, the base concentration is half of the hydroxide concentration.

$$[Ba(OH)_2] = \frac{1}{2}\ [OH^-]$$

EXAMPLE: Calculate the pH of 0.065 M KOH. This is a strong base with $1:1$ stoichiometry.

SOLUTION:

➤ $[KOH] = [OH^-] = 0.065$ M.
➤ $pOH = -\log 0.065 = 1.2$
➤ $pH = 14 - 1.2 = 12.8$

EXAMPLE: Calculate the pH of 0.065 M $Ba(OH)_2$. This is a strong base with $1:2$ stoichiometry.
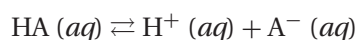
SOLUTION:

➤ $[Ba(OH)_2] = \frac{1}{2}\ [OH^-] = 0.065$
➤ $[OH^-] = 0.13$ M
➤ $pOH = -\log 0.13 = 0.9$
➤ $pH = 14 - 0.9 = 13.1$

Weak Acids and Bases

WEAK ACIDS

Weak acids have the word *acid* as part of their name, and they are not one of the six strong acids.

For weak acids, only 1 out of every 10,000–100,000 molecules undergoes dissociation to proton and conjugate base or

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

Most of the molecules are still in the HA form. This is an equilibrium process, with a very small K_a (for acid). The K_a values are typically in the range of 10^{-4} to 10^{-6}. The K_a expression is written as:

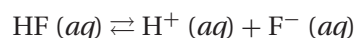$$K_a = \frac{[H^+]\,[A^-]}{[HA]}$$

EXAMPLE: Calculate the pH of 0.15 M HNO_3.

SOLUTION:

➤ This is a strong acid, so the proton concentration is equal to the acid concentration: $[H^+] = [HNO_3] = 0.15$ M.

➤ $pH = -\log 0.15 = 0.8$

EXAMPLE: Calculate the pH of 0.15 M HF. For this problem, $K_a = 6.7 \times 10^{-4}$.

SOLUTION: This is a weak acid. The steps for solving this problem are:

➤ Write the equation.

$$HF\,(aq) \rightleftharpoons H^+\,(aq) + F^-\,(aq)$$

➤ Fill in the table.

	HF	$\rightleftharpoons$	H^+	+	F^-
At equilibrium	0.15 M		x		x

(Small K so the initial HF concentration equals the HF concentration at equilibrium.)

➤ Write the K expression.

$$K_a = \frac{[H^+]\,[F^-]}{[HF]}$$

➤ Fill in the equilibrium values.

$$6.7 \times 10^{-4} = \frac{x^2}{0.15}$$

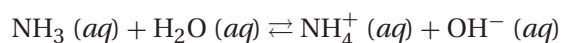➤ Solve the $[H^+]$ for x.

$$x = [H^+] = 1 \times 10^{-2}\ \text{M}$$

➤ Calculate the pH.

$$pH = -\log(1 \times 10^{-2}) = 2$$

WEAK BASES

We use ammonia for the weak base problems because almost all weak bases are organic derivatives of ammonia. When ammonia is dissolved in water, approximately 1 out of every 100,000 molecules produces an OH^- (hydroxide ion).

The equation is:

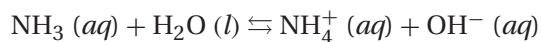$$NH_3\,(aq) + H_2O\,(aq) \rightleftharpoons NH_4^+\,(aq) + OH^-\,(aq)$$

This is an equilibrium process and the K_b (for base) is 1.8×10^{-5}. The K_b expression is written:
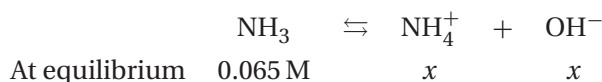
$$K_b = \frac{[NH_4{}^+]\,[OH^-]}{[NH_3]}$$

EXAMPLE: Calculate the pH of 0.065 M NH_3. In this example, $K_b = 1.8 \times 10^{-5}$.

SOLUTION: This is a weak base; there are certain steps to follow.

➤ Write the equation.

$$NH_3\;(aq) + H_2O\;(l) \leftrightharpoons NH_4^+\;(aq) + OH^-\;(aq)$$

➤ Fill in the table.

	NH_3	$\leftrightharpoons$	NH_4^+	+	OH^-
At equilibrium	0.065 M		x		x

➤ Write the K expression.

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

➤ Fill in the equilibrium values.
➤ Solve for x, i.e., $[OH^-]$.

$$1.8 \times 10^{-5} = \frac{x^2}{0.065}$$

$$x = [OH^-] = 1.1 \times 10^{-3}\;M$$

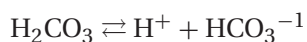➤ Calculate the pOH.

$$pOH = 3$$

➤ Calculate the pH.

$$pH = 11$$

POLYPROTIC ACIDS

Polyprotic acids are acids that have more than one proton; therefore, they have more than one K_a. There is just one K_a per proton removed. In the following equations, all substances are in aqueous solution.

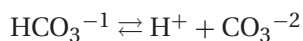➤ Carbonic acid has 2 protons (both weak):

$$H_2CO_3$$

➤ For the removal of the first proton,

$$H_2CO_3 \rightleftarrows H^+ + HCO_3{}^{-1}$$

➤ For the removal of the second proton,
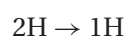
$$HCO_3{}^{-1} \rightleftarrows H^+ + CO_3{}^{-2}$$

➤ K_{a1} for the first proton $= 4.3 \times 10^{-7}$ Weak acid

➤ K_{a2} for the second proton $= 4.8 \times 10^{-11}$ Weaker acid
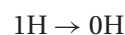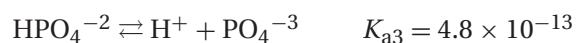
➤ Phosphoric acid has 3 protons (all weak):

$$H_3PO_4$$

➤ Removal of first proton,

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4{}^{-1} \qquad K_{a1} = 6.9 \times 10^{-3}$$

$$3H \rightarrow 2H$$
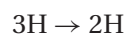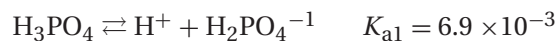
➤ Removal of second proton,

$$H_2PO_4{}^{-1} \rightleftharpoons H^+ + HPO_4{}^{-2} \quad K_{a2} = 6.2 \times 10^{-8}$$

$$2H \rightarrow 1H$$

➤ Removal of third proton,

$$HPO_4{}^{-2} \rightleftharpoons H^+ + PO_4{}^{-3} \qquad K_{a3} = 4.8 \times 10^{-13}$$

$$1H \rightarrow 0H$$

pH OF A POLYPROTIC ACID SOLUTION

If you are calculating the pH of a solution of carbonic acid or phosphoric acid, only the first (and largest) K_{a1} is used. The amount of proton produced by the subsequent K_a values is negligible compared to the first. In all of the equations that follow, every substance is in aqueous solution except the water, which is liquid.

SALTS OF POLYPROTIC ACIDS

$NaHCO_3$ is the salt of NaOH and H_2CO_3. It is a basic salt (K_b); thus, it produces OH^- and a conjugate acid:

$$HCO_3{}^{-1} + H_2O \rightleftharpoons OH^- + H_2CO_3 \quad K_{b1} = 2.3 \times 10^{-8}$$
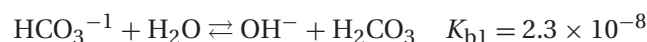
Na_2CO_3 is also a salt of NaOH and H_2CO_3. It is a basic salt (K_b); thus, it produces OH^- and a conjugate acid:

$$CO_3{}^{-2} + H_2O \rightleftharpoons OH^- + HCO_3{}^{-1} \quad K_{b2} = 2.1 \times 10^{-4}$$

There are three salts of phosphoric acid:

$$NaH_2PO_4$$
$$Na_2HPO_4$$
$$Na_3PO_4$$
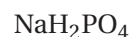
All of these are basic salts; they produce OH^- and a conjugate acid

$$H_2PO_4{}^{-1} + H_2O \rightleftharpoons OH^- + H_3PO_4 \qquad K_{b1} = 1.4 \times 10^{-12}$$
$$HPO_4{}^{-2} + H_2O \rightleftharpoons OH^- + H_2PO_4{}^{-1} \qquad K_{b2} = 1.6 \times 10^{-7}$$
$$PO_4{}^{-3} + H_2O \rightleftharpoons OH^- + HPO_4{}^{-2} \qquad K_{b3} = 2.1 \times 10^{-2}$$
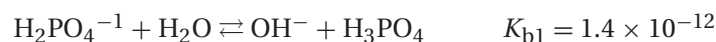
EXAMPLE: Calculate the pH of 0.1185 M phosphoric acid solution.

SOLUTION:

➤ For the pH of a polyprotic acid, we use only the K_{a1}.

$$K_{a1} = 6.9 \times 10^{-3}$$

➤ Write the equation.

$$H_3PO_4 \rightleftarrows H^+ + H_2PO_4^{-1}$$

➤ Fill in the table.

$$\begin{array}{cccc} H_3PO_4 & \leftrightarrows & H^+ & + & H_2PO_4^{-1} \\ 0.1185\,M & & x & & x \end{array}$$

➤ Write K_a expression.

$$K_a = \frac{[H^+]\,[H_2PO_4^{-1}]}{[H_3PO_4]}$$

➤ Fill in values and solve for x.
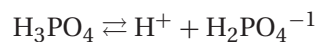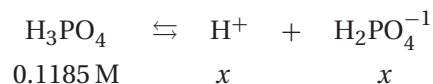
$$6.9 \times 10^{-3} = \frac{x^2}{0.1185\,M}$$

$$x = [H^+] = \sqrt{8.2 \times 10^{-4}} = 2.9 \times 10^{-2}\,M$$

➤ Calculate the pH.

$$pH = -\log[H^+] = 1.5$$

EXAMPLE: Calculate the pH of 0.0165 M sodium hydrogen phosphate.

SOLUTION:

➤ Write the formula.

$$Na_2HPO_4$$

➤ Recognize that this is a basic salt, so it is a base. So you need a K_b.

➤ Write the equation.

$$HPO_4^{-2} + H_2O \rightleftarrows OH^- + H_2PO_4^{-1}$$

➤ Fill in the table.

$$\begin{array}{cccc} HPO_4^{-2} & \leftrightarrows & OH^- & + & H_2PO_4^{-1} \\ 0.0165\,M & & x & & x \end{array}$$
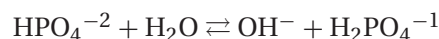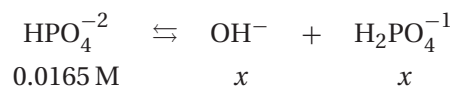
➤ Determine which K_b is needed.

K_{b1} involves $2H \rightarrow 3H$

K_{b2} involves $1H \rightarrow 2H$

K_{b3} involves $0H \rightarrow 1H$

➤ Because our salt has 1H and is going to the conjugate acid with 2H, we need K_{b2}.

$$K_{b2} = 1.6 \times 10^{-7}$$

➤ Write the K_b expression.

$$K_{b2} = \frac{[OH^-] \, [H_2PO_4^{\,-}]}{[HPO_4^{\,-2}]}$$

➤ Fill in the values and solve for x.

$$1.6 \times 10^{-7} = \frac{x^2}{0.0165 \text{ M}}$$

$$x = [OH^-] = 5.1 \times 10^{-5} \text{ M}$$

➤ Calculate pOH and pH.

$$pOH = 4.3$$
$$pH = 9.7$$

SOLUTIONS OF SALTS

When an acid reacts with a base, in stoichiometric quantities, an ionic compound (a salt) is formed, along with water:

$$acid + base \rightarrow salt + H_2O$$

The ionic compound is neutral, acidic, or basic (when dissolved in water), depending on which acid and base were used to make it.
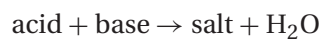
CASE 1:

$$\text{Strong acid} + \text{Strong base} \longrightarrow \text{Neutral salt} \qquad pH = 7$$

CASE 2:

$$\text{Strong acid} + \text{Weak base} \longrightarrow \text{Acidic salt} \qquad pH < 7$$

CASE 3:

$$\text{Weak acid} \;\; + \text{Strong base} \longrightarrow \text{Basic salt} \qquad pH > 7$$
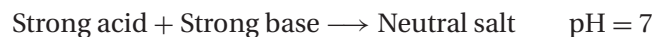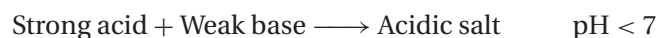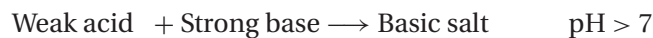
We look next at salts from cases 2 and 3 only. In the following equations, all substances are in aqueous solution except water, which is liquid.

CASE 2 EXAMPLES:

$$HCl + NH_4OH \longrightarrow NH_4Cl + H_2O$$

$$HNO_3 + NH_4OH \longrightarrow NH_4NO_3 + H_2O$$

CASE 3 EXAMPLES:

$$HF + LiOH \longrightarrow LiF + H_2O$$

$$HCN + KOH \longrightarrow KCN + H_2O$$

$$CH_3COOH + KOH^- \longrightarrow CH_3COO^-K^+ + H_2O$$
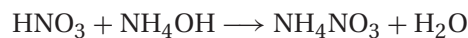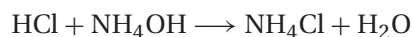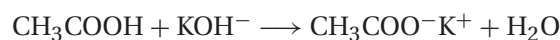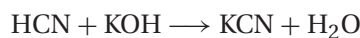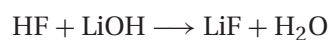
ACIDIC SALTS

Acidic salts are formed when a strong acid reacts with a weak base, as in case 2.

EXAMPLE: Calculate the pH of 0.078 M ammonium nitrate. For this problem, $K_a = 5.6 \times 10^{-10}$.

SOLUTION:

➤ Recognize that NH_4NO_3 is an acidic salt.
➤ Therefore, it is an acid (produces H^+).
➤ Write the equation.

$$NH_4^+ \ (aq) \rightleftarrows NH_3 \ (aq) + H^+ \ (aq)$$

➤ Fill in the table.

	NH_4^+	$\rightleftarrows$	NH_3	+	H^+
At equilibrium	0.078 M		x		x
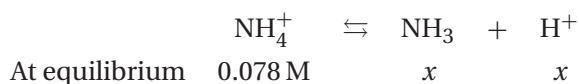
➤ Write the K expression.

$$K_a = \frac{[NH_3] \, [H^+]}{[NH_4^+]}$$

➤ Fill in the values and solve for x, the $[H^+]$.

$$5.6 \times 10^{-10} = \frac{x^2}{0.078 \text{ M}}$$
$$x = [H^+] = 6.6 \times 10^{-6} \text{ M}$$

➤ Calculate pH.

$$pH = 5.2$$

BASIC SALTS

Basic salts are formed when a strong base reacts with a weak acid, as in case 3.

EXAMPLE: Calculate the pH of 0.035 M KCN. For this problem, $K_b = 1.6 \times 10^{-5}$.

SOLUTION:

➤ Recognize that KCN is a basic salt.
➤ Therefore, it is a base (produces OH^-).
➤ Write the equation. The only ion here that can produce OH^- from water is the cyanide. You must have a negative ion to remove the H^+ from H_2O, leaving OH^-.

$$CN^- \ (aq) + H_2O \ (l) \rightleftarrows HCN \ (aq) + OH^- \ (aq)$$

➤ Fill in the table.

	CN^-	$\rightleftarrows$	HCN	+	OH^-
At equilibrium	0.035 M		x		x

➤ Write the K expression.

$$K_b = \frac{[HCN]\,[OH^-]}{[CN^-]}$$

➤ Fill in the values and solve for x, the $[OH^-]$.

$$1.6 \times 10^{-5} = \frac{x^2}{0.035\,M}$$

$$x = [OH^-] = 7.5 \times 10^{-4}\,M$$

➤ Calculate pOH.

$$pOH = 3.1$$

➤ Calculate pH.

$$pH = 10.9$$

Equilibrium Constants

You have just examined the **equilibrium constants** K_a and K_b for various acids and bases. Now see how they work together to produce the ionization constant for water, K_w. First consider the K_a expression for an acid and the K_b expression for a base:

$$K_a = \frac{[H_3O^+][A^-]}{HA} \qquad \text{and} \qquad K_b = \frac{[HA][OH^-]}{[A^-]}$$

When you multiply K_a by K_b, you get $K_a \times K_b = [H_3O^+][OH^-] = K_w = 1 \times 10^{-14}$. Prove it to yourself by multiplying the K_a value of HF (7.2×10^{-4}) by the K_b value of F^- (1.4×10^{-11}).

One other equilibrium constant to be examined in this chapter is the **solubility product constant** of a slightly soluble salt, K_{sp}. Keep in mind that this is an equilibrium constant between the ionic compound and a saturated solution of the ions that it forms. Consider the slight ability of AgCl (s) to dissolve in water. The equation for this is AgCl (s) → Ag^+ (aq) + Cl^- (aq). When you write the equilibrium constant expressions for a reaction, solids, liquids, and solvents are not included. This expression is written as $K_{sp} = [Ag^+][Cl^-]$ and has a value of 1.8×10^{-10}. When comparing this to the K_{sp} for $CaSO_4$ (2.4×10^{-5}), you see that the calcium sulfate is more soluble than the silver chloride.

Buffers

DEFINITION OF COMMON BUFFER SYSTEMS

A **buffer** is a solution that resists change in pH when small amounts of acid or base are added. It is usually a solution that is made of approximately equal concentrations of an acid and its conjugate base. The calculation of the pH of a buffer uses exactly the same method as for a common ion.

EXAMPLE: Calculate the pH of a buffer made by mixing 60.0 milliliters (mL) of 0.100 M NH_3 with 40.0 mL of 0.100 M NH_4Cl. The equilibrium constant, K_a, is

$$K_a = 5.6 \times 10^{-10}$$

SOLUTION:

➤ Calculate the molarity of each component in the mixture.

$$(0.0600 \text{ L}) (0.100 \text{ M}) = 0.006 \text{ mole}/0.100 \text{ L} = 0.060 \text{ M } NH_3$$

$$(0.0400 \text{ L}) (0.100 \text{ M}) = 0.004 \text{ mole}/0.100 \text{ L} = 0.040 \text{ M } NH_4Cl$$

➤ Write the equation and fill in the values.

	NH_4	$\rightleftarrows$	H^+	+	NH_3
Initial	0.040 M		0		0.060 M
Δ	$-x$		$+x$		$+x$
At equilibrium	$0.040 \text{ M} - x$		x		$0.060 \text{ M} + x$

➤ Assume the change is negligible.
➤ Write the K_a expression.

$$K_a = \frac{[H^+] [NH_3]}{[NH_4{}^+]}$$

➤ Plug in the values and solve for x.

$$5.6 \times 10^{-10} = \frac{x (0.060)}{0.040}$$

$$x = [H^+] = 3.7 \times 10^{-10} \text{ M}$$

➤ Calculate the pH.

$$pH = 9.4$$

INFLUENCE OF BUFFERS ON A TITRATION CURVE

While titration curves will be covered in more detail later in this chapter, you can use a titration curve to show the impact of a buffer on a solution and how it resists changes in pH. Buffers resist change in pH because they contain an acidic component to neutralize OH^- ions and a basic component to neutralize H^+ ions. Consider the following situation where a different number of moles of HCl in 1 liter of solution produce various pH values (see Figure 6-1). If a buffer is made from 0.2 M acetic acid and 0.2 M sodium acetate, you can see that adding a small amount of the acid has little effect on the pH, causing the line to remain more horizontal. In order for the line to remain horizontal, the buffer concentration must be sufficiently larger than the amount of acid being added.

Even if the buffer were made with half the concentration of acetic acid and sodium acetate, 0.1 M each, the 0.1 M HCl solution would have a pH of 2.72—still shy of the pH of 1 if there was no buffer present at all.
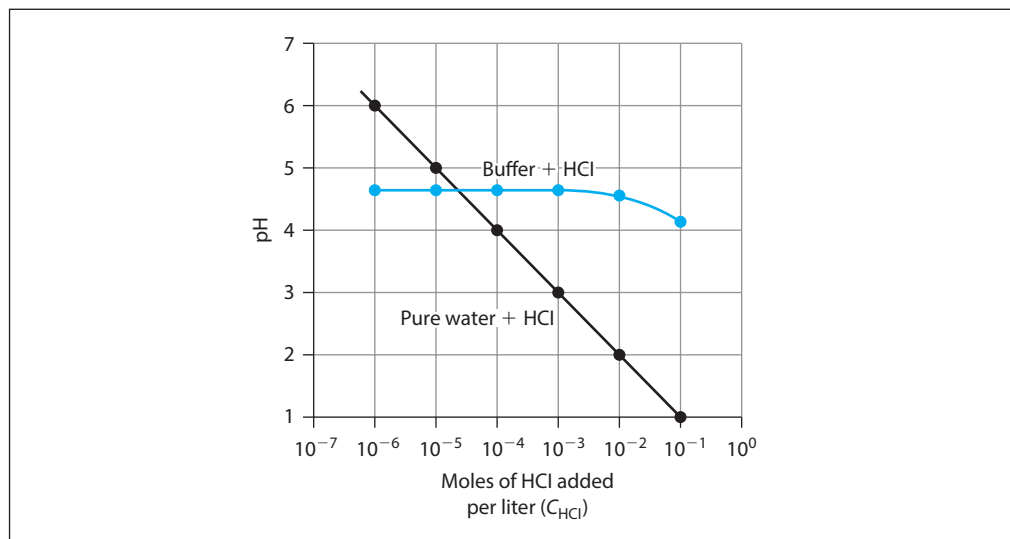
FIGURE 6-1 Influence of buffers on a titration curve.

IONS IN SOLUTIONS

Anions and Cations

When an ionic compound is dissolved in a solution, there is a formation of both negative and positive ions. The negative ions are called **anions**, while the positive ions are called **cations**. For example, when a salt such as sodium chloride is added to water, you get Na^+ and Cl^- as the cation and anion, respectively.

NOMENCLATURE OF IONIC COMPOUNDS

Ionic compounds consist of cations and anions. The name of the cation comes first, and it is named as the **element**. There are a few complex cations, but the most important one is ammonium ion, which has the formula NH_4^{+1}.

The main group elements form cations in a systematic manner. Elements from group I always form +1 cations. Elements from group II always form +2 cations. The metals Al and Ga from group III always form +3 cations. In general, the metals always form cations.

Anions are generally formed from nonmetals, or groups of nonmetals that are covalently bonded. The simple cations and anions and many of the complex anions are listed in the following table.

To name a compound such as Na_3N, the cation Na^{+1} is called **sodium** and the anion N^{-3} is called **nitride**. Therefore, the compound is sodium nitride. AlN is aluminum nitride; Mg_3N_2 is magnesium nitride; and MgO is magnesium oxide.

To write the formula of calcium hydride, the calcium cation is Ca^{+2} and the anion hydride is H^{-1}. Two hydrides are required to balance the +2 charge on the calcium ion, in order to net out to zero overall. So the formula is CaH_2.

TABLE 6-1 Simple and Complex Anions and Cations

Main Group Cations and Simple Anions						
Group IA	**IIA**	**IIIA**	**IVA**	**VA**	**VIA**	**VIIA**
H^+ Hydrogen						H^- Hydride
Li^+ Lithium	Be^{2+} Beryllium	Al^{3+} Aluminum		N^{3-} Nitride	O^{2-} Oxide	F^- Fluoride
Na^+ Sodium	Mg^{2+} Magnesium	Ga^{3+} Gallium			S^{2-} Sulfide	Cl^- Chloride
K^+ Potassium	Ca^{2+} Calcium	In^{3+} Indium			Se^{2-} Selenide	Br^- Bromide
Rb^+ Rubidium	Sr^{2+} Strontium				Te^{2-} Telluride	I^- Iodide
Cs^+ Cesium	Ba^{2+} Barium					

Complex Anions						
Cyanide	CN^-					
Hydroxide	OH^-					
Peroxide	$O_2{}^{-2}$					
Permanganate	$MnO_4{}^-$					
Chromate	$CrO_4{}^{-2}$					
Dichromate	$Cr_2O_7{}^{-2}$					
Carbonate	$CO_3{}^{-2}$	Hydrogen carbonate	$HCO_3{}^-$			
Phosphate	$PO_4{}^{-3}$	Hydrogen phosphate	$HPO_4{}^{-2}$	Dihydrogen phosphate	$H_2PO_4{}^-$	
Phosphite	$PO_3{}^{-3}$	Hydrogen phosphite	$HPO_3{}^{-2}$	Dihydrogen phosphite	$H_2PO_3{}^-$	
Sulfate	$SO_4{}^{-2}$	Hydrogen sulfate	$HSO_4{}^-$			
Sulfite	$SO_3{}^{-2}$	Hydrogen sulfite	$HSO_3{}^-$			
Nitrate	$NO_3{}^-$					
Nitrite	$NO_2{}^-$					
Perchlorate	$ClO_4{}^-$	Perbromate	$BrO_4{}^-$	Periodate	$IO_4{}^-$	
Chlorate	$ClO_3{}^-$	Bromate	$BrO_3{}^-$	Iodate	$IO_3{}^-$	
Chlorite	$ClO_2{}^-$	Bromite	$BrO_2{}^-$	Iodite	$IO_2{}^-$	
Hypochlorite	ClO^-	Hypobromite	BrO^-	Hypoiodite	IO^-	

Complex Cation	
Ammonium	$NH_4{}^+$

A good method to determine how many cations and how many anions are in a formula is the **lowest common denominator method**. The lowest common denominator of the charges is determined (ignoring the signs). This gives the total + charges and the total − charges necessary.

EXAMPLE: Determine the formula of sodium oxide.

SOLUTION: Sodium is Na^{+1} and oxide is O^{-2}. The lowest common denominator of 1 and 2 (the charges) is 2. Thus, the positive charges must total +2 and the negative charges must total −2. So there must be 2 sodium cations and 1 oxide anion, and the formula is Na_2O.

Transition metal cations vary in their possible charges; the charge of the metal must be written in the name as a roman numeral. Thus, copper (II) oxide means that the copper cation is Cu^{+2}. Because oxide is always O^{-2}, the charges balance, and the formula is CuO.

Copper (I) oxide means that the copper cation is Cu^{+1}. Oxide is O^{-2}. The lowest common denominator is 2; thus, there must be two Cu^{+1} cations for every oxide anion. The formula is Cu_2O.

The complex anions must be memorized. Their names, formulas, and net charge are given in the previous table.

EXAMPLE: Write the formula of sodium phosphate.

SOLUTION: The sodium cation is Na^{+1} and the phosphate anion is $PO_4{}^{-3}$. The lowest common denominator of the charges is 3. Thus, there must be 3 sodium cations and 1 phosphate anion to result in a net zero charge for the molecule. So the formula is Na_3PO_4.

HYDRATION AND THE HYDRONIUM ION

When a water solution contains cations and anions, the water molecules will orient themselves depending on whether an anion or cation is nearby. Because water is a polar molecule where oxygen is the negative end, the oxygen of a water molecule will be oppositely attracted to a cation. When a water molecule is oriented toward an anion, the hydrogen atoms of the water molecule will be attracted to the anion. This is because the hydrogen atoms of the water molecule are the positive ends of the molecule and will be attracted to the negative anions. When the ions are surrounded or solvated by water molecules, they are called **hydrated ions**.

Hydrogen ions can also interact with a water molecule. This is found in acid–base chemistry when a proton is in solution. When in solution, the hydrogen ions (protons) will form a coordinate covalent bond to a free pair of electrons on the oxygen atom of a water molecule. This forms the hydronium ion as shown in the reaction $H^+ + H_2O \rightarrow H_3O^+$.

SOLUBILITY

Concentration Units

There are various concentration units that can be used to describe how much solute is dissolved in a certain amount of solution. This section deals with reactions that take place in solution. The concentration unit that is used to make solutions for reaction is **molarity**, which has the symbol **M**, and is defined as:

M = mole solute/liter (L) solution

This definition is also a working equation. There are three variables; if two are known, the third can be calculated.

EXAMPLE: Calculate the molarity of a solution that is prepared by dissolving 1.192 grams (g) of oxalic acid ($C_2H_2O_4$) in water to a total of 100.0 milliliters (mL) of solution.

SOLUTION:

1. Convert the mass of oxalic acid to moles.

    (1.192 g) (1 mole/90.04 g) = 0.01324 mole oxalic acid

2. Convert the milliliters to liters.

    (100.0 mL) (1 L/1000 mL) = 0.1000 L
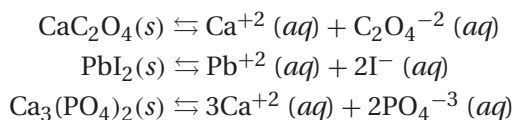
3. Calculate the molarity.

    M = 0.01324 mole/0.1000 L = 0.1324 M

Solubility Product Constant

Insoluble ionic compounds are actually soluble to a very small extent. These solubilities are equilibrium-based processes, with a very small equilibrium constant K.

The solubility equation is written with the solid on the left and the ions in solution on the right, as shown in the following examples:

$$CaC_2O_4(s) \leftrightarrows Ca^{+2}\ (aq) + C_2O_4^{-2}\ (aq)$$
$$PbI_2(s) \leftrightarrows Pb^{+2}\ (aq) + 2I^-\ (aq)$$
$$Ca_3(PO_4)_2(s) \leftrightarrows 3Ca^{+2}\ (aq) + 2PO_4^{-3}\ (aq)$$

The K expression for solubility product constant—called K_{sp}—is written as:

$$K_{sp} = [Ca^{+2}]\ [C_2O_4^{-2}]$$
$$K_{sp} = [Pb^{+2}]\ [I^-]^2$$
$$K_{sp} = [Ca^{+2}]^3\ [PO_4^{-3}]^2$$

The solubility of the compound (in M units) can be calculated from the K_{sp} data.

➤ Write the equation.

$$CaF_2\ (s) \leftrightarrows Ca^{+2}\ (aq) + 2F^-\ (aq)$$
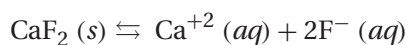
➤ Fill in the values.

	Ca^{+2}	+	$2F^-$
Initial	0		0
Δ	$+x$		$+2x$
At equilibrium	x		$2x$

➤ Write the K_{sp} expression.

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

➤ Plug in value for K_{sp} (found in the following table) and solve for x.

$$4.0 \times 10^{-11} = x(2x)^2 = 4x^3$$
$$x = [Ca^{+2}] = 2.2 \times 10^{-4} \text{ M}$$

TABLE 6-2 Solubility Products of Some Slightly Soluble Ionic Compounds at 25 °C

| Compound	K_{sp}
Aluminum hydroxide [Al(OH)$_3$]	1.8×10^{-33}
Barium carbonate (BaCO$_3$)	8.1×10^{-9}
Barium fluoride (BaF$_2$)	1.7×10^{-6}
Barium sulfate (BaSO$_4$)	1.1×10^{-10}
Bismuth sulfide (Bi$_2$S$_3$)	1.6×10^{-72}
Cadmium sulfide (CdS)	8.0×10^{-28}
Calcium carbonate (CaCO$_3$)	8.7×10^{-9}
Calcium fluoride (CaF$_2$)	4.0×10^{-11}
Calcium hydroxide [Ca(OH)$_2$]	8.0×10^{-6}
Calcium phosphate [Ca$_3$(PO$_4$)$_2$]	1.2×10^{-26}
Chromium (III) hydroxide [Cr(OH)$_3$]	3.0×10^{-29}
Cobalt (II) sulfide (CoS)	4.0×10^{-21}
Copper (I) bromide (CuBr)	4.2×10^{-8}
Copper (I) iodide (CuI)	5.1×10^{-12}
Copper (II) hydroxide [Cu(OH)$_2$]	2.2×10^{-20}
Copper (II) sulfide (CuS)	6.0×10^{-37}
Iron (II) hydroxide [Fe(OH)$_2$]	1.6×10^{-14}
Iron (III) hydroxide [Fe(OH)$_3$]	1.1×10^{-36}
Iron (II) sulfide (FeS)	6.0×10^{-19}
Lead (II) carbonate (PbCO$_3$)	3.3×10^{-14}
Lead (II) chloride (PbCl$_2$)	2.4×10^{-4}
Lead (II) chromate (PbCrO$_4$)	2.0×10^{-14}
Lead (II) fluoride (PbF$_2$)	4.1×10^{-8}
Lead (II) iodide (PbI$_2$)	1.4×10^{-8}
Lead (II) sulfide (PbS)	3.4×10^{-8}
Magnesium carbonate (MgCO$_3$)	4.0×10^{-5}
Magnesium hydroxide [Mg(OH)$_2$]	1.2×10^{-11}
Manganese (II) sulfide (MnS)	3.0×10^{-14}
Mercury (I) chloride (Hg$_2$Cl$_2$)	3.5×10^{-18}
Mercury (II) sulfide (HgS)	4.0×10^{-54}
Nickel (II) sulfide (NiS)	1.4×10^{-24}
Silver bromide (AgBr)	7.7×10^{-13}
Silver carbonate (Ag$_2$CO$_3$)	8.1×10^{-12}
Silver chloride (AgCl)	1.6×10^{-10}
Silver iodide (AgI)	8.3×10^{-17}
Silver sulfate (Ag$_2$SO$_4$)	1.4×10^{-5}
Silver sulfide (Ag$_2$S)	6.0×10^{-51}
Strontium carbonate (SrCO$_3$)	1.6×10^{-9}
Strontium sulfate (SrSO$_4$)	1.6×10^{-9}
Tin (II) sulfide (SnS)	1.0×10^{-26}
Zinc hydroxide [Zn(OH)$_2$]	1.8×10^{-14}
Zinc sulfide (ZnS)	3.0×10^{-23}

Conversely, the K_{sp} can be calculated using solubility data.

EXAMPLE: Calculate the K_{sp} of lead (II) iodide if the solubility is 1.2×10^{-3} M.

SOLUTION: The solubility equals x; therefore, $x = 1.2 \times 10^{-3}$.

➤ Write the equation.

$$PbI_2(s) \leftrightarrows Pb^{+2}\ (aq) + 2I^-\ (aq)$$
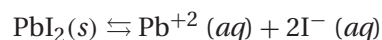
➤ Fill in the values.

	Pb^{+2}	$+$	$2I^-$
Initial	0		0
Δ	$+1.2 \times 10^{-3}$ (x)		$+2.4 \times 10^{-3}$ $(2x)$
At equilibrium	$+1.2 \times 10^{-3}$		$+2.4 \times 10^{-3}$

➤ Write the K_{sp} expression.

$$K_{sp} = [Pb^{+2}]\ [I^-]^2$$

➤ Plug in values and solve for K_{sp}.

$$K_{sp} = (1.2 \times 10^{-3})\ (2.4 \times 10^{-3})^2$$

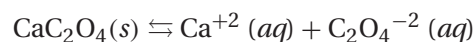$$K_{sp} = 6.9 \times 10^{-9}$$

Common Ion Effect

When one of the ions is added to a solution at equilibrium, the equilibrium shifts to remove the added ion; thus the solubility lessens and more precipitate forms.

EXAMPLE: Calculate the solubility of calcium oxalate in 0.15 M calcium chloride. The equilibrium constant, K_{sp}, is:

$$K_{sp} = 2.3 \times 10^{-9}$$

SOLUTION:

➤ Write the equation.

$$CaC_2O_4(s) \leftrightarrows Ca^{+2}\ (aq) + C_2O_4^{-2}\ (aq)$$

➤ Fill in the values.

	Ca^{+2}	$+$	$C_2O_4^{-2}$
Initial	0.15		0
Δ	$+x$		$+x$
At equilibrium	$0.15 + x$		x

➤ Assume the change is negligible.

➤ Write the K_{sp} expression.

$$K_{sp} = [Ca^{+2}]\ [C_2O_4^{-2}]$$

➤ Plug in values and solve for x.

$$2.3 \times 10^{-9} = (0.15)x$$

$$x = [C_2O_4{}^{-2}] = 1.5 \times 10^{-8} \text{ M}$$

The common ion effect occurs when you add strong acid or strong base to a solution of weak acid or weak base at equilibrium. The added base or acid reacts to form more of one of the components in equilibrium.

EXAMPLE: Calculate the concentration of acetate ion in a solution that is 0.10 M HAc and 0.010 M HCl. The equilibrium constant, K_a, is:

$$K_a = 1.8 \times 10^{-5}$$

SOLUTION:

➤ Write the equation.

$$\text{HAc } (aq) \rightleftharpoons \text{H}^+(aq) + \text{Ac}^- (aq)$$
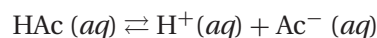
➤ Fill in the table.

	HAc	$\rightleftharpoons$	H$^+$	+	Ac$^-$
Initial	0.10		0.010		0
Δ	$-x$		$+x$		$+x$
At equilibrium	$0.10 - x$		$0.010 + x$		x

➤ Assume the change is negligible.
➤ Write the K_a expression.

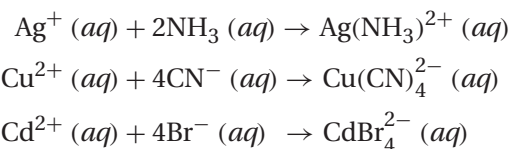$$K_a = \frac{[\text{H}^+]\,[\text{Ac}^-]}{[\text{HAc}]}$$

➤ Plug in values.

$$1.8 \times 10^{-5} = \frac{(0.010)\,x}{0.10}$$

➤ Solve for x.

$$x = [\text{Ac}^-] = 1.8 \times 10^{-4} \text{ M}$$

COMPLEX ION FORMATION

Many metal ions can accept electron pairs from other molecules (Lewis bases), causing the metal ions to act as Lewis acids. When these metal ions accept these electron pairs, a complex ion forms. Some examples are:

$$\text{Ag}^+ (aq) + 2\text{NH}_3 (aq) \rightarrow \text{Ag(NH}_3)^{2+} (aq)$$

$$\text{Cu}^{2+} (aq) + 4\text{CN}^- (aq) \rightarrow \text{Cu(CN)}_4^{2-} (aq)$$

$$\text{Cd}^{2+} (aq) + 4\text{Br}^- (aq) \rightarrow \text{CdBr}_4^{2-} (aq)$$

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CHAPTER 6:
The Unique Nature
of Water and
Its Solutions

Accompanying these complexes are equilibrium constants of formation, or formation constants, K_f. The greater the value of K_f, the more stable the complex of ions will be in aqueous solution.

COMPLEX IONS AND SOLUBILITY

The addition of a Lewis base can drive an equilibrium and allow a slightly soluble salt to be more soluble. For example, AgCl will be only slightly soluble in water according to the reaction:

$$AgCl\ (s) \rightarrow Ag^+\ (aq) + Cl^-\ (aq)$$
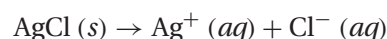
However, should an electron pair be introduced into the preceding reaction, the equilibrium can be shifted toward the right. If cyanide ion were then added to the preceding reaction, CN^- would bond to Ag^+ to form the complex ion $Ag(CN)_2^-$. This complex ion has an equilibrium constant of formation, which is on the order of 10^{21}. The cyanide ion does a terrific job of removing the silver ions from solution, driving the reaction to the right and increasing the solubility of AgCl.

SOLUBILITY AND pH

Lowering the pH increases the solubility of basic ionic compounds. If you calculate the solubility of a basic compound in pure water as a reference, you can compare the solubility at a lower pH.

EXAMPLE: (Part I—Reference): Calculate the solubility of nickel (II) hydroxide in pure water. The solubility constant, K_{sp}, is:

$$K_{sp} = 2.0 \times 10^{-15}$$

SOLUTION:

➤ Write the equation.

$$Ni(OH)_2(s) \leftrightarrows Ni^{+2}\ (aq) + 2OH^-\ (aq)$$
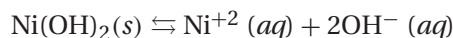
➤ Fill in the values.

	Ni^{+2}	+	$2OH^-$
Initial	0		0
Δ	$+x$		$+2x$
At equilibrium	x		$2x$

➤ Write the K_{sp} expression.

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

➤ Plug in values and solve for x.

$$2.0 \times 10^{-15} = x(2x)^2$$

$$x = [Ni^{+2}] = 7.9 \times 10^{-6}\ M$$

EXAMPLE: (Part II): Calculate the solubility of nickel (II) hydroxide at pH 8.

SOLUTION:

➤ The pOH $= 6$; therefore, $[OH^-] = 1 \times 10^{-6}$ M.

➤ Plug in values using this concentration of OH^-.

$$2.0 \times 10^{-15} = x(1 \times 10^{-6})^2$$

$$x = [Ni^{+2}] = 2 \times 10^{-3} \text{ M}$$

EXAMPLE: (Part III): What is the pH of a saturated solution of nickel (II) hydroxide in pure water?

SOLUTION:

$$[OH^-] = 2x = 2(7.9 \times 10^{-6}) = 1.6 \times 10^{-5} \text{ M}$$

$$pOH = 4.8$$

$$pH = 9.2$$

This says that at any pH less than 9.2, the solubility is $> 7.9 \times 10^{-6}$ M, and as shown previously, at pH 8, the solubility is 2×10^{-3} M.
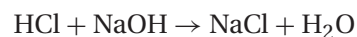
ACID–BASE TITRATIONS

An **acid–base titration** is the addition of a quantity of base of known concentration, using a burette, to a known volume of acid of unknown concentration, until the endpoint is reached. An **indicator compound**, such as phenolphthalein, is added so that a color change occurs at the endpoint. At that point, an equivalent amount of base has been added, and the volume that contains that amount is determined from the initial and final volumes on the burette. The concentration of the acid solution can then be calculated.

EXAMPLE: A 25.0-mL sample of HCl is titrated with 0.0750 M NaOH. The titration requires 32.7 mL of base to reach the endpoint. Calculate the molarity of the HCl.

SOLUTION:

➤ Write the equation for the reaction.

$$HCl + NaOH \rightarrow NaCl + H_2O$$

➤ The stoichiometry of HCl to NaOH is 1 : 1.

➤ Calculate the moles of base added in the titration.

$$(0.0750 \text{ M}) (0.0327 \text{ L}) = 0.00245 \text{ mole NaOH added}$$

➤ Calculate the moles of acid in the solution.

$$(0.00245 \text{ mole base}) (1 \text{ mole acid}/1 \text{ mole base}) = 0.00245 \text{ mole acid}$$

➤ Calculate the molarity of the acid.

$$M = \text{mole}/L = 0.00245 \text{ mole}/0.0250 \text{ L} = 0.098 \text{ M acid}$$

There are two major types of acid–base titrations. One is the addition of strong base to strong acid; the other is the addition of strong base to weak acid. The pH of the endpoint solution can be calculated for the second case.

Addition of Strong Base to Strong Acid

➤ The initial pH is the pH of the strong acid solution.

$$[H^+] = [HA]$$

➤ At the midpoint, calculate the moles of acid left.
➤ Then calculate the M of the acid solution.
➤ Calculate the pH at the midpoint.
➤ At the endpoint, the pH is 7, because the salt is neutral.

Addition of Strong Base to Weak Acid

➤ The initial pH is the pH of the weak acid solution.

$$K_a = x^2/[HA]$$
$$x = [H^+]$$
$$pH = -\log [H^+]$$

➤ At the midpoint, use the **Henderson–Hasselbach equation** after calculating the molarity of each component.

$$pH = pK_a + \log \frac{[A^-]}{[HA]} \quad \text{where } pK_a = -\log K_a$$

➤ At the endpoint, it's the pH of a basic salt solution.

  ➤ Calculate the molarity of the salt.
  ➤ Calculate the K_b.

$$K_b = x^2/[A^-]$$
$$x = [OH^-]$$
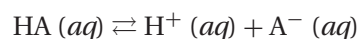
  ➤ Calculate pOH.
  ➤ Calculate pH.

EXAMPLE: A 25.0-mL sample of 0.0875 M acetic acid is titrated with 0.150 M NaOH. Consider the following given values:

$$K_a = 1.8 \times 10^{-5} \quad pK_a = 4.74$$

SOLUTION:

  ➤ Calculate the pH of the initial acid solution.

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

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

$1.8 \times 10^{-5} = x^2/0.0875$

$x = [H^+] = 1.25 \times 10^{-3}$ M

pH = 2.9

➤ Calculate the pH at the point when 5.0 mL of base has been added.

(0.005 L) (0.150 M NaOH) = 7.5×10^{-4} mole base added

➤ Reacts with 7.5×10^{-4} mole acid.

(0.0250 L) (0.0875 M acid) = 2.188×10^{-3} mole acid initially

➤ Subtract 7.5×10^{-4} mole acid that is now gone to get:

1.438×10^{-3} mole acid in 30 mL = 0.0479 M acid, and

7.5×10^{-4} mole conj base in 30 mL = 0.0250 M base

➤ Plug into the Henderson–Hasselbach equation.

$$pH = 4.74 + \log\frac{0.0250}{0.0479}$$

pH = 4.5

➤ Calculate the pH at the endpoint of the titration.

Here, you have added 2.188×10^{-3} mole NaOH to completely neutralize the initial amount of acid. This requires 2.188×10^{-3} mole/0.150 M = 0.0146 L NaOH solution.

$[A^-] = 2.188 \times 10^{-3}$ mole/0.0396 L total = 0.055 M conj base

➤ Calculate $K_b = K_w/K_a = 5.6 \times 10^{-10}$

$K_b = x^2/0.055$ M $= 5.6 \times 10^{-10}$

$x = [OH^-] = 5.5 \times 10^{-6}$ M

pOH = 5.3

pH = 8.7

Indicators

The easiest way to tell the approximate pH value of a solution is via the use of an indicator. **Universal indicators** are usually made from a blend of indicators and can have more than six distinct colors to give more exact pH values. Other indicators, such as **litmus**, have just two colors. When choosing an indicator for a titration, there is much to consider.

Indicators such as **phenolphthalein** are useful during a titration because their change in color tells you when the endpoint has been reached. The reaching of the endpoint is the reaching of the equivalence point as well. Not all indicators turn color at the same pH. This is why you need to pick an indicator with a pK that is close

to the equivalence point. For example, the equivalence point in a titration between NaOH and acetic acid is about 9.2. You would choose phenolphthalein for this reaction because it has a pK of 9.3. If you were to titrate a strong acid and a weak base, then **methyl orange** might be used as an indicator. The pK of this indicator is about 3.7, and it changes color at a pH range of 3.1–4.4.

Neutralization

Neutralization is the process by which an acid and base are mixed together to form a salt and water. A classic example is the reaction between HCl and NaOH to form NaCl and H_2O. Because the three ionic compounds in the reaction are all completely soluble electrolytes, the net ionic reaction for the neutralization of these substances will be:

$$H^+ + OH^- \rightarrow H_2O$$

However, this is not the only type of neutralization that you can find. For example, if you were to have an acid spill in the laboratory, you would use sodium bicarbonate ($NaHCO_3$) or sodium carbonate (Na_2CO_3) to neutralize the spill. In these cases, the acid is neutralized and carbon dioxide is formed. The equations for the reactions are:

$$HCl + NaHCO_3 \rightarrow NaCl \ + H_2O + CO_2$$
$$2HCl + Na_2CO_3 \ \rightarrow 2NaCl + H_2O + CO_2$$
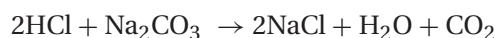
Interpretation of Titration Curves

As a base or acid is titrated, the pH can be measured and plotted to form a **titration curve**. In general, there are three more common shapes to be familiar with and one that is less popular. In Figure 6-2, you can see the titration curve of a strong acid and a strong base. As the strong base is titrated with the strong acid, the pH for the most part stays relatively high until the equivalence point is reached. At the equivalence point, the slope will be the steepest and the pH will be 7.

When a weak base is titrated with a strong acid, the pH will start at a lower basic value and the endpoint will occur at a pH that is on the acidic side of the pH scale. The opposite will occur when a strong base is titrated with a weak acid; the pH will start very basic and the pH at the equivalence point will be in the basic range.

One more case to consider is when a diprotic or polyprotic acid is involved (see Figure 6-3.). In the case of acids such as H_2CO_3 or H_3PO_4, the curves will have more than one equivalence point. Consider the titration of 25 mL of 0.100 M H_2CO_3 with 0.100 M NaOH. The pH starts low as there is just acid present. When the first H^+ ion is completely removed from the acid, you have the first equivalence point, which takes place after 25 mL of base are added. Now the base is titrating against the HCO_3^-. The second equivalence point at 50 mL of base added shows another equivalence point and a steep part of the curve. This shows the complete removal of the H^+ ion from the HCO_3^- to form CO_3^{2-}.
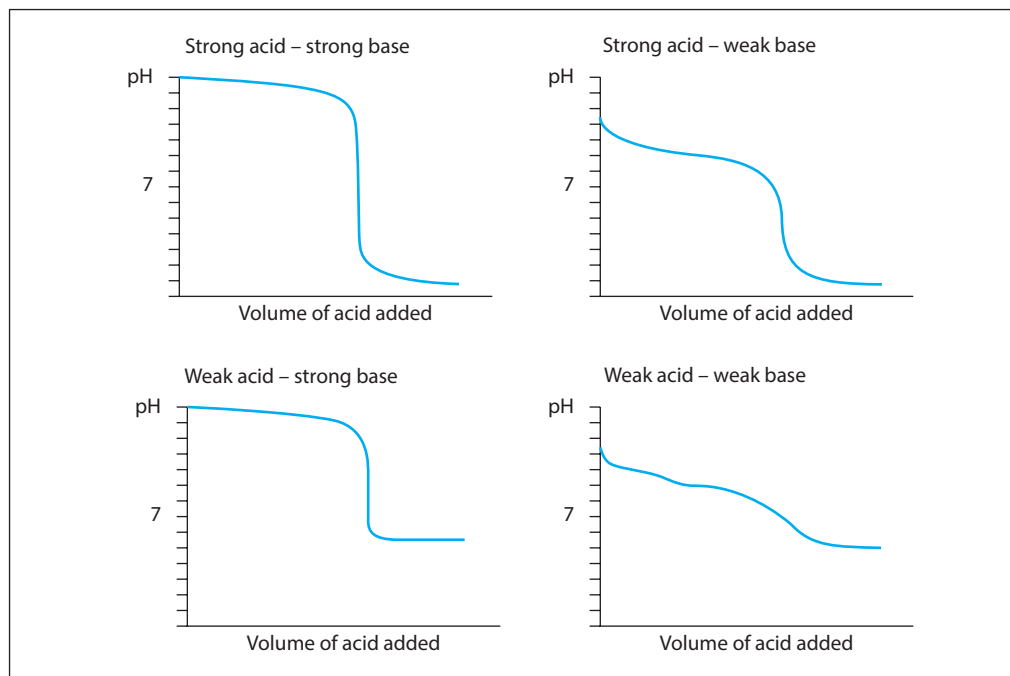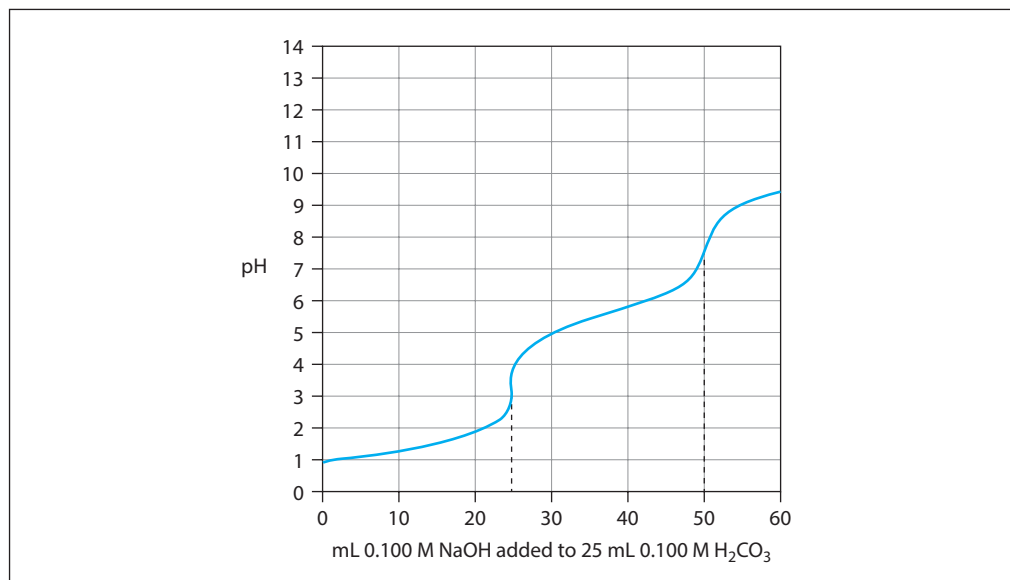
FIGURE 6-2 Titration curves.

FIGURE 6-3 Titration curve when a diprotic or polyprotic acid is involved.

Oxidation–Reduction Reactions

Oxidation–reduction reactions, the third type of reaction in solution (next to precipitation reactions and acid-base reactions), involve the transfer of one or more electrons from one species in the reaction to another.

Any species that loses electrons is **oxidized**. Any species that gains electrons is **reduced**. Oxidation and reduction can be tracked using the oxidation number of each

atom. Each atom in a formula has an oxidation number. It is similar to a charge; for simple ions, the charge and the oxidation number are the same. For atoms of an element, the oxidation number is always zero.

RULES FOR OXIDATION NUMBERS

➤ The oxidation number of an atom in a pure element is zero.

➤ The oxidation number of a simple ion is the same as its charge.

➤ The oxidation number of oxygen is usually -2, except in peroxides, where it is -1.

➤ The oxidation number of hydrogen in a covalent compound is $+1$ unless it is bonded to boron, where it is -1.

➤ The oxidation number of hydrogen in an ionic compound is -1.

➤ The oxidation number of fluorine is always -1.

➤ The sum of all the oxidation numbers in a neutral compound is always zero.

When the oxidation number of an atom decreases from one side of the equation to the other side, that atom is reduced. If an oxidation number increases, that atom is oxidized.

EXAMPLE: State which atom is oxidized and which is reduced in the following equation:

$$Fe + Cu^{+2} \rightarrow Fe^{+2} + Cu$$
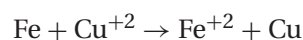
SOLUTION:

1. Because Fe is an element, its oxidation number is 0.
2. Because Cu^{+2} is a simple ion, its oxidation number is $+2$.
3. Fe^{+2} is a simple ion; its oxidation number is $+2$.
4. Cu is an element; its oxidation number is 0.
5. Therefore, Fe is going from 0 to $+2$; Fe is being oxidized.
6. Cu is going from $+2$ to 0; Cu is reduced.

EXAMPLE: Try another problem. Which atom is oxidized and which is reduced?

$$2Sb + 3Cl_2 \rightarrow 2SbCl_3$$
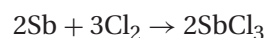
SOLUTION:

1. Because Sb is an element; its oxidation number is 0.
2. Because Cl_2 is an element; its oxidation number of each Cl is 0.
3. Sb in $SbCl_3$ is the ion Sb^{+3}; oxidation number $+3$.
4. Cl in $SbCl_3$ is the ion Cl^{-1}; oxidation number -1.
5. Therefore,

$$Sb^0 \rightarrow Sb^{+3} \qquad \text{oxidation}$$
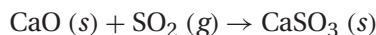$$Cl^0 \rightarrow Cl^{-1} \qquad \text{reduction}$$

COMMON TYPES OF OXIDATION–REDUCTION REACTIONS

A few of the more common classifications of oxidation–reduction reactions are combination reactions, decomposition reactions, single displacement reactions, and combustion reactions.
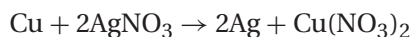
A **combination reaction** occurs when two substances combine to form a third substance.

$$CaO\ (s) + SO_2\ (g) \rightarrow CaSO_3\ (s)$$

A **decomposition reaction** occurs when a single substance decomposes to two or more substances.

$$2KClO_3 \rightarrow 2KCl + 3O_2$$
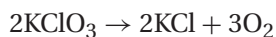
A **single displacement reaction** occurs when an element reacts with an ionic compound and replaces the cation in the compound. The original cation becomes an element.

$$Cu + 2AgNO_3 \rightarrow 2Ag + Cu(NO_3)_2$$

A **combustion reaction** occurs when a substance reacts with oxygen to produce one or more oxides.

$$4Fe + 3O_2 \rightarrow 2Fe_2O_3$$
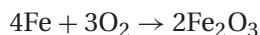
OXIDATION–REDUCTION TITRATIONS

Oxidation–reduction titration typically does not require an indicator compound to be added, because there is often an automatic color change on reaction.

EXAMPLE: A 25.0 mL sample of $MnO_4{}^-$ is titrated with 0.0485 M I^- solution. To reach the endpoint, 18.7 mL of the I^- solution is required. Calculate the molarity of the $MnO_4{}^-$ solution. The balanced equation is:

$$10I^- + 16H^+ + 2MnO_4{}^- \rightarrow 5I_2 + 2Mn^{+2} + 8H_2O$$
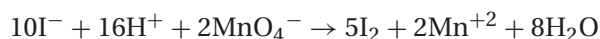
➤ Calculate the moles of I^- added.

$$(0.0485\ \text{mole/L})\ (0.0187\ \text{L}) = 9.07 \times 10^{-4}\ \text{mole}\ I^-\ \text{added}$$

➤ Calculate the moles of $MnO_4{}^-$.

$$(9.07 \times 10^{-4}\ \text{mole}\ I^-)\ (2\ \text{mole}\ MnO_4{}^-/10\ \text{mole}\ I^-)$$
$$= 1.81 \times 10^{-4}\ \text{mole}\ MnO_4{}^-$$

➤ Calculate the molarity of $MnO_4{}^-$.

$$M = 1.81 \times 10^{-4}\ \text{mole}/0.0250\ \text{L} = 0.00726\ \text{M}\ MnO_4{}^-$$