EXHIBIT J

PRINCIPLES OF MODERN CHEMISTRY

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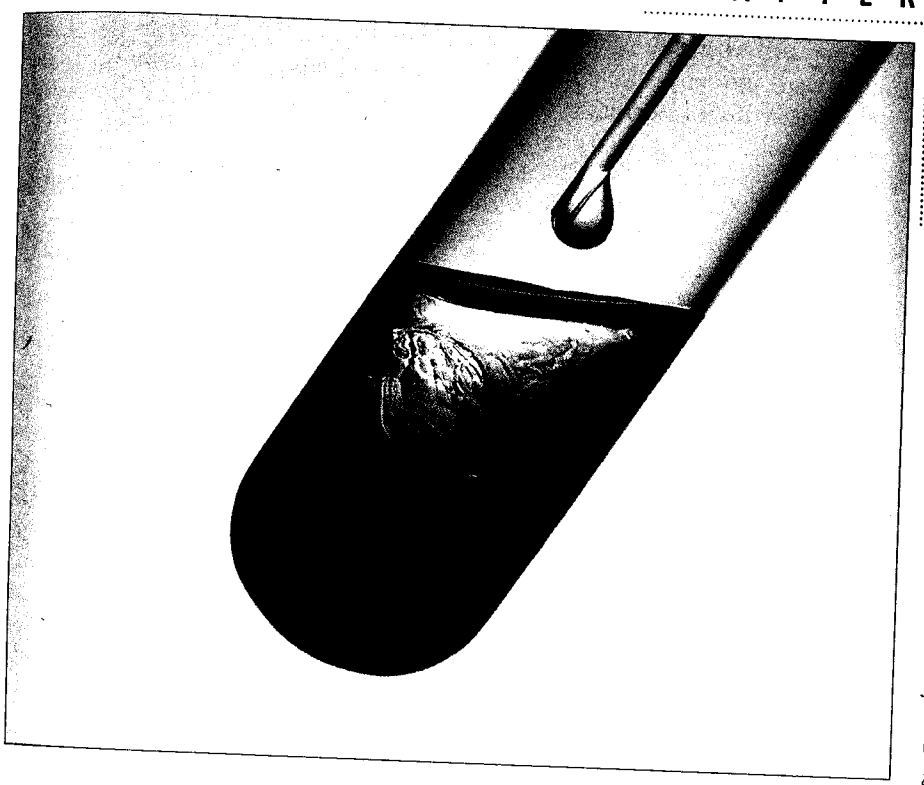
CHAPTER 6



Cobalt chloride: chemical equilibrium in HCl. A solution of $Co(H_2O)_6^{2+}$ + 4 $Cl^- \rightleftarrows CoCl_4^{2-}$ + 6 H_2O shows a concentration of pink $Co(H_2O)_6^{2+}$ ions formed by the addition of water. The $CoCl_4^{2-}$ solution has greater density. (Richard Megna/Fundamental Photographs, New York)

Acid–Base Equilibria

We have established acid–base reactions as one of the major categories of chemical action (Chapter 2) and discussed the use of acid–base titrations (Chapter 4). Now the ideas about chemical equilibrium developed in Chapter 5 are applied to an especially important aspect of acid–base chemistry: calculating how far such reactions proceed before reaching equilibrium.

Although many acid–base reactions take place in the gaseous and solid states and in nonaqueous solutions, in this chapter the focus is on acid–base reactions in aqueous solutions. Such solutions play roles in everyday life. Vinegar, orange juice, and battery fluid are familiar acidic aqueous solutions; basic solutions are produced when such common products as borax, baking soda, and antacids are dissolved in water. Acid–base chemistry will appear many times throughout the rest of this book. We will consider the effects of acidity on the dissolution of solids in Chapter 7, on redox reactions in electrochemical cells in Chapter 10, and on the rates of reaction in Chapter 11. Chapter 21 discusses the manufacture and uses of the workhorse industrial acids (nitric, phosphoric, and sulfuric). Chapter 23 points out the central biochemical roles of amino acids and nucleic acids. The reactions of acids and bases lie at the heart of all chemistry.

6-1 PROPERTIES OF ACIDS AND BASES

In Section 2-5, where the nature of acids and bases was discussed, it was stated that acids increase the concentration of hydrogen ion (H^+) above that in pure water, and bases increase the concentration of hydroxide ion (OH^-). A broader definition of acids and bases, which will be useful in quantitative calculations in this chapter, was proposed independently by Johannes Brønsted and Thomas Lowry in 1923. A **Brønsted–Lowry acid** is defined as a substance that can donate a hydrogen ion, and a **Brønsted–Lowry base** is a substance that can accept a hydrogen ion. In a Brønsted–Lowry acid–base reaction, hydrogen ions are transferred from the acid to the base. For example, when acetic acid is dissolved in water,

$$\underset{\text{Acid}_1}{CH_3COOH(aq)} + \underset{\text{Base}_2}{H_2O(\ell)} \rightleftharpoons \underset{\text{Acid}_2}{H_3O^+(aq)} + \underset{\text{Base}_1}{CH_3COO^-(aq)}$$

hydrogen ions are transferred from acetic acid to water. Acids and bases occur as **conjugate acid–base pairs.** CH_3COOH and CH_3COO^- form such a pair, where CH_3COO^- is the conjugate base of CH_3COOH (equivalently, CH_3COOH is the conjugate acid of CH_3COO^-). In the same way, H_3O^+ and H_2O form a conjugate acid–base pair. [Throughout this chapter, the hydronium ion, $H_3O^+(aq)$, will be used in place of the hydrogen ion, $H^+(aq)$. Chemically the two are equivalent, but the former is a more accurate representation of the true nature of hydrogen ions in water.] The equilibrium that is established may be pictured as the competition between two bases for hydrogen ions. For example, when ammonia is dissolved in water,

$$\underset{\text{Acid}_1}{H_2O(\ell)} + \underset{\text{Base}_2}{NH_3(aq)} \rightleftharpoons \underset{\text{Acid}_2}{NH_4^+(aq)} + \underset{\text{Base}_1}{OH^-(aq)}$$

the two bases NH_3 and OH^- compete for hydrogen ions.

One advantage of the Brønsted–Lowry approach is that it is not limited to aqueous solutions. An example with liquid ammonia as the solvent is

$$\underset{\text{Acid}_1}{HCl(\text{in } NH_3)} + \underset{\text{Base}_2}{NH_3(\ell)} \rightleftharpoons \underset{\text{Acid}_2}{NH_4^+(\text{in } NH_3)} + \underset{\text{Base}_1}{Cl^-(\text{in } NH_3)}$$

The NH_3 acts as a base even though hydroxide ion, OH^-, is not present. The Arrhenius scheme that was introduced in Chapter 2 has been extended and freed from its limitation to aqueous solution.

Some molecules and ions function either as acids or bases depending on reaction conditions, and are called **amphoteric.** The most common example is water itself. Water acts as an acid in donating a hydrogen ion to NH_3 (its conjugate base here is OH^-) and as a base in accepting a hydrogen ion from CH_3COOH (its conjugate acid here is H_3O^+). In the same way, the hydrogen carbonate ion can act as an acid

$$HCO_3^-(aq) + H_2O(\ell) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq)$$

or as a base:

$$HCO_3^-(aq) + H_2O(\ell) \rightleftharpoons H_2CO_3(aq) + OH^-(aq)$$

Autoionization of Water

What happens when water acts as both acid and base in the same reaction? The resulting equilibrium is

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$$\underset{\text{Acid}_1}{} + \underset{\text{Base}_2}{H_2O(\ell)} \rightleftharpoons \underset{\text{Acid}_2}{} + \underset{\text{Base}_1}{OH^-(aq)}$$

or

$$2\,H_2O(\ell) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

This reaction is responsible for the small but measurable **autoionization** of water. The equilibrium expression that results is

$$[H_3O^+][OH^-] = K_w$$

where K_w, the ion product constant for water, has the numerical value 1.0×10^{-14} at 25°C. Note that $H_2O(\ell)$, as the solvent, does not enter the equilibrium expression. The temperature dependence of K_w is given in Table 6-1; all problems in this chapter are assumed to refer to 25°C unless otherwise stated.

Pure water contains no ions other than H_3O^+ and OH^-, and because there is overall electrical neutrality, there must be an equal number of ions of each type. Using the equilibrium expression, this gives

$$[H_3O^+] = [OH^-] = y$$

$$y^2 = 1.0 \times 10^{-14}$$

$$y = 1.0 \times 10^{-7}$$

so that in pure water at 25°C the concentrations of both H_3O^+ and OH^- are 1.0×10^{-7} M.

Table 6-1 Temperature Dependence of K_w

t (°C)	K_w	pH of Water
0	0.114×10^{-14}	7.47
10	0.292×10^{-14}	7.27
20	0.681×10^{-14}	7.08
25	1.01×10^{-14}	7.00
30	1.47×10^{-14}	6.92
40	2.92×10^{-14}	6.77
50	5.47×10^{-14}	6.63
60	9.61×10^{-14}	6.51

Strong Acids and Bases

An aqueous acidic solution contains an excess of H_3O^+ over OH^- ions. A **strong acid** is one that ionizes essentially completely in aqueous solution. When the strong acid HCl (hydrochloric acid) is put in water, the reaction that occurs is

$$\underset{}{} + \underset{}{H_2O(\ell)} \longrightarrow \underset{}{} + \underset{}{Cl^-(aq)}$$

A single rather than a double arrow is used here to indicate that the reaction is essentially complete. Another strong acid is perchloric acid ($HClO_4$). If 0.10 mol of either of these acids is dissolved in enough water to make 1.0 L of solution, a 0.10 M concentration of $H_3O^+(aq)$ results. The acid–base properties of solutions are determined by the concentrations of $H_3O^+(aq)$, so these two strong acids have the same apparent strength in water despite differences in their intrinsic abilities to donate hydrogen ions. Water is said to have a **leveling effect** on a certain group of acids (HCl, HBr, HI, H_2SO_4, HNO_3, and $HClO_4$) in that they all behave as strong acids when water is the solvent; the reactions of these acids with water all lie so far to the right at equilibrium that the differences between the acids are undetectably small. The concentration of H_3O^+ in a 0.10 M solution of *any* strong acid that donates one hydrogen ion per molecule is simply 0.10 M; the OH^- concentration is

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{0.10} = 1.0 \times 10^{-13}\ \text{M}$$

A **strong base** is defined in an analogous fashion, as a base that reacts essentially completely to give $OH^-(aq)$ ion when put in water. The amide ion (NH_2^-) and

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the hydride ion (H^-) are both strong bases. For every mole per liter of either of these ions that is added to water, one mole per liter of $OH^-(aq)$ forms. The other products are NH_3 and H_2, respectively (see Fig. 2-18):

$$H_2O(\ell) + NH_2^-(aq) \longrightarrow NH_3(aq) + OH^-(aq)$$

$$H_2O(\ell) + H^-(aq) \longrightarrow H_2(aq) + OH^-(aq)$$

The important base sodium hydroxide, a solid, increases the OH^- concentration in water when it dissolves:

$$NaOH(s) \longrightarrow Na^+(aq) + OH^-(aq)$$

For every mole of NaOH that dissolves in water, one mole of $OH^-(aq)$ forms, making NaOH a strong base. Strong bases are leveled in aqueous solution in the same way that strong acids are leveled. If 0.10 mol of NaOH or NH_2^- or H^- is put into enough water to make 1.0 L of solution, then in every case

$$[OH^-] = 0.10 \text{ M}$$

$$[H_3O^+] = \frac{1.0 \times 10^{-14}}{0.10} = 1.0 \times 10^{-13} \text{ M}$$

The OH^- contribution from the autoionization of water is negligible in these cases, as was the contribution of H_3O^+ from that source in the case of the 0.10 M HCl or $HClO_4$ solution. Of course, if only a very small amount of strong acid or base were added to pure water (for example, 10^{-7} mol L^{-1}), the autoionization of water would have to be taken into account.

The pH Function

In aqueous solution, the concentration of hydronium ion can range from 10 M to 10^{-15} M. It is convenient to compress this enormous range by introducing a logarithmic acidity scale, called **pH** and defined by

$$pH = -\log_{10}[H_3O^+]$$

Pure water at 25°C has $[H_3O^+] = 1.0 \times 10^{-7}$ M, so

$$pH = -\log_{10}(1.0 \times 10^{-7}) = -(-7.00) = 7.00$$

A 0.10 M solution of HCl has $[H_3O^+] = 0.10$ M, so

$$pH = -\log_{10}(0.10) = -\log_{10}(1.0 \times 10^{-1}) = -(-1.00) = 1.00$$

and at 25°C a 0.10 M solution of NaOH has

$$pH = -\log_{10}\left(\frac{1.0 \times 10^{-14}}{0.10}\right) = -\log_{10}(1.0 \times 10^{-13}) = -(-13.00) = 13.00$$

As these examples show, calculating the pH is especially easy when the concentration of H_3O^+ is exactly a power of 10, because the logarithm is then just the power to which 10 is raised. In other cases, a calculator is needed. If the pH is given, the concentration of H_3O^+ can be calculated by raising 10 to the power (−pH).

The most commonly encountered H_3O^+ concentrations are less than 1 M, so the pH function is defined with a negative sign in order to produce a number that is

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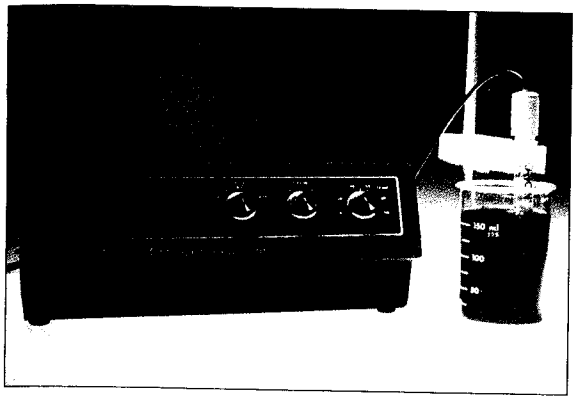


Figure 6–1
A simple pH meter with a digital read-out.

positive in most cases. A *high* pH means a *low* concentration of H_3O^+, and vice versa. At 25°C,

$pH < 7$	Acidic solution
$pH = 7$	Neutral solution
$pH > 7$	Basic solution

At other temperatures the pH of water differs from 7.00 (see Table 6-1). A change of one pH unit implies a change of a factor of 10 (that is, one order of magnitude) in the concentrations of H_3O^+ and OH^-. The pH is most directly measured with a **pH meter** (Fig. 6-1). The mechanism by which pH meters operate will be considered in Chapter 10. Figure 6-2 shows the pH values for several common fluids.

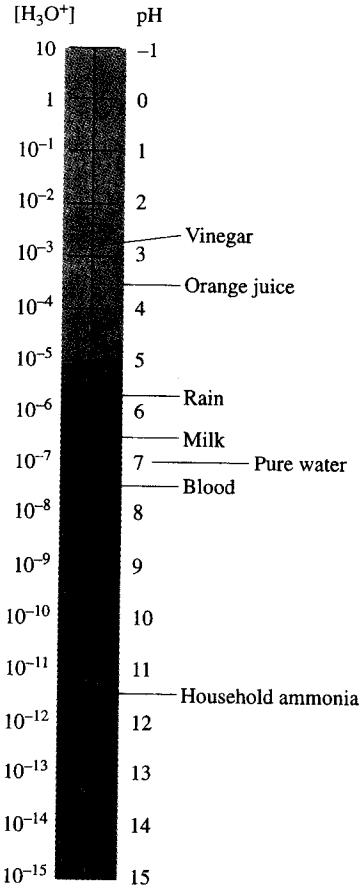


Figure 6–2
Many everyday materials are acidic or basic aqueous solutions with a wide range of pH values.

Example 6-1

(a) A solution is prepared by dissolving 0.23 mol of NaH(*s*) in 2.8 L of water. Calculate its pH.
(b) The pH of some orange juice at 25°C is 2.85. Calculate $[H_3O^+]$ and $[OH^-]$.

Solution

(a) Because H^- is a strong base, it reacts to give 0.23 mol of OH^-:

$$NaH(s) + H_2O(\ell) \longrightarrow Na^+(aq) + OH^-(aq) + H_2(g)$$

The concentration is

$$[OH^-] = \frac{0.23 \text{ mol}}{2.8 \text{ L}} = 8.2 \times 10^{-2} \text{ M}$$

$$[H_3O^+] = \frac{1.0 \times 10^{-14}}{8.2 \times 10^{-2}} = 1.22 \times 10^{-13} \text{ M}$$

The pH is then

$$pH = -\log_{10}(1.22 \times 10^{-13}) = 12.91$$

(b)

$$pH = 2.85 = -\log_{10}[H_3O^+]$$

$$[H_3O^+] = 10^{-2.85}$$

This can be evaluated by using a calculator to give

$$[H_3O^+] = 1.4 \times 10^{-3}\ \text{M}$$

$$[OH^-] = \frac{1.0 \times 10^{-14}}{1.4 \times 10^{-3}} = 7.1 \times 10^{-12}$$

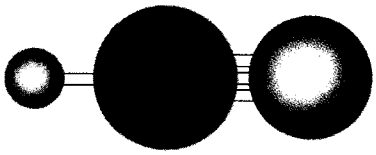
Related Problems: 5, 6, 7, 8

6-2 ACID AND BASE STRENGTH

Acids are classified as strong or weak, depending on whether they are fully or partially ionized in solution. In a **weak acid,** the transfer of hydrogen ions to water does not proceed to completion. A weak acid such as acetic acid is thus also a **weak electrolyte;** its aqueous solutions conduct electricity less well than a strong acid of the same concentration because fewer ions are present. A weak acid produces smaller colligative properties than a strong acid (recall the effect of dissolved acetic acid on the freezing point of water in Fig. 4-17).

The Brønsted–Lowry theory helps to establish a quantitative scale for acid strength. The ionization of an acid (symbolized by "HA") in aqueous solution can be written as

$$HA(aq) + H_2O(\ell) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$



Hydrogen cyanide, HCN, is a highly toxic gas that dissolves in water to form equally toxic solutions of hydrocyanic acid.

where A^- is the conjugate base of HA. The equilibrium expression for this chemical reaction is

$$\frac{[H_3O^+][A^-]}{[HA]} = K_a$$

where the subscript "a" stands for "acid." For example, if the symbol A^- refers to the cyanide ion (CN^-), we write

$$\frac{[H_3O^+][CN^-]}{[HCN]} = K_a$$

where K_a is the **acid ionization constant** for hydrogen cyanide in water and has a numerical value of 6.17×10^{-10} at 25°C. Table 6-2 gives values of K_a for a number of important acids. The useful quantity $pK_a = -\log_{10} K_a$ is also given. The acid ionization constant is a quantitative measure of the strength of the acid in a given solvent (here, water). A strong acid has K_a greater than 1, so [HA] in the denominator is small and the acid ionizes almost completely. In a weak acid, K_a is smaller than 1 and the ionized species have low concentrations; reaction with water proceeds to a limited extent before equilibrium is reached.

The strength of a base is inversely related to the strength of its conjugate acid; the weaker the acid, the stronger its conjugate base, and vice versa. To see this, note that the equation representing the ionization of a base such as ammonia in water can be written as

$$\underset{\text{Acid}_1}{H_2O(\ell)} + \underset{\text{Base}_2}{NH_3(aq)} \rightleftharpoons \underset{\text{Acid}_2}{NH_4^+(aq)} + \underset{\text{Base}_1}{OH^-(aq)}$$

which gives an equilibrium expression of the form