## 10.2.4 ACIDS AND BASES

### 10.2.4.1 Defining Acids and Bases

10.2.4.1.1 Arrhenius Definition

The essential nature of acids and bases was first recognised by the Swedish chemist Svante Arrhenius (1859–1927). On the basis of his experiments with electrolytes, in 1884 Arrhenius postulated that **acids** produce hydrogen ions (H^+) in aqueous solution, whereas **bases** produce hydroxide ions (OH^-).
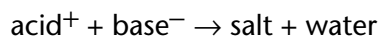
For example:

$$HCl_{(g)} + H_2O \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$$

and

$$NaOH_{(s)} + H_2O \rightarrow Na^+_{(aq)} + OH^-_{(aq)}$$
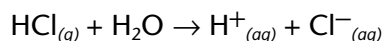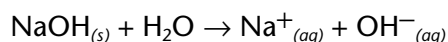
Note that the use of H^+ is regarded as shorthand for H_3O^+, the **hydronium ion**, since it is now known that the bare proton H^+ does not exist as a free species in solution.

This leads to the definition that in Arrhenius acid-base reactions, an acid and a base react to form a salt and water:

$$acid^+ + base^- \rightarrow salt + water$$

The positive ion from the base forms a salt with the negative ion from the acid, while hydrogen ions and hydroxide ions combine to form water, so this is effectively a neutralization reaction. For example, two moles of the base sodium hydroxide ($NaOH$) can combine with one mole of sulphuric acid (H_2SO_4) to form two moles of water and one mole of sodium sulphate:

$$2\ NaOH + H_2SO_4 \rightarrow 2\ H_2O + Na_2SO_4$$
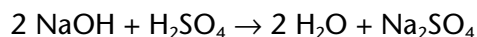
Since the ions of the salt that is formed often remain in solution and are generally unchanged, the essential reaction defined by the Arrhenius concept acids and bases is the formation of water from hydrogen and hydroxide ions:
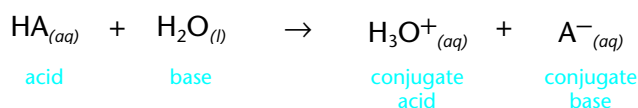
$$H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O$$
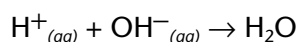
The Arrhenius concept is somewhat limited, however, because it only defines one kind of base—the hydroxide ion.

10.2.4.1.2 Brønsted-Lowry Definition

The Brønsted-Lowry definition of acids and bases, formulated independently by its two proponents Danish chemist Johannes Brønsted (1879–1947) and English chemist Martin Lowry (1874–1936) in 1923, is derived from the notion of *protonation* of bases through the *de-protonation* of acids—that is, the ability of acids to *donate* hydrogen ions (H^+) or protons to bases, which *accept* them. Unlike the Arrhenius definition, the Brønsted-Lowry definition does not refer to the formation of a salt and water, but instead to the formation of conjugate acids and conjugate bases, produced by the transfer of a proton from the acid to the base.

When an acid (HA) dissolves in water, it donates a proton to a water molecule to form a new acid (the **conjugate acid**) and a new base (the **conjugate base**). For example:

$$\underset{\text{acid}}{HA_{(aq)}} + \underset{\text{base}}{H_2O_{(l)}} \rightarrow \underset{\substack{\text{conjugate} \\ \text{acid}}}{H_3O^+_{(aq)}} + \underset{\substack{\text{conjugate} \\ \text{base}}}{A^-_{(aq)}}$$

A **conjugate acid-base pair** comprises two substances related to each other by the donating and accepting of a *single proton*. In the previous equation, there are two conjugate acid-base pairs: HA (acid) and A^- (base), and H_2O (base) and H_3O^+ (acid).

In this definition, an acid is a compound that can donate a proton, and a base is a compound that can receive a proton. An acid-base reaction is thus the removal of a hydrogen ion from the acid and its addition to the base. This does not refer to the removal of a proton from the nucleus of an atom, as that requires levels of energy not attainable through the simple dissociation of acids, but to removal of a hydrogen ion (H^+).

The Brønsted-Lowry definition encompasses the Arrhenius definition, but also extends the concept of acid-base reactions to systems where water is not involved, such as the protonation of ammonia, a base, to form the ammonium ion, its conjugate acid:

$$H^+ + NH_3 \rightarrow NH_4^+$$
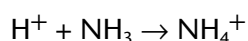
This process may proceed in the absence of water, such as in the reaction of ammonia with acetic acid:

$$CH_3COOH + NH_3 \rightarrow NH_4^+ + CH_3COO^-$$
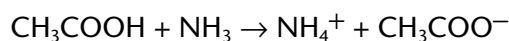
In practice, the Brønsted-Lowry definition is the one most widely used—acid-base reactions are assumed to involve the transfer of a proton (H^+) from an acid to a base.

10.2.4.1.3   Lewis Definition

The Lewis definition of acid-base reactions, devised in 1923 by American chemist Gilbert Lewis (1875–1946), is a further generalisation that encompasses both the Arrhenius and Brønsted-Lowry definitions. Instead of defining acid-base reactions in terms of protons or other bonded substances, the Lewis definition defines a base (referred to as a Lewis base) to be a compound that can donate an **electron pair**, and an acid (a Lewis acid) to be compound that can receive this election pair.

For example, in the classical aqueous acid-base reaction:

$$HCl_{(aq)} + NaOH_{(aq)} \rightarrow H_2O_{(l)} + NaCl_{(aq)}$$
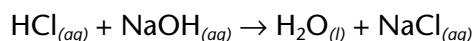
the Lewis definition does not regard this reaction as the formation of salt and water or the transfer of H^+ from HCl to OH^-. Instead, the Lewis definition regards the acid to be the H^+ ion itself, and the base to be the OH^- ion, which has an *unshared electron pair*. Therefore, the acid-base reaction here, according to the Lewis definition, is the donation of the electron pair from OH^- to the H^+ ion. This forms a covalent bond between H^+ and OH^-, producing water (H_2O).

By treating acid-base reactions in terms of electron pairs instead of specific substances, the Lewis definition can be applied to reactions that are not covered by either of the previously discussed definitions. For example, a silver cation behaves as an acid with respect to ammonia, which behaves as a base, in the following reaction:

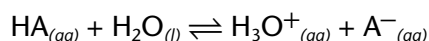$$Ag^+ + 2 : NH_3 \rightarrow [H_3N : Ag : NH_3]^+$$
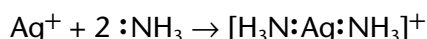
The result of this reaction is the formation of an ammonia-silver adduct.

Lewis acids are sometimes described as **electrophiles** (literally *electron-lover*, from the Greek *philia*, meaning love or affection).

10.2.4.2   Acid Strength

The general reaction that occurs when an acid is dissolved in water can be represented as follows:

$$HA_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)}$$

The double arrows ($\rightleftharpoons$) indicate that reactions actually occur in both directions, and that the two are in **equilibrium**. The equation really represents a competition for the proton between the two bases H_2O and A^-. If H_2O is a much stronger base than A^-, that is, if H_2O has a much greater affinity for H^+ than does A^-, the equilibrium position will be far to the right: most of the acid dissolved will be in the ionised form. Conversely, if A^- is a much stronger base than H_2O, the equilibrium position will *i.e.* far to the left. In this case most of the acid dissolved will be present at equilibrium as HA.

A **strong acid** is one that **completely dissociates** in water: referring to the above equation, the equilibrium lies far to the right. Conversely, a **weak acid** is one where **only a small fraction of the molecules dissociate** in water: where equilibrium position in the above equation lies far to the left (Figure 10.2.4.1).
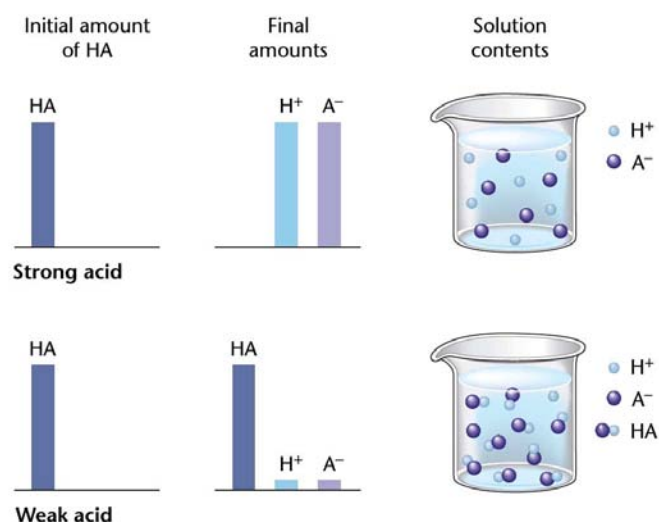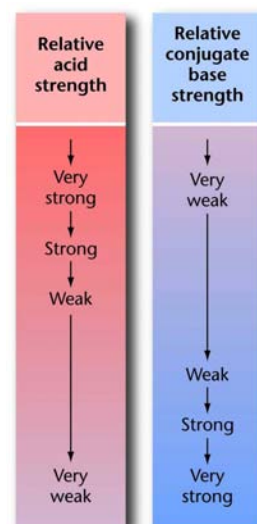

Figure 10.2.4.1   Dissociation in Strong and Weak Acids

Furthermore, a strong acid has a weak conjugate base, and a weak acid a strong conjugate base.

Common strong acids include hydrochloric acid (HCl), nitric acid (HNO_3), perchloric acid ($HClO_4$) and sulphuric acid (H_2SO_4).

Most acids are **oxyacids**, in which the acidic hydrogen is attached to an oxygen atom.

10.2.4.3 Water as an Acid and a Base

A substance is said to be **amphoteric** if it can behave as either an acid or a base. Water is the most common amphoteric substance. Its ionisation involves the transfer of a proton from one water molecule to another to produce a hydroxide ion and a hydronium ion:

$$H_2O_{(l)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$$
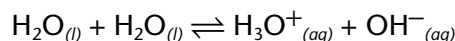
The forward reaction for this process does not occur to a very great extent. In pure water, only a tiny amount of H_3O^+ and OH^- exist. At 25 °C the actual concentrations are:

$$[H_3O^+] = [OH^-] = 1.0 \times 10^{-7} \ M$$

Note that in pure water the concentrations of H_3O^+ and OH^- (written as $[H_3O^+]$ and $[OH^-]$ respectively) are the same, since the two ions are produced in equal numbers in the ionisation reaction. Further, it has been observed that the product of $[H_3O^+]$ and $[OH^-]$ is constant, no matter what the acidity of an aqueous solution. This constant, K_w, is known as the **ion-product constant** for water.

In pure water:

$$K_w = [H_3O^+][OH^-] = (1.0 \times 10^{-7})(1.0 \times 10^{-7}) = 1.0 \times 10^{-14}$$

Thus, in any aqueous solution at **25 °C**, no matter what it contains:, the product of $[H_3O^+]$ (usually simply written as $[H^+]$) and $[OH^-]$ is always equal to 1.0×10^{-14}. If $[H^+]$ goes up, then $[OH^-]$ must go down, and vice versa.

In summary:

1. In a **neutral solution**, $[H^+] = [OH^-]$
2. In an **acidic solution**, $[H^+] > [OH^-]$
3. In a **basic solution**, $[OH^-] > [H^+]$

In each case however:

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

10.2.4.4 The pH Scale

The pH scale is used to describe the acidity of a solution. The pH of a solution is defined as the *negative logarithm of the hydrogen ion concentration*:
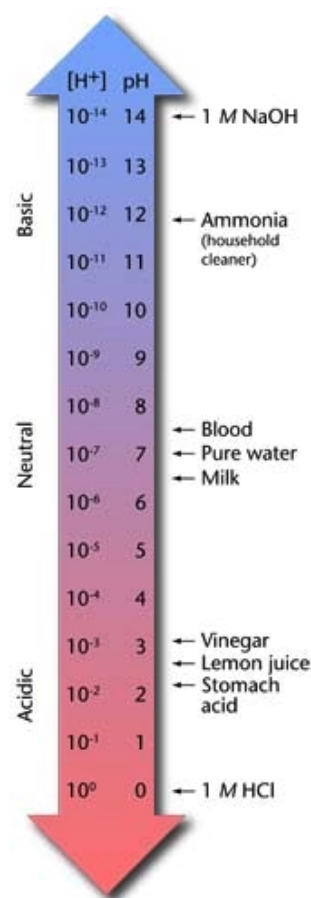
$$pH = -\log[H^+]$$

For example, if:

$$[H^+] = 1.0 \times 10^{-5} \ M$$

then

$$pH = 5.00$$

Note that pH increases as [H+] decreases and vice versa.

Work through the examples in the text to become familiar with pH calculations.

10.2.4.5 Buffered Solutions

A **buffered solution** is one that resists a change in its pH even when a strong acid is added to it. For example, when 0.01 mol of HCl is added to 1 L of pure water, the pH changes from its initial value of 7 to 2, a change of 5 pH units. However, when 0.01 mol of HCl is added to a solution containing both 0.1 *M* acetic acid (CH_3COOH) and 0.1 *M* sodium acetate (CH_3COONa), the pH changes from an initial value of 4.74 to 4.66, a change of only 0.08 of a pH unit. The latter solution is buffered—it undergoes only a very slight change in pH when a strong acid or base is added to it.

A solution is **buffered** by the *presence of a weak acid and its conjugate base*. In the above example, the solution contains both the weak acid, acetic acid, and its conjugate base, the acetate ion.

To understand why we observe this behaviour, consider what happens in an aqueous solution of hydrochloric acid. Since HCl is a strong acid, it effectively dissociates completely to form hydrogen and chloride ions:

$$HCl_{(aq)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$$
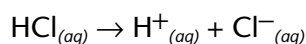
When added to pure water then, this results in a significant change in H^+ ion concentration and pH. If, however, a strong conjugate base such as CH_3COO^- is present, it reacts with most of the H^+ ions:

$$H^+_{(aq)} + CH_3COO^-_{(aq)} \rightarrow CH_3COOH_{(aq)}$$
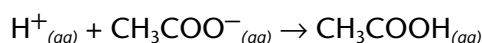
thus reducing the H^+ ion concentration and the magnitude of the change in pH.

Similarly, if a strong base such as $NaOH$ is added to this acetic acid/acetate buffer, most of the OH^- ions combine with protons from the acetic acid present:

$$OH^-_{(aq)} + CH_3COOH_{(aq)} \rightarrow H_2O_{(l)} + CH_3COO^-_{(aq)}$$
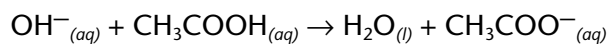
in this case reducing the OH^- ion concentration and the magnitude of the change in pH.

Thus, the general properties of a buffered solution are:

1. The solution contains a weak acid HA and its conjugate base A^-;
2. The buffer resists changes in pH by reacting with any added H^+ or OH^- so that these ions do not accumulate;
3. Any added H^+ reacts with the base A^-:

    $$H^+_{(aq)} + A^-_{(aq)} \rightarrow HA_{(aq)}$$
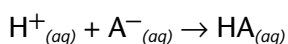
4. Any added OH^- reacts with the weak acid HA:

    $$OH^-_{(aq)} + HA_{(aq)} \rightarrow H_2O_{(l)} + A^-_{(aq)}$$
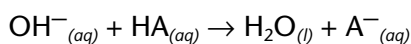
References

Introductory Chemistry—A Foundation (6th Ed), Zumdahl, S.S. and DeCoste, D.J. (Houghton Mifflin, 2009) [ISBN 13: 978-0-618-80327-9]

http://en.wikipedia.org/wiki/

Work directly from text, with exercises:

Chapter 16   Acids and Bases