Solution Equilibria: Acids and Bases

Key Concepts

5-2 Ionization of water and the pH scale. Ion-product constant, $K_w$.
5-8 Salts of weak acids and strong bases. Hydrolysis. $K_b$ as a hydrolysis constant.
5-9 Polyprotic acids. Second and third dissociation constants. Predominant species as function of pH.
5-10 Equilibria with slightly soluble salts. Solubility and solubility-product constant $K_{sp}$. Common-ion effect. Separation by selective precipitation.
The words "acid" and "base" are functional terms, and not labels. They describe what a substance does, rather than what it is.

R. von Handler (b. 1931)

Almost all the reactions that a chemist is concerned with take place in solution rather than in gaseous or solid phases. Most of these reactions occur in aqueous solution, where water is the solvent. There are good reasons for this preference for liquid media. Molecules must come into contact to react, and the rates of migration of atoms or molecules within crystals usually are too slow to be useful. In contrast, molecules of gases are mobile, but gas volumes are inconveniently large, and many substances cannot be brought into the gas phase without decomposing. Solutions of reacting molecules in liquids offer an optimum combination of compactness, ease of handling, and rapidity of mixing of different substances.

As we saw in Chapter 1, water has special virtues as a solvent. It is polar, in the sense illustrated in Figure 5-1. The oxygen atom draws the electrons of the O—H bonds toward itself, acquiring a slight negative charge and leaving small positive charges on the two hydrogen atoms. Water therefore can interact with other polar molecules. Moreover, water molecules dissociate to a small extent into H⁺ and OH⁻ ions, a property that is important in acid–base reactions. This chapter is concerned with reactions and equilibria in aqueous solution, especially those involving acids and bases.

5-1 EQUILIBRIA IN AQUEOUS SOLUTIONS
If reactants and products in a chemical reaction are in solution, the form of the equilibrium-constant expression is the same as for gas reactions, but
Water is a polar molecule, with excess electrons and a partial negative charge on the oxygen atom, and an electron deficiency and a partial positive charge on each hydrogen atom. (b) The methane molecule, CH₄, is nonpolar: its electrons are distributed evenly over the molecule. It has no local regions of positive and negative charge to attract water molecules, so water is a poor solvent for methane. (c) Methanol, CH₃OH, is polar, although less so than water. It has an excess of electrons and a small negative charge on the oxygen atom, and a small positive charge on the attached hydrogen atom. Methanol interacts well with water molecules by electrostatic forces, making it soluble in water. (d) Sodium hydroxide, NaOH, dissociates into positive and negative ions. These ions interact strongly with the polar water molecules, so NaOH is extremely soluble in water. Each Na⁺ and OH⁻ ion has a cluster of water molecules surrounding it, with their negative charges closest to the sodium ions and their positive charges closest to the hydroxide ions. The ions are said to be hydrated.
the logical units of concentration are moles per liter of solution (units of molarity).

\[ aA + bB \rightleftharpoons cC + dD \]  \hfill (4-7)

\[ K_{eq} = \frac{[C]^c[D]^d}{[A]^a[B]^b} \]  \hfill (4-8)

Some reactions in aqueous solution involve water as a participant. A well-studied example is the hydrolysis ("splitting by water") of the ethyl acetate molecule to yield acetic acid and ethyl alcohol (ethanol):

\[
\begin{array}{cccc}
\text{O} & & & \\
\text{CH}_3 - \text{C} - \text{O} - \text{C}_2\text{H}_5 + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3 - \text{C} - \text{OH} + \text{HO} - \text{C}_2\text{H}_5 & & & \\
\text{ethyl acetate} & \text{water} & \text{acetic acid} & \text{ethyl alcohol}
\end{array}
\]  \hfill (5-1)

Because all the other participant molecules themselves are polar, they dissolve well in water, which is therefore a good dispersing agent. In addition, water plays a direct role as a reactant molecule.

The equilibrium-constant expression for this reaction, in principle, is

\[ K'_{eq} = \frac{[\text{CH}_3\text{COOH}][\text{C}_2\text{H}_5\text{OH}]}{[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]} \]  \hfill (5-2)

However, since water is present in such excess in its role as solvent, the water concentration is virtually unchanged during the reaction. In dilute solutions this is approximately the concentration of water in its pure state.

\[ [\text{H}_2\text{O}] = \frac{1000 \text{ g liter}^{-1}}{18.0 \text{ g mole}^{-1}} = 55.6 \text{ moles liter}^{-1} \]  \hfill (5-3)

This constant water concentration can be brought over to the left side of equation 5-2 and incorporated into the equilibrium constant, as we saw for condensed phases in Chapter 4, so the equilibrium-constant expression becomes

\[ K_{eq} = K'_{eq}[\text{H}_2\text{O}] = \frac{[\text{CH}_3\text{COOH}][\text{C}_2\text{H}_5\text{OH}]}{[\text{CH}_3\text{COOC}_2\text{H}_5]} \]  \hfill (5-4)

Other reactions in aqueous solution involve ions; an example is the precipitation of silver ions with chloride ions, in the form of insoluble silver chloride:

\[ \text{Ag}^+ + \text{Cl}^- \rightleftharpoons \text{AgCl}(s) \]
In this process water is not a direct reactant or product, but it does interact with the ions to keep them in solution. Any ion in aqueous solution is hydrated, or surrounded by polar water molecules as in Figure 5-1d. If the central ion is positive (a cation), then the negatively charged oxygen atoms of the water molecules are pointed toward it; if the central ion is negative (an anion), the positively charged hydrogen atoms of the water molecules are closest.

Each hydrated ion thus is stabilized by an immediate environment of charges opposite in sign to its own charge. When a salt crystal dissolves in water, the attractions between ions of opposite charge in the crystal are broken. In compensation, similar attractions are set up between ions and the hydrating water molecules. Solubility of salt crystals is the result of a balance or competition between crystal forces and hydration forces. This is why salts do not dissolve in nonpolar solvents such as benzene, which cannot offer hydrating attractions.

5-2  IONIZATION OF WATER AND THE pH SCALE

Water itself ionizes to a small extent:

\[ \text{H}_2\text{O}(l) \rightleftharpoons \text{H}^+ + \text{OH}^- \quad (5-5) \]

Each ion is surrounded with polar water molecules (as Na\(^+\) and OH\(^-\) are in Figure 5-1d). The hydrated state of the proton, H\(^+\), is sometimes represented as \(\text{H}_3\text{O}^+\), meaning \(\text{H}^+ \cdot \text{H}_2\text{O}\). But this is an unnecessary and even misleading notation. A more accurate representation of a hydrated proton would be \(\text{H}_5\text{O}^+\), or \(\text{H}^+ \cdot (\text{H}_2\text{O})_4\), to represent the cluster:

We will assume that H\(^+\) and OH\(^-\), like all other ions, are hydrated in aqueous solution, and we will therefore represent them simply as H\(^+\) and OH\(^-\).
Table 5-1

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$K_w$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>$0.115 \times 10^{-14}$</td>
</tr>
<tr>
<td>25</td>
<td>$1.008 \times 10^{-14}$</td>
</tr>
<tr>
<td>40</td>
<td>$2.95 \times 10^{-14}$</td>
</tr>
<tr>
<td>60</td>
<td>$9.5 \times 10^{-14}$</td>
</tr>
</tbody>
</table>

The equilibrium-constant expression for the dissociation of water is

$$K'_{eq} = \frac{[H^+][OH^-]}{[H_2O]}$$

(5-6)

The constant $[H_2O]$ form can be combined with $K'_{eq}$ as before, producing

$$K_w = 55.6K'_{eq} = [H^+][OH^-]$$

(5-7)

This new equilibrium constant, $K_w$, is called the ion-product constant for water. Like most equilibrium constants, $K_w$ varies with temperature. Some experimental values of the ion-product constant are given in Table 5-1.

Example 1

From the data in Table 5-1 and Le Chatelier’s principle, predict whether the dissociation of water liberates or absorbs heat.

Solution

Since a higher temperature favors dissociation, dissociation is an endothermic or heat-absorbing process. From Appendix 3, $\Delta H_{(diss of H_2O)} = +55.90 \text{ kJ mole}^{-1}$. This is the energy required to break one $\text{O}--\text{H}$ bond, thereby leaving both electrons with the oxygen atom.

It is customary to take $K_w = 1.00 \times 10^{-14}$ as being accurate enough for room-temperature equilibrium calculations. (It is also customary in acid base equilibrium calculations to write $K_w$ as if it were an exact number, $10^{-14}$, rather than $1.00 \times 10^{-14}$.) This means that in pure water, where the concentrations of hydrogen and hydroxide ions are equal,

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

(5-8)

Since large powers of 10 are clumsy to deal with, a logarithmic notation has been devised, called the pH scale (Figure 5-2). (The symbol pH stands for "negative power of hydrogen ion concentration.") The pH is the negative logarithm of $[H^+]$:

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

(5-9)
If the hydrogen ion concentration is $10^{-7}$ mole liter$^{-1}$, then

$$\text{pH} = -\log_{10}(10^{-7}) = 7$$

By an analogous definition,

$$\text{pOH} = -\log_{10}([\text{OH}^-])$$

and the pOH of pure water is also 7. The equilibrium constant $K_w$ also can be expressed in logarithmic terms:

$$\text{p}K_w = -\log_{10}K_w = 14$$

Finally, the equilibrium expression for dissociation of water,

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

can be written

$$\text{pH} + \text{pOH} = 14$$

In an acid solution, $[\text{H}^+]$ is greater than $10^{-7}$, so the pH is less than 7. The ion-product equilibrium still holds, and $[\text{OH}^-]$ can be found from the expression

$$[\text{OH}^-] = \frac{K_w}{[\text{H}^+]} = \frac{10^{-14}}{[\text{H}^+]}$$

or

$$\text{pOH} = \text{p}K_w - \text{pH} = 14 - \text{pH}$$

The approximate pH values of some common solutions are given in Table 5-2.

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**Example 2**

From Table 5-2, what is the hydrogen ion concentration of orange juice? What is the hydroxide ion concentration?
Table 5-2

Acidity of Some Common Solutions

<table>
<thead>
<tr>
<th>Substance</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial concentrated HCl (37% by weight)</td>
<td>~1.1</td>
</tr>
<tr>
<td>1M HCl solution</td>
<td>0.0</td>
</tr>
<tr>
<td>Gastric juice</td>
<td>1.4</td>
</tr>
<tr>
<td>Lemon juice</td>
<td>2.1</td>
</tr>
<tr>
<td>Orange juice</td>
<td>2.8</td>
</tr>
<tr>
<td>Wine</td>
<td>3.5</td>
</tr>
<tr>
<td>Tomato juice</td>
<td>4.1</td>
</tr>
<tr>
<td>Black coffee</td>
<td>5.0</td>
</tr>
<tr>
<td>Urine</td>
<td>6.0</td>
</tr>
<tr>
<td>Rainwater</td>
<td>6.5</td>
</tr>
<tr>
<td>Milk</td>
<td>6.9</td>
</tr>
<tr>
<td>Pure water at 24°C</td>
<td>7.0</td>
</tr>
<tr>
<td>Blood</td>
<td>7.4</td>
</tr>
<tr>
<td>Baking soda solution</td>
<td>8.5</td>
</tr>
<tr>
<td>Borax solution</td>
<td>9.2</td>
</tr>
<tr>
<td>Limewater</td>
<td>10.5</td>
</tr>
<tr>
<td>Household ammonia</td>
<td>11.9</td>
</tr>
<tr>
<td>1M NaOH solution</td>
<td>14.0</td>
</tr>
<tr>
<td>Saturated NaOH solution</td>
<td>~15.0</td>
</tr>
</tbody>
</table>

Solution

Since the pH of orange juice is 2.8, the hydrogen ion concentration is

\[
[H^+] = 10^{-2.8} = 10^{+0.2} \times 10^{-3} = 1.6 \times 10^{-3}
\]

\[= 0.0016 \text{ mole liter}^{-1}\]

The hydroxide ion concentration can be obtained by either of two equivalent methods:

\[
[OH^-] = \frac{10^{-14}}{1.6 \times 10^{-3}} = 6.3 \times 10^{-12} \text{ mole liter}^{-1}
\]

or

\[
pOH = 14 - \text{pH} = 11.2
\]

\[
[OH^-] = 10^{-11.2} = 10^{+0.8} \times 10^{-12} = 6.3 \times 10^{-12} \text{ mole liter}^{-1}
\]

Example 3

What is the ratio of hydrogen ions to hydroxide ions in pure water? In orange juice?
Solution

In pure water the ratio is $10^{-7}$ to $10^{-7}$ or 1 to 1. In orange juice, from Table 5-2, the ratio is $1.6 \times 10^{-3}$ to $6.3 \times 10^{-12}$ or 250,000,000 to 1.

To maintain equilibrium, the added $H^+$ ions from the juice have pushed the water dissociation reaction in the direction of undissociated $H_2O$, thereby removing $OH^-$ ions from the solution. Orange juice is not a particularly strong acid, and the enormous fluctuation of ionic ratios even in this example illustrates the usefulness of power-of-ten and logarithmic (pH, pOH, pK) notation.

5-3 STRONG AND WEAK ACIDS

Arrhenius defined an acid (Chapter 2) as a substance that increases the hydrogen ion concentration of an aqueous solution, and a base as a substance that increases the hydroxide ion concentration. A more general definition was proposed in 1923 by Johannes Brønsted and T. M. Lowry. The Brønsted–Lowry definition can be applied to nonaqueous solutions as well: An acid is any substance that is capable of giving up a hydrogen ion, or proton, and a base is any substance that can combine with and therefore remove a hydrogen ion. Now that we understand that water molecules exist in equilibrium with their dissociated $H^+$ and $OH^-$ ions, we can see that the two definitions are equivalent when water is the solvent. Arrhenius and Brønsted acids are both hydrogen-ion-releasing substances. If a Brønsted base combines with hydrogen ions, it shifts the equilibrium of equation 5-5 in favor of dissociation until balance is restored. More hydroxide ions are formed in the process, so in water a Brønsted base is an Arrhenius base as well.

In aqueous solution, acids are classified as either strong or weak. Strong acids are completely dissociated or ionized, and they include hydrogen acids such as hydrochloric acid ($HCl$) and hydroiodic acid ($HI$), and oxyacids (oxygen-containing acids) such as nitric acid ($HNO_3$), sulfuric acid ($H_2SO_4$), and perchloric acid ($HClO_4$). Each of these acids loses one proton in solution, and the acid-dissociation constant, $K_a$, is so large ($> 10^3$) that too little undissociated acid remains to be measured. ($HSO_4^-$ loses a second proton and is a weak acid.)

Weak acids have measurable ionization constants in aqueous solution, because they do not dissociate completely. Examples (at 25°C) are

\[
\text{Sulfuric: } \quad HSO_4^- \rightleftharpoons H^+ + SO_4^{2-} \quad K_a = \frac{[H^+][SO_4^{2-}]}{[HSO_4^-]} = 1.2 \times 10^{-2}
\] (5-16)
Hydrofluoric: \[ \text{HF} \rightleftharpoons \text{H}^+ + \text{F}^- \quad K_a = \frac{[\text{H}^+][\text{F}^-]}{[\text{HF}]} = 3.5 \times 10^{-4} \quad (5-17) \]

Acetic: \[ \text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+ \quad K_a = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = 1.76 \times 10^{-5} \quad (5-18) \]

Hydrocyanic: \[ \text{HCN} \rightleftharpoons \text{H}^+ + \text{CN}^- \quad K_a = \frac{[\text{H}^+][\text{CN}^-]}{[\text{HCN}]} = 4.9 \times 10^{-10} \quad (5-19) \]

The distinction between strong and weak acids is somewhat artificial. The ionization of HCl is not simply a dissociation; it is, rather, the result of successful competition of H\(_2\)O molecules with Cl\(^-\) ions for the proton, H\(^+\):

\[ \text{HCl} + \text{xH}_2\text{O} \rightleftharpoons \text{H}^+ \cdot (\text{H}_2\text{O})_x + \text{Cl}^- \quad (5-20) \]

In the Brønsted–Lowry theory, any proton donor is an acid, and any proton acceptor is a base (Figure 5-3). Therefore, HCl is an acid, and Cl\(^-\) is its conjugate base. Since HCl loses a proton readily it is a strong acid, and since Cl\(^-\) has so little affinity for the proton it is a weak base. In contrast, HCN is a very weak acid, because relatively few HCN molecules release their proton. Its conjugate base, CN\(^-\), is a strong base by virtue of its high affinity for a proton.

Water is a somewhat stronger base than Cl\(^-\), and when it is present in excess, as in an aqueous solution of HCl, it takes virtually all the protons from HCl, leaving it completely ionized. CN\(^-\) is a much stronger base than H\(_2\)O, so only a small fraction of the protons from HCN become bound to the water molecules. In other words, HCN is only slightly ionized in aqueous solution, as its \(K_a\) of \(4.9 \times 10^{-10}\) indicates.

Because water is present in great excess, any acid whose conjugate base is weaker than H\(_2\)O (i.e., has a lesser affinity for protons than has H\(_2\)O) will be ionized almost completely in aqueous solution. We cannot distinguish between the behavior of HCl and of HClO\(_4\) (perchloric acid) in water solution. Both are completely dissociated and are therefore strong acids. However, for a solvent with a lesser attraction for protons than water, we do find differences between HCl and HClO\(_4\). With diethyl ether as a solvent, perchloric acid is still a strong acid, but HCl is only partially ionized and hence is a weak acid. Diethyl ether does not solvate a proton as strongly as water does (Figure 5-4). (Solvation is a generalization of the concept of hydration, which applies to solvents other than water.) The equilibrium point in the reaction

\[ \text{HCl} + \text{xC}_2\text{H}_5\text{OC}_2\text{H}_5 \rightleftharpoons \text{H}^+ \cdot (\text{C}_2\text{H}_5\text{OC}_2\text{H}_5)_x + \text{Cl}^- \quad (5-21) \]
Browns-Lowry acids and bases in the theory of Brown and Lowry. An acid is any substance that releases protons in solution, and a base is any substance that removes protons by combining with them. HCl is a strong acid because it readily releases H⁺ ions. Cl⁻ is a weak base. From Dickerson and Geis. Chemistry, Matter, and the Universe.

<table>
<thead>
<tr>
<th></th>
<th>Acid</th>
<th>Base</th>
<th>Acidity</th>
<th>$pK_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>Weak acid</td>
<td>Strong base</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HCN</td>
<td>Weak acid</td>
<td>Strong base</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH₃</td>
<td>Weak acid</td>
<td>Strong base</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HF</td>
<td>Moderately weak acid</td>
<td>Strong acid</td>
<td>3.45</td>
<td></td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>Strong acid</td>
<td>Strong acid</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂O</td>
<td>Strong acid</td>
<td>Strong base</td>
<td>1.92</td>
<td></td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>Strong acid</td>
<td>Strong base</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>H⁺</td>
<td>Strong acid</td>
<td>Weak base</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl⁻</td>
<td>Weak base</td>
<td>Strong base</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The table shows the acids and bases with their $pK_a$ values.
Comparison of relative strengths of solvation of a hydrogen ion in (a) liquid ammonia, (b) water, and (c) diethyl ether. The binding between proton and solvent ammonia molecules is extremely strong, and liquid ammonia will take protons from and make strong acids of substances that in aqueous solution are only weak acids. In contrast, diethyl ether is such an ineffectual proton-solvating molecule that many substances that are strong acids in water can retain their proton and be only partially dissociated weak acids in ethyl ether. The + and − represent partial charges arising from local deficiencies and excesses of electrons.

lies far to the left, so HCl is only partially dissociated in ether. Only in an extremely strong acid, such as perchloric acid, does the anion have so little attraction for the proton that it will release it to ether as an acceptor solvent. Clearly, by using solvents other than water, we can see differences in acidity (or proton affinity) that are masked in aqueous solution. This masking of relative acid strengths by solvents such as water is known as the leveling effect.

The dissociation constants for a number of acids in aqueous solution are listed in Table 5-3, with estimates of the $K_a$ for strong acids that are “leveled” by the solvent in aqueous solution. The dissociation of protonated solvent, $\text{H}_3\text{O}^+$, into hydrated protons and $\text{H}_2\text{O}$, represents merely a shuffling of protons from one set of water molecules to another, and must have a $K_{eq}$ of 1.00. In liquid ammonia as a solvent, all acids whose conjugate bases are weaker than $\text{NH}_3$ would be leveled by the solvent and would be totally ionized strong acids. Thus hydrofluoric acid and acetic acid are both strong acids in liquid ammonia.

The leveling effect of solvent and the origin of strong and weak acids are summarized in Figure 5-4. The distinction between strong and weak acids depends on the solvent as much as it does on the inherent properties of the acids themselves. Nevertheless, in aqueous solution the distinction is
<table>
<thead>
<tr>
<th>Acid</th>
<th>HA</th>
<th>A⁻</th>
<th>$K_a$</th>
<th>$pK_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perchloric</td>
<td>HClO₄⁻</td>
<td>ClO₄⁻</td>
<td>$\sim 10^{+8}$</td>
<td>$\sim -8$</td>
</tr>
<tr>
<td>Permanganic</td>
<td>HMnO₄⁻</td>
<td>MnO₄⁻</td>
<td>$\sim 10^{+8}$</td>
<td>$\sim -8$</td>
</tr>
<tr>
<td>Chloric</td>
<td>HClO₃⁻</td>
<td>ClO₃⁻</td>
<td>$\sim 10^{+3}$</td>
<td>$\sim -3$</td>
</tr>
<tr>
<td>Nitric</td>
<td>HNO₃⁻</td>
<td>NO₃⁻</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrobromic</td>
<td>HBr⁻</td>
<td>Br⁻</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrochloric</td>
<td>HCl⁻</td>
<td>Cl⁻</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulfuric (1)</td>
<td>H₂SO₄⁻</td>
<td>HSO₄⁻</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Trichloroacetic</td>
<td>CCl₃COOH⁻</td>
<td>CCl₃COO⁻</td>
<td>$2 \times 10^{-1}$</td>
<td>0.70</td>
</tr>
<tr>
<td>Oxalic (1)</td>
<td>HOOC─COOH</td>
<td>HOOC─COO⁻</td>
<td>$5.9 \times 10^{-2}$</td>
<td>1.23</td>
</tr>
<tr>
<td>Dichloroacetic</td>
<td>CHCl₂COOH⁻</td>
<td>CHCl₂COO⁻</td>
<td>$3.32 \times 10^{-2}$</td>
<td>1.48</td>
</tr>
<tr>
<td>Sulfurous (1)</td>
<td>H₂SO₃⁻</td>
<td>HSO₃⁻</td>
<td>$1.54 \times 10^{-2}$</td>
<td>1.81</td>
</tr>
<tr>
<td>Sulfuric (2)</td>
<td>HSO₄⁻</td>
<td>SO₄²⁻</td>
<td>$1.20 \times 10^{-2}$</td>
<td>1.92</td>
</tr>
<tr>
<td>Phosphoric (1)</td>
<td>H₃PO₄⁻</td>
<td>H₂PO₄⁻</td>
<td>$7.52 \times 10^{-3}$</td>
<td>2.12</td>
</tr>
<tr>
<td>Bromoacetic</td>
<td>CH₂BrCOOH⁻</td>
<td>CH₂BrCOO⁻</td>
<td>$2.05 \times 10^{-3}$</td>
<td>2.69</td>
</tr>
<tr>
<td>Malonic (1)</td>
<td>HOOC─CH₂─COOH⁻</td>
<td>HOOC─CH₂─COO⁻</td>
<td>$1.40 \times 10^{-3}$</td>
<td>2.83</td>
</tr>
<tr>
<td>Chloroacetic</td>
<td>CH₂ClCOOH⁻</td>
<td>CH₂ClCOO⁻</td>
<td>$1.40 \times 10^{-3}$</td>
<td>2.85</td>
</tr>
<tr>
<td>Nitrous</td>
<td>HNO₂⁻</td>
<td>NO₂⁻</td>
<td>$4.6 \times 10^{-4}$</td>
<td>3.34</td>
</tr>
<tr>
<td>Hydrofluoric</td>
<td>HF⁻</td>
<td>F⁻</td>
<td>$3.53 \times 10^{-4}$</td>
<td>3.45</td>
</tr>
<tr>
<td>Formic</td>
<td>HCOOH⁻</td>
<td>HCOO⁻</td>
<td>$1.77 \times 10^{-4}$</td>
<td>3.75</td>
</tr>
<tr>
<td>Benzoic</td>
<td>C₆H₅COOH⁻</td>
<td>C₆H₅COO⁻</td>
<td>$6.46 \times 10^{-5}$</td>
<td>4.19</td>
</tr>
<tr>
<td>Oxalic (2)</td>
<td>HOOC─COO⁻</td>
<td>OOC─COO⁻</td>
<td>$6.4 \times 10^{-5}$</td>
<td>4.19</td>
</tr>
<tr>
<td>Acetic</td>
<td>CH₃COOH⁻</td>
<td>CH₃COO⁻</td>
<td>$1.76 \times 10^{-5}$</td>
<td>4.75</td>
</tr>
<tr>
<td>Propionic</td>
<td>CH₃CH₂COOH⁻</td>
<td>CH₃CH₂COO⁻</td>
<td>$1.34 \times 10^{-5}$</td>
<td>4.87</td>
</tr>
<tr>
<td>Malonic (2)</td>
<td>HOOC─CH₂─COO⁻</td>
<td>OOC─CH₂─COO⁻</td>
<td>$2.03 \times 10^{-6}$</td>
<td>5.69</td>
</tr>
<tr>
<td>Carbonic (1)</td>
<td>CO₃⁻ + H₂O</td>
<td>HCO₃⁻</td>
<td>$4.3 \times 10^{-7}$</td>
<td>6.37</td>
</tr>
<tr>
<td>Sulfurous (2)</td>
<td>HSO₄⁻</td>
<td>SO₄²⁻</td>
<td>$1.02 \times 10^{-7}$</td>
<td>6.91</td>
</tr>
<tr>
<td>Hydrogen sulfide (1)</td>
<td>H₂S⁻</td>
<td>HS⁻</td>
<td>$9.1 \times 10^{-8}$</td>
<td>7.04</td>
</tr>
<tr>
<td>Phosphoric (2)</td>
<td>H₃PO₄⁻</td>
<td>HPO₄²⁻</td>
<td>$6.23 \times 10^{-8}$</td>
<td>7.21</td>
</tr>
<tr>
<td>Ammonium ion</td>
<td>NH₄⁺</td>
<td>NH₃⁻</td>
<td>$5.6 \times 10^{-10}$</td>
<td>9.25</td>
</tr>
<tr>
<td>Hydrocyanic</td>
<td>HCN⁻</td>
<td>CN⁻</td>
<td>$4.93 \times 10^{-10}$</td>
<td>9.31</td>
</tr>
<tr>
<td>Silver ion</td>
<td>Ag⁺ + H₂O</td>
<td>AgOH⁻</td>
<td>$9.1 \times 10^{-11}$</td>
<td>10.04</td>
</tr>
<tr>
<td>Carbonic (2)</td>
<td>HCO₃⁻</td>
<td>CO₃²⁻</td>
<td>$5.61 \times 10^{-11}$</td>
<td>10.25</td>
</tr>
<tr>
<td>Hydrogen peroxide</td>
<td>H₂O₂⁻</td>
<td>HO₂⁻</td>
<td>$2.4 \times 10^{-12}$</td>
<td>11.62</td>
</tr>
<tr>
<td>Hydrogen sulfide (2)</td>
<td>HS⁻</td>
<td>S²⁻</td>
<td>$1.1 \times 10^{-12}$</td>
<td>11.96</td>
</tr>
<tr>
<td>Phosphoric (3)</td>
<td>HPO₄²⁻</td>
<td>PO₄³⁻</td>
<td>$2.2 \times 10^{-13}$</td>
<td>12.67</td>
</tr>
<tr>
<td>Water</td>
<td>H₂O⁻</td>
<td>OH⁻</td>
<td>$1.8 \times 10^{-16}$</td>
<td>15.76</td>
</tr>
</tbody>
</table>

Subscripts:
- HA is the acid form, with acid strength decreasing down the table. A⁻ is the conjugate base, with base strength increasing down the table. The equilibrium is HA⇌H⁺ + A⁻ and the equilibrium-constant expression is $K_a = \frac{[H^+][A^-]}{[HA]}$. $pK_a = -\log_{10} K_a$.

The notation (1) indicates a first dissociation or proton-transfer reaction; (2) indicates a second dissociation; and (3) indicates a third dissociation.

This $K_w$ value for water explicitly uses [H₂O] = 55.6 moles liter⁻¹ in the denominator, for the sake of consistency with the other entries in the table. The standard $K_w$ is obtained by noting that 55.6 $\times$ 1.8 $\times$ 10⁻¹⁶ = 1.0 $\times$ 10⁻¹⁴ = $K_w$. 

Note: The table contains a mix of acid dissociation constants and their corresponding acid dissociation equilibria.
real. As long as the discussion is confined to aqueous solutions (as ours will be from now on), we shall find it useful to think about and to treat the two classes of acids separately.

5-4 STRONG AND WEAK BASES

In Arrhenius’ terminology a base is a substance that decreases the hydrogen ion concentration of a solution. Sodium hydroxide, potassium hydroxide, and similar compounds are bases because they dissolve and dissociate completely in aqueous solution to yield hydroxide ions:

\[
\text{NaOH} \rightleftharpoons \text{Na}^+ + \text{OH}^- \\
\text{KOH} \rightleftharpoons \text{K}^+ + \text{OH}^- \tag{5-22}
\]

These excess hydroxide ions then disturb the water dissociation equilibrium, and combine with some of the protons normally found in pure water:

\[
\text{H}^+ + \text{OH}^- \rightleftharpoons \text{H}_2\text{O} \quad [\text{H}^+] = \frac{K_w}{[\text{OH}^-]} < 10^{-7} \tag{5-23}
\]

In the more generalized Brønsted–Lowry definition, the hydroxide ion itself is the base, because it is the substance that combines with the proton. The Na\(^+\) and K\(^+\) ions merely provide the positive ions that are necessary for overall electrical neutrality for the chemical compound.

The commonly encountered hydroxides of alkali metals (Li, Na, K) all dissolve and dissociate completely to produce the same Brønsted–Lowry base, OH\(^-\). These hydroxides all are strong bases, analogous to strong acids such as HCl and HNO\(_3\). Other substances such as ammonia and many organic nitrogen compounds also can combine with protons in solution and act as Brønsted–Lowry bases. These compounds are generally weaker bases than the hydroxide ion, because they have a smaller attraction for protons. For example, when ammonia competes with OH\(^-\) for protons in an aqueous solution, it is only partially successful. It can combine with only a portion of the H\(^+\) ions, thus

\[
\text{NH}_3 + \text{H}^+ \rightleftharpoons \text{NH}_4^+ \tag{5-24}
\]

will have a measurable equilibrium constant.

There is no logical reason why this reaction cannot be described by an acid-dissociation constant, as in Table 5-3. The ammonium ion, NH\(_4^+\), is the Brønsted–Lowry conjugate acid of the base NH\(_3\). There is no reason why, in an acid–base pair, it is the acid that must be neutral and the base charged, as in HCl/Cl\(^-\) and HCN/CN\(^-\). The NH\(_4^+\) ion is just as respectable an acid as HCl or HCN, and although weaker than HCl, it is actually stronger than HCN. Thus, we can describe the ammonia reaction as an acid dissociation:

\[
\text{NH}_4^+ \rightleftharpoons \text{NH}_3 + \text{H}^+ \quad K_a = 5.6 \times 10^{-10} \quad \text{(from Table 5-3)} \tag{5-25}
\]
or, if we want to focus on the basic behavior of NH₃,

\[
\text{NH}_3 + \text{H}^+ \rightleftharpoons \text{NH}_4^+ \quad K_{\text{eq}} = \frac{1}{K_a} = 1.8 \times 10^{+9} \tag{5-26}
\]

However, chemical language has become trapped by the older acid–base terminology introduced by Arrhenius, and you should be aware of this. Arrhenius thought of a base as a substance that releases OH⁻ ions into aqueous solution. For alkali metal hydroxides such as NaOH the process was straightforward:

\[
\text{NaOH} \rightleftharpoons \text{Na}^+ + \text{OH}^- \tag{5-27}
\]

But what about NH₃? Where do the hydroxide ions come from? Arrhenius assumed that when ammonia dissolved in water the reaction was

\[
\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4\text{OH} \rightleftharpoons \text{NH}_4^+ + \text{OH}^- \tag{5-28}
\]

This brought NH₃ into line by postulating an intermediate—ammonium hydroxide—that dissociated like any other hydroxide. Sodium hydroxide is a strong base that dissociates completely; ammonium hydroxide would be a weak base that dissociates only partially. Arrhenius defined a base-dissociation constant, \( K_b \), as

\[
\text{BOH} \rightleftharpoons \text{B}^+ + \text{OH}^- \quad K_b = \frac{[\text{B}^+][\text{OH}^-]}{[\text{BOH}]} \tag{5-29}
\]

where B usually represents a metal. For ammonia, \( K_a \) and \( K_b \) would be related by

\[
K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{[\text{NH}_4^+][\text{OH}^-][\text{H}^+]}{[\text{NH}_3][\text{H}^+]} = \frac{K_w}{K_a} \tag{5-30}
\]

\[
K_b = \frac{10^{-14}}{5.6 \times 10^{-10}} = 1.8 \times 10^{-5} \tag{5-31}
\]

Unfortunately for Arrhenius’ theory, there is no evidence that ammonium hydroxide, \( \text{NH}_4\text{OH} \), exists as a real compound. It is more accurate to say that the polar ammonia molecule is hydrated like any other polar molecule: \( \text{NH}_3 \cdot (\text{H}_2\text{O})_x \). Ammonia, \( \text{NH}_3 \), combines directly with a proton and with water molecules:

\[
\begin{align*}
\text{NH}_3 + \text{H}^+ + x\text{H}_2\text{O} & \rightleftharpoons \text{NH}_4^+ & \text{(in acid solutions)} \\
\text{NH}_3 + x\text{H}_2\text{O} & \rightleftharpoons \text{NH}_4^+ + \text{OH}^- & \text{(in basic solutions)} \tag{5-32}
\end{align*}
\]

Nevertheless, Arrhenius’ notation is too deeply embedded in the fabric of chemistry to dislodge, and we often will use \( K_b \) for weak bases rather than \( K_a \) for their conjugate acids. In general, the completely dissociated strong bases that we shall encounter will be hydroxide compounds, and the weak bases will be ammonia and organic nitrogen compounds such as those listed in Table 5-4. \( K_b \) always can be found from \( K_a \) and \( K_w \) and the expression

\[
K_a \times K_b = K_w \tag{5-33}
\]
Table 5-4

Dissociation Constants of Some Weak Bases* at 25 °C

<table>
<thead>
<tr>
<th>Base</th>
<th>B</th>
<th>BH⁺</th>
<th>(K_b)</th>
<th>p(K_b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aniline</td>
<td><img src="image" alt="Aniline structure" /></td>
<td><img src="image" alt="Aniline structure" /></td>
<td>4.3 (\times) 10⁻¹⁰</td>
<td>9.37</td>
</tr>
<tr>
<td>Pyridine</td>
<td><img src="image" alt="Pyridine structure" /></td>
<td><img src="image" alt="Pyridine structure" /></td>
<td>1.8 (\times) 10⁻⁹</td>
<td>8.75</td>
</tr>
<tr>
<td>Imidazol</td>
<td><img src="image" alt="Imidazol structure" /></td>
<td><img src="image" alt="Imidazol structure" /></td>
<td>9.1 (\times) 10⁻⁸</td>
<td>7.05</td>
</tr>
<tr>
<td>Hydrazine</td>
<td>N₂H₄</td>
<td>N₂H₅⁺</td>
<td>9.8 (\times) 10⁻⁷</td>
<td>6.01</td>
</tr>
<tr>
<td>Ammonia</td>
<td>NH₃</td>
<td>NH₄⁺</td>
<td>1.79 (\times) 10⁻⁵</td>
<td>4.75</td>
</tr>
<tr>
<td>Trimethylamine</td>
<td>(CH₃)₃N</td>
<td>(CH₃)₃NH⁺</td>
<td>6.4 (\times) 10⁻⁵</td>
<td>4.19</td>
</tr>
<tr>
<td>Methylamine</td>
<td>CH₃—NH₂</td>
<td>CH₃—NH₃⁺</td>
<td>3.7 (\times) 10⁻⁴</td>
<td>3.34</td>
</tr>
<tr>
<td>Dimethylamine</td>
<td>(CH₃)₂NH</td>
<td>(CH₃)₂NH₂⁺</td>
<td>5.4 (\times) 10⁻⁴</td>
<td>3.27</td>
</tr>
</tbody>
</table>

*If B represents the base, the equilibrium equation is B + H₂O ⇌ BH⁺ + OH⁻, in which BH⁺ is the conjugate acid. Base strengths increase down the table, and conjugate acid strengths decrease. The equilibrium-constant expression is

\[K_b = \frac{[BH^+] [OH^-]}{[B]}\]

\[pK_b = -\log_{10} K_b\]

5-5 SOLUTIONS OF STRONG ACIDS AND BASES: NEUTRALIZATION AND TITRATION

When an amount of strong acid is added to water, the effect is that of adding the same amount of hydrogen ions, since the acid is totally dissociated.

Example 4

What is the hydrogen ion concentration of a 0.0100\(M\) nitric acid solution? What is the pH?
**Solution**

\[ [H^+] = 0.010 \text{ mole liter}^{-1} \]
\[ \text{pH} = -\log_{10}(10^{-2}) = 2.00 \]

The solution is quite acidic.

---

**Example 5**

What are the hydrogen ion concentration and the pH of a 0.0050M sodium hydroxide solution?

**Solution**

The hydroxide ion contribution from completely dissociated NaOH is

\[ [OH^-] = 0.0050 \text{ mole liter}^{-1} \]

This large quantity of hydroxide ions will repress the normal dissociation of water and enhance the reaction to the left:

\[ H_2O \leftrightarrow H^+ + OH^- \]

The hydrogen ion concentration is found from the water equilibrium expression:

\[ [H^+] = \frac{K_w}{[OH^-]} = \frac{10^{-14}}{0.0050} = 2.0 \times 10^{-12} \text{ mole liter}^{-1} \]

\[ \text{pH} = -\log_{10}(2.0) - \log_{10}(10^{-12}) = -0.30 + 12.0 = 11.7 \]

The solution is quite basic.

---

**Example 6**

If we mix equal volumes of the solutions of the previous two examples, what will be the pH of the resulting solution?

**Solution**

If equal volumes are mixed, then the concentration of each solute will be halved, since the final volume is twice the volume of each starting solution. The final solution would be 0.0025M in nitric acid and 0.0025M in sodium hydroxide. But acid and base will react and neutralize one another until one or the other is used up:

\[ H^+ + NO_3^- + Na^+ + OH^- \rightleftharpoons H_2O + NO_3^- + Na^+ \]

or simply

\[ H^+ + OH^- \rightleftharpoons H_2O \]

since sodium and nitrate ions take no part in the neutralization reaction. In this case, sodium hydroxide is in shorter supply. When all the base has been neutralized, we still have
0.0050 - 0.0025 = 0.0025 mole liter\(^{-1}\) excess nitric acid

\[ [\text{H}^+] = 0.0025 = 2.5 \times 10^{-3} \text{ mole liter}^{-1} \]

\[ \text{pH} = -\log_{10}(2.5) + 3.0 = 2.6 \]

### Example 7

How many milliliters of 0.10\(M\) HCl must we add to 200 ml of 0.0050\(M\) KOH to bring the pH down to 10.0?

**Solution**

Without HCl, the pH of the potassium hydroxide solution would be 11.7, as in Example 5. Let \(y\) equal the number of milliliters of HCl solution needed to yield a pH of 10.0. Since 0.0050 mole liter\(^{-1}\) is the same as 0.0050 millimoles ml\(^{-1}\), the total number of millimoles (mmoles) of KOH is

\[ n_{\text{KOH}} = 0.0050 \text{ mmmole ml}^{-1} \times 200 \text{ ml} = 1.0 \text{ mmmole} \]

The total number of millimoles of HCl that must be added is

\[ n_{\text{HCl}} = 0.10 \text{ mmmole ml}^{-1} \times y \text{ ml} = 0.10y \text{ mmmole} \]

Since the final solution is basic, \(n_{\text{KOH}} > n_{\text{HCl}}\). The net amount of hydroxide ions left over after partial neutralization by HCl is

\[ n_{\text{base}} = n_{\text{KOH}} - n_{\text{HCl}} = 1.0 - 0.10y \]

The final volume is

\[ V = 200 + y \text{ ml} \]

and therefore the final hydroxide in concentration is

\[ [\text{OH}^-] = \frac{n_{\text{base}}}{V} = \frac{1.0 - 0.10y}{200 + y} \]

A pH of 10.0 means a pOH of 4.0 and \([\text{OH}^-] = 10^{-4} \text{ mole liter}^{-1}\), thus

\[ \frac{1.0 - 0.10y}{200 + y} = 10^{-4} \]

and

\[ y = 9.8 \text{ ml of 0.10 M HCl to be added.} \]

---

**Titration and Titration Curves**

If we add equal numbers of equivalents of a strong acid and a strong base, they will neutralize one another completely, and the pH will be 7.0. As we saw in Chapter 2, this makes possible the titration method of measuring quantities of acid or base.
Example 8

One hundred fifty milliliters of HCl solution of unknown concentration are titrated with 0.10 M NaOH. Eighty milliliters of base solution are required to neutralize the acid. How many moles of HCl were present originally, and what was the acid-solution concentration?

Solution

The number of millimoles of base used is

\[ n_{\text{NaOH}} = 0.10 \text{ mmole ml}^{-1} \times 80 \text{ ml} = 8.0 \text{ mmoles} \]

This must be the same as the number of millimoles of acid originally present, if neutralization was complete.

Thus the original concentration of HCl was

\[ [\text{HCl}]_0 = \frac{8.0 \text{ mmoles}}{150 \text{ ml}} = 0.053 \text{ mmole ml}^{-1} \text{ or mole liter}^{-1} \]

A common way of determining the equivalence point of titration (the point at which neutralization occurs) is with an acid–base indicator. Indicators are weak organic acids or bases that have different colors in their ionized and neutral states (or in two ionized states). If their color change occurs in the neighborhood of pH 7, and if we add a few drops of indicator solution to the solution being titrated, we see this color change at the end point of the titration. We will discuss some common indicators in the section on weak acids. The matching of indicator color-change point and the end point of a titration does not have to be very exact, because the pH swings drastically through several units as neutralization becomes complete. This can make life easy for the analytical chemist, and it is worth looking more closely at the behavior of pH during titration. To illustrate what we have just said, let us calculate the titration curve for a typical strong acid and strong base.

Example 9

Fifty milliliters of 0.10M HNO₃ are titrated with 0.10M KOH, in an experimental arrangement such as that shown in Figure 2-3. Calculate the pH of the solution as a function of the volume of KOH solution added (v, in milliliters).

Solution

It is easiest to treat this calculation in three parts: before neutralization, at neutralization (equivalence point), and after neutralization. Before the equivalence point, calculate how much base has been added, assume that all of this base was used to neutralize some of the acid, and calculate how much acid would remain unneutralized, as a function of the volume of base solution added.
### Table 5-5

**Titration of 50 ml of 0.10/M Nitric Acid by 0.10/M Potassium Hydroxide**

<table>
<thead>
<tr>
<th>Before equivalence point</th>
<th>Base solution added, v (ml)</th>
<th>$50 - v$</th>
<th>$50 + v$</th>
<th>$[\text{H}^+]$</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
<td>1.00</td>
<td>0.100</td>
<td>1.00</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>$\frac{40}{10}$</td>
<td>0.067</td>
<td>1.18</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>$\frac{30}{20}$</td>
<td>0.043</td>
<td>1.37</td>
<td></td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>$\frac{20}{30}$</td>
<td>0.025</td>
<td>1.60</td>
<td></td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>$\frac{10}{40}$</td>
<td>0.011</td>
<td>1.95</td>
<td></td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>$\frac{5}{45}$</td>
<td>0.0053</td>
<td>2.28</td>
<td></td>
</tr>
<tr>
<td></td>
<td>48</td>
<td>$\frac{2}{48}$</td>
<td>0.0020</td>
<td>2.69</td>
<td></td>
</tr>
<tr>
<td></td>
<td>49</td>
<td>$\frac{1}{49}$</td>
<td>0.0010</td>
<td>3.00</td>
<td></td>
</tr>
<tr>
<td></td>
<td>49.9</td>
<td>$\frac{0.1}{49.9}$</td>
<td>0.0001</td>
<td>4.00</td>
<td></td>
</tr>
<tr>
<td></td>
<td>49.99</td>
<td>$\frac{0.01}{49.99}$</td>
<td>0.00001</td>
<td>5.00</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>After equivalence point</th>
<th>Base solution added, v (ml)</th>
<th>$\frac{v - 50}{v + 50}$</th>
<th>$[\text{OH}^-]$</th>
<th>pOH</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>50.01</td>
<td>$\frac{0.01}{50.01}$</td>
<td>0.00001</td>
<td>5.00</td>
<td>9.00</td>
<td></td>
</tr>
<tr>
<td>50.1</td>
<td>$\frac{0.1}{50.1}$</td>
<td>0.0001</td>
<td>4.00</td>
<td>10.00</td>
<td></td>
</tr>
<tr>
<td>51</td>
<td>$\frac{1}{51}$</td>
<td>0.0010</td>
<td>3.00</td>
<td>11.00</td>
<td></td>
</tr>
<tr>
<td>52</td>
<td>$\frac{2}{52}$</td>
<td>0.0020</td>
<td>2.71</td>
<td>11.29</td>
<td></td>
</tr>
<tr>
<td>55</td>
<td>$\frac{5}{55}$</td>
<td>0.0048</td>
<td>2.32</td>
<td>11.68</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>$\frac{10}{60}$</td>
<td>0.0091</td>
<td>2.04</td>
<td>11.96</td>
<td></td>
</tr>
<tr>
<td>70</td>
<td>$\frac{20}{70}$</td>
<td>0.0167</td>
<td>1.78</td>
<td>12.22</td>
<td></td>
</tr>
<tr>
<td>80</td>
<td>$\frac{30}{80}$</td>
<td>0.023</td>
<td>1.64</td>
<td>12.36</td>
<td></td>
</tr>
<tr>
<td>90</td>
<td>$\frac{40}{90}$</td>
<td>0.029</td>
<td>1.54</td>
<td>12.46</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>$\frac{50}{100}$</td>
<td>0.033</td>
<td>1.48</td>
<td>12.52</td>
<td></td>
</tr>
</tbody>
</table>

Original: $n_{\text{HNO}_3} = 50 \text{ ml} \times 0.10 \text{ mmole ml}^{-1} = 5.0 \text{ mmoles}$

Added: $n_{\text{KOH}} = v \text{ ml} \times 0.10 \text{ mmole ml}^{-1}$

Net acid: $n_{\text{acid}} = 5.0 \text{ mmoles} - 0.10v \text{ mmole}$

Total volume: $V = 50 + v \text{ ml}$

Hydrogen ion concentration: $[\text{H}^+]_{\text{net}} = \frac{5.0 - 0.10v}{50 + v} = \frac{50 - v}{50 + v} (0.10) \text{ mmole ml}^{-1}$

The calculation of $[\text{H}^+]$ for various values of $v$ is shown in Table 5-5, and these calculations are plotted with open circles at the left of Figure 5-5. At the equivalence point, the amounts of acid and base are equal and the
Titration curve for typical strong acid and base. Fifty milliliters of 0.10 M HNO₃ are titrated with increasing amounts of 0.10 M KOH. Data are given in Table 5-5. Notice how rapidly the pH changes in the region of the end point, or of exact neutralization of acid by base. Any acid—base indicator that changes color between pH 4 and pH 10 could be used to detect the equivalence point in this titration.

pH is 7.0. After the equivalence point, we only need to calculate how much base was added in excess of that required to neutralize the acid, and use this to find [OH⁻], pOH, and pH:

Original: \( n_{\text{HNO}_3} = 5.0 \) mmole (as before)
Added: \( n_{\text{KOH}} = \nu \text{ ml} \times 0.10 \text{ mmole ml}^{-1} \)
Net base: \( n_{\text{base}} = 0.10\nu - 5.0 \) mmole
Final volume: \( V = 50 + \nu \text{ ml} \)

Hydroxide ion concentration:

\[
[\text{OH}^-] = \frac{0.10\nu - 5.0}{50 + \nu} = \frac{\nu - 50}{\nu + 50} (0.10) \text{ mmole ml}^{-1}
\]

This calculation for several values of \( \nu \) and the corresponding pH values are listed in Table 5-5 and are plotted with solid circles on the right of Figure 5-5. It now is obvious why the choice of an indicator is not too critical in such a titration. Any indicator that changes color between pH 4 and pH 10 will do.

Titrating a weak acid with a strong base, or a weak base with a strong acid, is more complicated because the weak component is only partially
dissociated. Dissociation equilibria of the type discussed in the next section must be used. We will not be concerned in this chapter with such titrations, but they are treated in Appendix 5, with an example of a titration curve corresponding to Figure 5-5.

5-6 EQUILIBRIA WITH WEAK ACIDS AND BASES

Because weak acids are only partially dissociated in water, the contribution of a weak acid such as acetic acid to the hydrogen ion concentration is less than the total concentration of added acid. The equilibrium-constant expression for dissociation of the acid must be used explicitly. These general principles can be illustrated with a concrete example, that of calculating the pH of a solution of 0.0100M acetic acid. As we saw in Example 5-4 for nitric acid, a strong acid, a 0.0100M solution has a pH of 2.00. Because acetic acid is a weak acid and only partially dissociated, a 0.0100M solution will have a hydrogen ion concentration of less than 0.0100M, and a pH greater than 2.0.

It is common to represent the acetate ion, CH₃COO⁻, simply by Ac⁻, and the undissociated acetic acid molecule, CH₃COOH, by HAc as if it were a simple inorganic acid. (The forms OAc⁻ and HOAc also are used, to indicate that acetic acid is an oxyacid with the dissociating proton attached to an oxygen atom.) The dissociation of HAc is incomplete:

$$
HAc \rightleftharpoons H^+ + Ac^- 
$$

and the equilibrium expression describing dissociation is

$$
K_a = \frac{[H^+][Ac^-]}{[HAc]} = 1.76 \times 10^{-5} \quad \text{(from Table 5-3)}
$$

We know the initial overall concentration, c₀, of acetic acid:

$$
c_0 = 0.0100 \text{ mole liter}^{-1}
$$

and we know that at equilibrium some of this acetic acid remains undisassociated and some of it has ionized to acetate ions, Ac⁻:

$$
c_0 = [HAc] + [Ac^-] \quad \text{(mass-balance equation)}
$$

This is called a mass-balance equation, because it states that total acetate is neither created nor destroyed during dissociation. We also know that the concentrations of hydrogen ions and acetate ions are equal, since dissociation of HAc is the only source of H⁺. (It is legitimate to neglect H⁺ from the dissociation of water, since acetic acid represses water dissociation even below its normal small extent.) Thus

$$
[H^+] = [Ac^-] \quad \text{(charge-balance equation)}
$$

This is known as a charge-balance equation, because it states that the total positive charge in the solution must equal the total negative charge. We now
can use these data about conservation of acetate and neutrality of the solution to simplify the equilibrium-constant expression. Let the hydrogen ion concentration that we are seeking be \([\text{H}^+] = y\), and eliminate \([\text{Ac}^-]\) at once using the charge-balance equation:

\[
K_a = \frac{y^2}{[\text{HAc}]} \quad \text{(equilibrium equation)}
\]

\[
c_0 = [\text{HAc}] + y \quad \text{(mass-balance equation)}
\]

The second equation tells us that the concentration of undissociated \(\text{HAc}\) equals the original overall concentration, \(c_0\), minus the amount that has dissociated, \(y\):

\([\text{HAc}] = c_0 - y\)

The equilibrium expression then is

\[
K_a = \frac{y^2}{c_0 - y} \tag{5-34}
\]

Substituting the value of \(K_a\) from Table 5-3, we get

\[
1.76 \times 10^{-5} = \frac{y^2}{0.0100 - y}
\]

or

\[
y^2 + 1.76 \times 10^{-5}y - 1.76 \times 10^{-7} = 0
\]

This is a quadratic equation, which can be solved with the quadratic formula. If \(ay^2 + by + c = 0\), then

\[
y = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \tag{5-35}
\]

For this problem, \(a = 1\), \(b = 1.76 \times 10^{-5}\), and \(c = -1.76 \times 10^{-7}\).

\[
y = \frac{-1.76 \times 10^{-5} \pm \sqrt{3.10 \times 10^{-10} + 7.04 \times 10^{-7}}}{2}
\]

or

\[
y = \frac{-1.76 \times 10^{-5} \pm 8.39 \times 10^{-4}}{2}
\]

Only the positive answer is reasonable, because one cannot have a negative concentration. Thus the answer is

\[
y = 4.11 \times 10^{-4} \text{ mole liter}^{-1}
\]

Under certain physical conditions you can take a shortcut to avoid the quadratic formula. In this example, since you know that the acid is only
slightly dissociated, you can try neglecting \( y \) in the denominator of the equilibrium expression for \( K_a \), thereby assuming that it is small in comparison with 0.0100 mole liter\(^{-1}\), and that the concentration of undisassociated acetic acid is virtually the same as the total acetic acid present. This assumption gives

\[
1.76 \times 10^{-5} = \frac{y^2}{0.0100}
\]

and an approximate answer of

\[
y = 4.2 \times 10^{-4} = 0.00042 \text{ mole liter}^{-1}
\]

This is close to the correct answer of 0.000411 mole liter\(^{-1}\). You can make a quick improvement by using this approximate value in the undisassociated acetate concentration in the denominator:

\[
1.76 \times 10^{-5} = \frac{y^2}{0.0100 - 0.00042}
\]

\[
y = 4.11 \times 10^{-4} \text{ mole liter}^{-1}
\]

Repetition of the foregoing process until the answer remains constant from one cycle to the next is called the method of successive approximation. If your intuition for how much dissociation the acid undergoes is good enough, you can often solve an equilibrium problem by an approximate solution and a quick correction in less time than it takes to solve the quadratic formula. If your original guess is not so good, two or three cycles of approximation may be required before you arrive at an unchanging value for \( y \).

As our results show, acetic acid is indeed only slightly dissociated at 0.0100\(M\) concentration. Of the initial 0.0100 mole liter\(^{-1}\), 0.000411 mole has dissociated, and 0.0096 mole remains as dissolved but undisassociated HAc molecules. The percent dissociation is

\[
\frac{4.11 \times 10^{-4} \text{ mole}}{0.0100 \text{ mole}} \times 100 = 4.11\%
\]

Since the hydrogen ion concentration is \([H^+] = 4.11 \times 10^{-4} M\), the pH of this solution is 3.39.

What happens if we dilute the acetic acid solution? Does a greater or lesser percent of the acetic acid then dissociate? Does the pH increase or decrease?

---

**Example 10**

What are the pH and percent dissociation in a solution of 0.00100\(M\) acetic acid?
Solution

The equilibrium expression is as before:

\[ K_a = \frac{y^2}{c_0 - y} \]

\[ 1.76 \times 10^{-5} = \frac{y^2}{0.00100 - y} \]

Neglecting \( y \) in comparison with \( c_0 \), the approximate solution is

\[ 1.76 \times 10^{-5} = \frac{y^2}{0.00100} \]

\[ y = 1.33 \times 10^{-4} \text{ mole liter}^{-1} \]

and the solution obtained by using this value to correct the undissociated HAc concentration is

\[ y = 1.24 \times 10^{-4} \text{ mole liter}^{-1} \]

Using this second value to correct \( c_0 \) in another cycle of approximation makes no change in \( y \), so the process can be halted. Now the pH is 3.91 instead of 3.39, and the percent dissociation is

\[ \frac{1.24 \times 10^{-4} \text{ mole}}{0.00100 \text{ mole}} \times 100 = 12.4\% \]

Although the actual hydrogen ion concentration is lower (witness the larger pH), a greater fraction of the HAc present is dissociated into ions. This is Le Chatelier’s principle again. If a solution containing HAc, H\(^+\), and Ac\(^-\) is diluted, thereby lowering its total concentration of all ions and molecules, the equilibrium will attempt to reestablish itself, as reactions change, in the direction that will increase the total concentration of solute particles of one kind or another. Compare this behavior with the effect of increasing the pressure on the ammonia gas equilibrium in Chapter 4.

Indicators

An indicator is a weak acid (or a weak base) that has sharply different colors in its dissociated and undissociated states. Methyl orange (Figure 5-6) is a complex organic compound that is red in its neutral, un-ionized form and yellow when ionized. It can be represented as the weak acid HIn:

\[ \text{HIn} \rightleftharpoons \text{H}^+ + \text{In}^- \]

red \quad yellow

Adding acid shifts the indicator equilibrium to the left, and adding base shifts it to the right. Hence methyl orange is red in acids and yellow in bases.
The basic form (a) and acid form (b) of the indicator methyl orange. The different colors of the two structures, yellow and red, give methyl orange its usefulness in displaying the pH of a solution into which it has been introduced. The complex structure can be symbolized by an ion, $\text{In}^-$, which can combine with a proton as shown at the bottom of the figure.

The intensity of color from indicators such as methyl orange is so great that the colors can be seen easily even when the amount added to a solution is too small to have an appreciable influence on the pH of the solution. Nevertheless, the ratio of dissociated to undissociated indicator depends on the hydrogen ion concentration

$$K_a = \frac{[\text{H}^+][\text{In}^-]}{[\text{HIn}]} \quad (5-36)$$

and

$$\frac{[\text{In}^-]}{[\text{HIn}]} = \frac{K_a}{[\text{H}^+]} \quad (5-37)$$

$$\log_{10}\left(\frac{[\text{In}^-]}{[\text{HIn}]}\right) = \text{pH} - pK_a \quad (5-38)$$

For methyl orange, $K_a = 1.6 \times 10^{-4}$ and $pK_a = 3.8$. The neutral (red) and dissociated (yellow) forms of the indicator are present at equal concentrations when the pH = 3.8. The eye is sensitive to color changes over a range of concentration ratios of approximately 100, or over two pH units. Below pH 2.8, a solution containing methyl orange is red, and above ap-
proximately 4.8 it is clearly yellow. As you can see from Figure 5-5, an indicator change over two pH units is quite satisfactory for strong acid–base titrations.

Methyl orange could be used for the titration in Figure 5-5, even though its pK_a is far from the titration equivalence point of 7.0, only because the change in pH at the equivalence point is so large. For titrations of weak acids, this would not be true, and it would be better to pick an indicator with a pK_a closer to the expected equivalence point. Other indicators are shown in Figure 5-7, along with the pH range in which their color changes occur. Phenolphthalein is a particularly convenient and common indicator, which changes from colorless to pink in the range of pH 8 to 10.

**Contribution to [H^+] from Dissociation of Water**

Nothing has been said in the discussions of either strong acids or weak acids about a contribution to the hydrogen ion concentration from the dissociation of water itself. It has been tacitly assumed that all H^+ comes from the acid. This is a valid assumption for all but the most dilute solutions of very weak acids such as HCN. The correction for water dissociation seldom is necessary, so it will not be covered in this chapter. A complete treatment is given in Appendix 5.

**Figure 5-7**

Some common acid–base indicators, with the pH ranges in which their color changes occur. The choice of an indicator for an acid–base titration depends on the expected pH at the equivalence point of the titration and the width of swing of pH values as the equivalence point is passed.
5-7 WEAK ACIDS AND THEIR SALTS

What will happen to a weak acid such as acetic acid if we add some sodium acetate (NaAc), which is the salt of a strong base (NaOH) and acetic acid? The salt will dissolve and dissociate completely into sodium and acetate ions. From Le Chatelier’s principle, we would expect these added acetate ions to force the weak acetic acid equilibrium system in the direction of less dissociation. This is exactly what happens. The acid-equilibrium expression is the same:

\[ K_a = \frac{[H^+][Ac^-]}{[HAc]} \]  \hspace{1cm} (5-39)

However, two sources of acetate ions now exist: NaAc and HAc. The acetate ion supplied by sodium acetate is measured by \( c_s \), the total molarity of the salt, since dissociation is complete. Acetate concentration from acetic acid is measured by the hydrogen ion concentration, since every dissociation of HAc to produce \( \text{Ac}^- \) also produces a proton. Therefore, the total acetate ion concentration is

\[ [\text{Ac}^-]_{\text{total}} = [\text{Ac}^-]_{\text{NaAc}} + [\text{Ac}^-]_{\text{HAc}} = c_s + [H^+] \]  \hspace{1cm} (5-40)

(Again, we have neglected any protons contributed by the dissociation of water.) The concentration of un-ionized acetic acid is the overall acid concentration, \( c_a \), less the acetate from dissociation:

\[ [\text{HAc}] = c_a - [\text{Ac}^-]_{\text{HAc}} = c_a - [H^+] \]  \hspace{1cm} (5-41)

If we represent the hydrogen ion concentration by \( y \), we have

\[ K_a = \frac{y(c_s + y)}{(c_a - y)} \]  \hspace{1cm} (5-42)

When the added salt concentration, \( c_s \), is zero, this is the simple weak acid-dissociation equilibrium expression that we have seen previously in equation 5-34.

Example 11

What are the pH and percent dissociation of a solution of 0.010\( M \) acetic acid in the presence of (a) no NaAc, (b) 0.0050\( M \) NaAc, and (c) 0.010\( M \) NaAc?

Solution

From Le Chatelier’s principle, we would expect the dissociation of HAc to be repressed as more NaAc is added. The pH should increase and the percent dissociation should decrease. (a) This problem was already solved in Section 5-6, yielding pH 3.39 and 4.11% dissociation. (b) For \( c_s = 0.0050 \) mole liter\(^{-1} \),
\[ 1.76 \times 10^{-5} = \frac{y(0.0050 + y)}{0.010 - y} \] (from equation 5-42)

This is most easily solved by successive approximations. As a first approximation we can assume that \( y \) will be smaller than 0.0050 or 0.010, and we can therefore neglect it when it is added to or subtracted from these quantities:

\[ y_1 = 1.76 \times 10^{-5} \times \frac{0.010}{0.0050} = 3.52 \times 10^{-5} = 0.000035 \text{ mole liter}^{-1} \]

As a second approximation, we can use this trial value of \( y \) to “correct” 0.0050 to 0.005035, and 0.010 to 0.009965, and solve the equation again:

\[ y_2 = 1.76 \times 10^{-5} \times \frac{0.009965}{0.005035} = 3.48 \times 10^{-5} \text{ mole liter}^{-1} \]

A third approximation is unnecessary, and the answer should be rounded to \( 3.5 \times 10^{-5} \) mole liter\(^{-1}\):

\[ \text{pH} = 5 - \log_{10} 3.5 = 5 - 0.54 = 4.46 \]

\[ \text{Percent dissociation} = \frac{3.5 \times 10^{-5}}{0.010} \times 100 = 0.35\% \]

(c) For \( c_s = 0.010 \text{ mole liter}^{-1} \),

\[ y = [H^+] = 1.76 \times 10^{-5} \text{ mole liter}^{-1} \]
\[ \text{pH} = 4.75 \]
\[ \text{Percent dissociation} = 0.18\% \]

Notice that the acetic acid now dissociates so little that even the first approximation is adequate.

Results for these and a few other sodium acetate concentrations are listed in Table 5-6 and are plotted in Figure 5-8. The first salt added has a

| Table 5-6 |
|---|---|---|---|---|---|---|
| **Effect of Adding Sodium Acetate to 0.010M Acetic Acid Solution** |
| \( c_s \): & 0.0 & 0.001 & 0.002 & 0.005 & 0.010 & 0.020 |
| pH: & 3.4 & 3.8 & 4.1 & 4.5 & 4.8 & 5.1 |
| Percent dissociation of acetic acid: & 4.1 & 1.5 & 0.84 & 0.35 & 0.18 & 0.09 |
Figure 5-8

The effect of added sodium acetate on the dissociation of acetic acid. Data plotted here are listed in Table 5-6, and were calculated as explained in the text. The first salt added represses acetic acid dissociation to a great extent and causes a rapid increase in pH. Later additions are not as effective.

large effect on the degree of dissociation and pH; later additions of salt cause less change. When acid and salt are present in equal concentrations, the pH is equal to the $pK_a$ of the acid.

Buffers

If the concentrations of a solution of a weak acid and a salt of the acid anion are reasonably high, then the solution is resistant to changes in hydrogen ion concentration.

Example 12

A solution is 0.050$M$ in HAc and 0.050$M$ in NaAc. Calculate the change in pH when 0.0010 mole of hydrochloric acid (HCl) is added to a liter of solution, assuming that the volume increase upon adding the HCl is negligible. Compare this to the pH if the same amount of HCl is added to a liter of pure water.
Solution

Before adding HCl the acetic acid equilibrium is

$$K_a = \frac{[H^+][Ac^-]}{[HAc]} = \frac{y(0.050)}{(0.050)}$$

Thus

$$y = K_a = 1.76 \times 10^{-5} \text{ mole liter}^{-1}$$
$$\text{pH} = pK_a = 4.75$$

(Again, we were justified in ignoring $y$ in the [Ac$^-$] and [HAc] terms because the value is small compared to 0.050.)

The added protons from HCl combine with acetate ions to form more acetic acid:

$$\text{Ac}^- + \text{H}^+ \text{ (from HCl)} \rightarrow \text{HAc}$$

Thus to a good approximation, all the added protons are used up, and the new acetic acid and acetate concentrations are

$$[\text{HAc}] = 0.050 + [\text{H}^+]_{\text{HCl}} = 0.051 \text{ mole liter}^{-1}$$
$$[\text{Ac}^-] = 0.050 - [\text{H}^+]_{\text{HCl}} = 0.049 \text{ mole liter}^{-1}$$

$$K_a = \frac{y(0.049)}{(0.051)}$$

$$y = 1.76 \times 10^{-5} \times \frac{0.051}{0.049} = 1.83 \times 10^{-5} \text{ mole liter}^{-1}$$

$$\text{pH} = 5 - 0.26 = 4.74$$

The pH changes from 4.75 to 4.74, a difference of only 0.01 unit. In the absence of HAc and NaAc, the same concentration of HCl would produce a pH of 3.0.

This resistance to pH change is called **buffering action**, and the solution of HAc and NaAc is an acetate buffer. Buffers are used widely for pH control in laboratory chemistry, in the chemical industry, and in living organisms. A carbonate buffer system in your bloodstream, involving the reaction

$$\text{H}^+ + \text{HCO}_3^- \Leftrightarrow \text{H}_2\text{CO}_3 \Leftrightarrow \text{CO}_2 + \text{H}_2\text{O}$$ (5-43)

maintains the blood pH around 7.4. When a biochemist studies enzyme activity in the laboratory, he must use a buffer system to maintain a constant pH during the experiments, otherwise his results may have little meaning. One of the sillier disputes in commercial advertising is that between two pharmaceutical companies as to whether buffers added to aspirin to combat an acid reaction in the stomach are a benefit or an adulterant.
In general, if the concentration of strong acid added to a buffer solution is \( y \) moles liter\(^{-1} \), the equilibrium equation becomes

\[
K_a = \frac{[H^+][A^-]}{[HA]} = \frac{[H^+](c_s - y)}{c_a + y}
\]  \hspace{1cm} (5-44)

in which \( c_s \) and \( c_a \) are the salt and buffering acid concentrations, respectively. After addition of the foreign acid, the hydrogen ion concentration is

\[
[H^+] = K_a \frac{(c_a + y)}{(c_s - y)}
\]  \hspace{1cm} (5-45)

and the pH is

\[
pH = pK_a + \log_{10} \frac{(c_s - y)}{(c_a + y)}
\]  \hspace{1cm} (5-46)

If base is added, hydrogen ions are removed, and the same expressions can be used with a negative value of \( y \).

**Example 13**

A formic acid buffer is prepared with 0.010 mole liter\(^{-1} \) each of formic acid (HCOOH) and sodium formate (HCOONa). What is the pH of the solution? What is the pH if 0.0020 mole liter\(^{-1} \) of solid sodium hydroxide (NaOH) is added to a liter of buffer? What would be the pH of the sodium hydroxide solution without buffer? What would the pH have been after adding sodium hydroxide if the buffer concentrations had been 0.10 mole liter\(^{-1} \) instead of 0.010?

**Solution**

The answers are

- **Buffer:** \( pH = 3.75 \)
- **After adding NaOH:** \( pH = 3.92 \)
- **Without buffer:** \( pH = 11.30 \)
- **With stronger buffer:** \( pH = 3.77 \)

In the preceding example, you can see the dramatic effect of the formate buffer in keeping the solution acidic in spite of the added base, and the importance of reasonably high buffer concentrations if the buffering capacity of the solution is not to be exceeded.

**5-8 SALTS OF WEAK ACIDS AND STRONG BASES: HYDROLYSIS**

A sodium chloride solution is neutral, with a pH of 7.0. This is reasonable, because sodium hydroxide is a strong base and hydrochloric acid is a strong
acid, and if equal amounts of each were added, neutralization would be complete. In contrast, sodium acetate is the salt of a strong base and a weak acid. Intuitively we would expect a sodium acetate solution to be somewhat basic, and it is. Some of the acetate ions from the salt combine with water to form undissociated acetic acid and hydroxide ions:

$$\text{Ac}^- + \text{H}_2\text{O} \rightleftharpoons \text{HAc} + \text{OH}^- \quad (5-47)$$

This sometimes is called a **hydrolysis reaction**, the implication being that $\text{H}_2\text{O}$ breaks up crystals of sodium acetate. It does, when the salt crystal dissolves in water, but this is not the point. In solution the acetate ion acts as a base. It is as good a Brønsted base as ammonia, and the ammonium ion is a perfectly good acid, like HAc.

$$\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$$

We should not let the different charges on the acetate ion (−1) and ammonia (0) obscure the similarity of their acid–base behavior.

The equilibrium constant for acetate hydrolysis has the same form as any other base dissociation:

$$K_b = \frac{[\text{HAc}][\text{OH}^-]}{[\text{Ac}^-]} \quad (5-48)$$

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} \quad (5-30)$$

where, as usual, the virtually unchanging water concentration is incorporated into the equilibrium constant. This constant sometimes is written $K_h$ for “hydrolysis constant,” but the added nomenclature is unnecessary. It is a simple base-equilibrium constant of the kind we have seen before, except that acetate ion is the base.

As always, $K_b$ is related to the corresponding acid-dissociation constant, $K_a$, by

$$K_b = \frac{[\text{HAc}][\text{OH}^-]}{[\text{Ac}^-]} = \frac{[\text{HAc}][\text{OH}^-][\text{H}^+]}{[\text{Ac}^-][\text{H}^+]} = \frac{K_w}{K_a} \quad (5-49)$$

Thus

$$K_b = \frac{10^{-14}}{1.76 \times 10^{-5}} = 5.68 \times 10^{-10}$$

(Recall the ammonia–water equilibrium expressions at the end of Section 5.4.) This value is all we need to calculate the pH of a sodium acetate solution.

**Example 14**

What is the pH of a solution of 0.010M NaAc?

**Solution** Acetate ions from NaAc combine with $\text{H}_2\text{O}$ to produce undissociated HAc
molecules and OH\(^-\) ions (equation 5-47). The equilibrium expression is

\[
5.68 \times 10^{-10} = \frac{[\text{HAc}][\text{OH}^-]}{[\text{Ac}^-]}
\]

Let the hydroxide ion concentration be \(y\). Since every reaction of an acetate ion with water produces one hydroxide ion and one undissociated HAc molecule, the concentration of each of the latter two species must be \(y\) moles liter\(^{-1}\). The remaining acetate ions are those originally present from NaAc minus those that have combined with water:

\[ [\text{Ac}^-] = 0.010 - y \]

and we arrive at the familiar expression

\[
K_b = \frac{y^2}{0.010 - y} = \frac{y^2}{0.010 - y} = 5.68 \times 10^{-10} \tag{5-50}
\]

This is even easier to solve than the weak-acid problems. Since the equilibrium constant is so small, \(y\) will be correspondingly small and can be neglected in the denominator in comparison to 0.010. The result is

\[
y^2 = 0.010 \times 5.68 \times 10^{-10} = 5.7 \times 10^{-12}
\]

\[ y = 2.4 \times 10^{-6} \text{ mole liter}^{-1} = [\text{OH}^-] \]

\[
[H^+] = \frac{K_w}{[\text{OH}^-]} = \frac{10^{-14}}{2.4 \times 10^{-6}} = 4.2 \times 10^{-9}
\]

\[ \text{pH} = 9 - 0.6 = 8.4 \]

(As before, we have neglected any contribution to the hydrogen ion concentration from water molecules. Our procedure is accurate enough for most situations, including the purposes of this chapter. The full derivation is found in Appendix 5.)

---

5-9 **POLYPROTIC ACIDS: ACIDS THAT LIBERATE MORE THAN ONE HYDROGEN ION**

If water is the solvent, sulfuric acid, \(\text{H}_2\text{SO}_4\), loses one proton as a strong acid with an immeasurably large dissociation constant.

\[ \text{H}_2\text{SO}_4 \rightarrow \text{H}^+ + \text{HSO}_4^- \]

It also can lose a second proton as a weak acid with a measurable dissociation constant. Acids that can liberate more than one proton are called polyprotic acids.

\[ \text{HSO}_4^- \rightleftharpoons \text{H}^+ + \text{SO}_4^{2-} \quad K_{a_2} = 1.20 \times 10^{-2} \quad \text{p}K_{a_2} = 1.92 \]

For carbonic acid, \(\text{H}_2\text{CO}_3\), both dissociations are weak:
\[
\begin{align*}
\text{H}_2\text{CO}_3 & \rightleftharpoons \text{H}^+ + \text{HCO}_3^- & K_{a_1} &= 4.3 \times 10^{-7} & \text{p}K_{a_1} &= 6.37 \\
\text{HCO}_3^- & \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-} & K_{a_2} &= 5.61 \times 10^{-11} & \text{p}K_{a_2} &= 10.25
\end{align*}
\]

The relative values of \(K_{a_1}\) and \(K_{a_2}\) for a given acid are intuitively reasonable. One would expect \(\text{HCO}_3^-\), which already has a negative charge, to be less ready than neutral \(\text{H}_2\text{CO}_3\) to lose another proton.

Phosphoric acid, \(\text{H}_3\text{PO}_4\), has three dissociations:

\[
\begin{align*}
\text{H}_3\text{PO}_4 & \rightleftharpoons \text{H}^+ + \text{H}_2\text{PO}_4^- & \text{p}K_{a_1} &= 2.12 \\
\text{H}_2\text{PO}_4^- & \rightleftharpoons \text{H}^+ + \text{HPO}_4^{2-} & \text{p}K_{a_2} &= 7.21 \\
\text{HPO}_4^{2-} & \rightleftharpoons \text{H}^+ + \text{PO}_4^{3-} & \text{p}K_{a_3} &= 12.67
\end{align*}
\]

Thus, in an aqueous solution of phosphoric acid there will be seven ionic and molecular species present: \(\text{H}_3\text{PO}_4\), \(\text{H}_2\text{PO}_4^-\), \(\text{HPO}_4^{2-}\), \(\text{PO}_4^{3-}\), \(\text{H}_2\text{O}\), \(\text{H}^+\), and \(\text{OH}^-\). Life might appear impossibly complicated, were we not able to make some approximations.

At a pH equal to the \(\text{p}K_a\) for a particular dissociation, the two forms of the dissociating species are present in equal concentrations. For the second dissociation of phosphoric acid, for which \(\text{p}K_{a_2} = 7.21\),

\[
K_{a_2} = \frac{[\text{H}^+][\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]}
\]

\[
\log \frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} = \text{pH} - \text{p}K_{a_2}
\]

When \(\text{pH} = \text{p}K_{a_2}\), we have the ratio

\[
\frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} = 1.00
\]

Hence, in a neutral solution, \(\text{H}_2\text{PO}_4^-\) and \(\text{HPO}_4^{2-}\) are present in about the same concentrations. Very little undissociated \(\text{H}_3\text{PO}_4\) will be found, since from the first dissociation constant,

\[
K_{a_1} = \frac{[\text{H}^+][\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]}
\]

\[
\log \frac{[\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]} = \text{pH} - \text{p}K_{a_1} = 7.00 - 2.12 = 4.88
\]

\[
\frac{[\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]} = 10^{4.88} = 7.6 \times 10^4 = 76,000
\]

Similarly, little \(\text{PO}_4^{3-}\) will exist:

\[
\log \frac{[\text{PO}_4^{3-}]}{[\text{HPO}_4^{2-}]} = \text{pH} - \text{p}K_{a_3} = 7.00 - 12.67 = -5.67
\]

\[
\frac{[\text{PO}_4^{3-}]}{[\text{HPO}_4^{2-}]} = 10^{-5.67} = 2.1 \times 10^{-6} = \frac{1}{480,000}
\]
The only phosphate species that we have to consider near pH = 7 are H$_2$PO$_4^-$ and HPO$_4^{2-}$. Similarly, in strong acid solutions near pH = 3, only H$_3$PO$_4$ and H$_2$PO$_4^-$ are important. As long as the pK$_a$’s of successive dissociations are separated by three or four units (as they almost always are), matters are simplified.

There is still another simplification. When a polyprotic acid such as carbonic acid, H$_2$CO$_3$, dissociates, most of the protons present come from the first dissociation:

\[
H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \quad pK_{a1} = 6.37
\]

Since the second dissociation constant is smaller by four orders of magnitude (and the pK$_a_2$ larger by four units), the contribution of hydrogen ions from the second dissociation will be only one ten-thousandth as large. Correspondingly, the second dissociation has a negligible effect on the concentration of the product of the first dissociation, HCO$_3^-$. 

**Example 15**

At room temperature and 1 atm CO$_2$ pressure, water saturated in CO$_2$ has a carbonic acid concentration of approximately 0.040 mole liter$^{-1}$. Calculate the pH and the concentrations of all carbonate species for a 0.040 M H$_2$CO$_3$ solution.

**Solution**

Considering initially only the first dissociation:

\[
K_{a1} = 4.3 \times 10^{-7} = \frac{y^2}{0.040 - y} \quad \text{in which } y = [H^+]
\]

From our experience with acetic acid, which has an even larger K$_a$, we should expect to be able to neglect $y$ in the denominator. The extent of dissociation of an acid with such a small K$_a$ will be very small:

\[
y^2 = 4.3 \times 10^{-7} \times 0.040 = 1.7 \times 10^{-8}
\]

\[
y = 1.3 \times 10^{-4} \text{ mole liter}^{-1}
\]

This is the concentration of both hydrogen ion and bicarbonate ion, HCO$_3^-$:

\[
[H^+] = 1.3 \times 10^{-4} \text{ mole liter}^{-1}
\]

\[
[HCO_3^-] = 1.3 \times 10^{-4} \text{ mole liter}^{-1}
\]

\[
[H_2CO_3] = 0.040 - 0.00013 = 0.040 \text{ mole liter}^{-1}
\]

\[
\text{pH} = 4 - 0.12 = 3.88
\]

Consequently, carbonated beverages have an acidity somewhere between those of wine and tomato juice (see Table 5-2). For the second dissociation:

\[
HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}
\]

\[
K_{a2} = 5.6 \times 10^{-11} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}
\]
Since this second dissociation has only a minor effect on the first one, we can assume that the hydrogen ion and bicarbonate ion concentrations are effectively the same:

$$[\text{CO}_3^{2-}] = \frac{[\text{HCO}_3^-]}{[\text{H}^+]} \times K_{a_2} = K_{a_2} = 5.6 \times 10^{-11} \text{ mole liter}^{-1}$$

Note the rather surprising result that the concentration of the second dissociation product is equal to the second dissociation constant!

**Example 16**

Calculate the sulfide ion concentration in a solution saturated in $\text{H}_2\text{S}$ (0.10 mole liter$^{-1}$) (a) if the solution is made from distilled water and (b) if the solution is made pH = 3.0 with HCl. Use $K_a$ values in Table 5-3.

**Solution**

In distilled water, the first dissociation is

$$K_{a_1} = 9.1 \times 10^{-8} = \frac{y^2}{0.10}$$

The dissociation constant is so small that $y$ in the denominator can be neglected immediately. Dissociation will be extremely slight:

$$y = [\text{H}^+] = [\text{HS}^-] = 9.5 \times 10^{-5} \text{ mole liter}^{-1}$$

$$\text{pH} = 5 - 0.98 = 4.02$$

From the second dissociation:

$$[\text{S}_2^-] = \frac{[\text{HS}^-]}{[\text{H}^+]} \times K_{a_2} = K_{a_2} = 1.1 \times 10^{-12} \text{ mole liter}^{-1}$$

As with the $\text{H}_2\text{CO}_3$ example, the anion produced by the second dissociation has a concentration equal to the second dissociation constant.

In contrast, in HCl solution at pH = 3.0:

$$K_{a_1} = \frac{[\text{H}^+][\text{HS}^-]}{[\text{H}_2\text{S}]} = \frac{1.0 \times 10^{-3}[\text{HS}^-]}{0.10} = 9.1 \times 10^{-8}$$

$$[\text{HS}^-] = 9.1 \times 10^{-6} \text{ mole liter}^{-1}$$

$$K_{a_2} = \frac{[\text{H}^+][\text{S}_2^-]}{[\text{HS}^-]} = \frac{1.0 \times 10^{-3}[\text{S}_2^-]}{9.1 \times 10^{-6}} = 1.1 \times 10^{-12}$$

$$[\text{S}_2^-] = \frac{9.1 \times 10^{-6} \times 1.1 \times 10^{-12}}{1.0 \times 10^{-3}} = 1.0 \times 10^{-14}$$

The acid has repressed the dissociation of $\text{H}_2\text{S}$, making the sulfide ion concentration only one-hundredth of what it is in pure water. As we shall see in the next section, we can use acids to exert a fine control on sulfide concentration in analytical methods by controlling the pH.
5-10 EQUILIBRIA WITH SLIGHTLY SOLUBLE SALTS

When most solid salts dissolve in water, they dissociate almost completely into hydrated positive and negative ions. The solubility of a salt in water represents a balance between the attraction of the ions in the crystal lattice and the attraction between these ions and the polar water molecules. This balance may be a delicate one, easily changed in going from one compound to an apparently similar one, or from one temperature to another. It is not possible to give hard-and-fast rules as to whether a compound is soluble, or even to account for all observed behavior.

One important factor certainly is the electrostatic attraction between ions. Crystals made up of small ions that can be packed closely together are generally harder to pull apart than crystals made up of large ions. Therefore, for a given cation, fluorides (F⁻) and hydroxides (OH⁻) are less soluble than nitrates (NO₃⁻) and perchlorates (ClO₄⁻). Chlorides are intermediate in size, and their behavior is difficult to predict from general principles.

The charge on the ions also is important. More highly charged ions such as phosphates (PO₄³⁻) and carbonates (CO₃²⁻) interact strongly with cations and are less soluble than the singly charged nitrates and perchlorates.

The terms soluble and insoluble are relative, and the degree of solubility can be related to an equilibrium constant. For a “slightly soluble” salt such as silver chloride, an equilibrium exists between the dissociated ions and the solid compound:

\[ \text{AgCl}(s) \rightleftharpoons \text{Ag}^+ + \text{Cl}^- \]  \hspace{1cm} (5-51)

The equilibrium expression for this reaction is

\[ K_{eq} = \frac{[\text{Ag}^+][\text{Cl}^-]}{[\text{AgCl}(s)]} \]  \hspace{1cm} (5-52)

As long as solid AgCl remains, its effect on the equilibrium does not change. As with the H₂O concentration in the water dissociation equilibrium, the concentration of the solid salt can be incorporated into the equilibrium constant:

\[ K_{sp} = K_{eq}[\text{AgCl}(s)] = [\text{Ag}^+][\text{Cl}^-] \]  \hspace{1cm} (5-53)

This new equilibrium constant, \( K_{sp} \), is called the solubility-product constant. For substances in which the ions are not in a 1:1 ratio, the form of the solubility-product expression is analogous to our previous equilibrium expressions:

\[
\begin{align*}
\text{PbCl}_2 & \rightleftharpoons \text{Pb}^{2+} + 2\text{Cl}^- \quad K_{sp} = [\text{Pb}^{2+}][\text{Cl}^-]^2 \\
\text{Al(OH)}_3 & \rightleftharpoons \text{Al}^{3+} + 3\text{OH}^- \quad K_{sp} = [\text{Al}^{3+}][\text{OH}^-]^3 \\
\text{Ag}_2\text{CrO}_4 & \rightleftharpoons 2\text{Ag}^+ + \text{CrO}_4^{2-} \quad K_{sp} = [\text{Ag}^+]^2[\text{CrO}_4^{2-}] \\
\text{Ba}_3(\text{PO}_4)_2 & \rightleftharpoons 3\text{Ba}^{2+} + 2\text{PO}_4^{3-} \quad K_{sp} = [\text{Ba}^{2+}]^3[\text{PO}_4^{3-}]^2
\end{align*}
\]

Solubility equilibria are useful in predicting whether a precipitate will form
under specified conditions, and in choosing conditions under which two chemical substances in solution can be separated by selective precipitation.

The solubility-product constant of a slightly soluble compound can be calculated from its solubility in moles liter\(^{-1}\).

**Example 17**

The solubility of AgCl in water is 0.000013 mole liter\(^{-1}\) at 25°C. What is its solubility-product constant, \(K_{sp}\)?

**Solution**

The equilibrium expression is

\[
\text{AgCl} \rightleftharpoons \text{Ag}^+ + \text{Cl}^-
\]

The concentrations of \(\text{Ag}^+\) and \(\text{Cl}^-\) are equal because for each mole of solid AgCl that dissolves, 1 mole each of \(\text{Ag}^+\) and \(\text{Cl}^-\) ions is produced. Hence the concentration of each ion is equal to the overall solubility, \(s\), of the solid in moles liter\(^{-1}\):

\[
[\text{Ag}^+] = [\text{Cl}^-] = s = 1.3 \times 10^{-5} \text{ mole liter}^{-1}
\]

\[
K_{sp} = [\text{Ag}^+][\text{Cl}^-] = s^2 = 1.7 \times 10^{-10}
\]

**Example 18**

At a certain temperature the solubility of Fe(OH)\(_2\) in water is 7.7 \(\times\) 10\(^{-6}\) mole liter\(^{-1}\). Calculate its \(K_{sp}\) at that temperature.

**Solution**

The equilibrium equation is

\[
\text{Fe(OH)}_2 \rightleftharpoons \text{Fe}^{2+} + 2\text{OH}^-
\]

and the solubility-product expression is

\[
K_{sp} = [\text{Fe}^{2+}][\text{OH}^-]^2
\]

Since one mole of dissolved Fe(OH)\(_2\) produces one mole of Fe\(^{2+}\) and two moles of OH\(^-\),

\[
[\text{Fe}^{2+}] = s = 7.7 \times 10^{-6} \text{ mole liter}^{-1}
\]

\[
[\text{OH}^-] = 2s = 1.54 \times 10^{-5} \text{ mole liter}^{-1}
\]

\[
K_{sp} = 7.7 \times 10^{-6} \times (1.54 \times 10^{-5})^2 = 1.8 \times 10^{-15}
\]

The solubility-product constants of a number of substances are listed in Table 5-7. Substances are grouped by anion and listed in the order of decreasing \(K_{sp}\); anions are listed roughly in the order of decreasing solubility. Once the solubility-product constant is known, it can be used to calculate the solubility of a compound at a specified temperature.
### Table 5-7

**Solubility-Product Constants, \( K_{sp} \), at 25°C**

<table>
<thead>
<tr>
<th>Fluorides</th>
<th>Chromates (cont.)</th>
<th>Hydroxides (cont.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaF(_2)</td>
<td>2.4 ( \times ) 10(^{-5} )</td>
<td>Ag(_2)CrO(_4)</td>
</tr>
<tr>
<td>MgF(_2)</td>
<td>8 ( \times ) 10(^{-8} )</td>
<td>PbCrO(_4)</td>
</tr>
<tr>
<td>PbF(_2)</td>
<td>4 ( \times ) 10(^{-8} )</td>
<td>Carbonates</td>
</tr>
<tr>
<td>SrF(_2)</td>
<td>7.9 ( \times ) 10(^{-10} )</td>
<td>CaCO(_3)</td>
</tr>
<tr>
<td>CaF(_2)</td>
<td>3.9 ( \times ) 10(^{-11} )</td>
<td>BaCO(_3)</td>
</tr>
<tr>
<td>Clorides</td>
<td></td>
<td>SrCO(_3)</td>
</tr>
<tr>
<td>PbCl(_2)</td>
<td>1.6 ( \times ) 10(^{-5} )</td>
<td>CuCO(_3)</td>
</tr>
<tr>
<td>AgCl</td>
<td>1.7 ( \times ) 10(^{-10} )</td>
<td>ZnCO(_3)</td>
</tr>
<tr>
<td>Hg(_2)Cl(_2)(^a)</td>
<td>1.1 ( \times ) 10(^{-18} )</td>
<td>MnCO(_3)</td>
</tr>
<tr>
<td>Bromides</td>
<td></td>
<td>FeCO(_3)</td>
</tr>
<tr>
<td>PbBr(_2)</td>
<td>4.6 ( \times ) 10(^{-6} )</td>
<td>Ag(_2)CO(_3)</td>
</tr>
<tr>
<td>AgBr</td>
<td>5.0 ( \times ) 10(^{-13} )</td>
<td>CdCO(_3)</td>
</tr>
<tr>
<td>Hg(_2)Br(_2)(^a)</td>
<td>1.3 ( \times ) 10(^{-22} )</td>
<td>PbCO(_3)</td>
</tr>
<tr>
<td>Iodides</td>
<td></td>
<td>MgCO(_3)</td>
</tr>
<tr>
<td>Pbl(_2)</td>
<td>8.3 ( \times ) 10(^{-9} )</td>
<td>Hg(_2)CO(_3)(^a)</td>
</tr>
<tr>
<td>AgI</td>
<td>8.5 ( \times ) 10(^{-17} )</td>
<td>Hydroxides</td>
</tr>
<tr>
<td>Hg(_2)I(_2)(^a)</td>
<td>4.5 ( \times ) 10(^{-29} )</td>
<td></td>
</tr>
<tr>
<td>Sulfates</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaSO(_4)</td>
<td>2.4 ( \times ) 10(^{-5} )</td>
<td></td>
</tr>
<tr>
<td>Ag(_2)SO(_4)</td>
<td>1.2 ( \times ) 10(^{-5} )</td>
<td></td>
</tr>
<tr>
<td>SrSO(_4)</td>
<td>7.6 ( \times ) 10(^{-7} )</td>
<td></td>
</tr>
<tr>
<td>PbSO(_4)</td>
<td>1.3 ( \times ) 10(^{-8} )</td>
<td></td>
</tr>
<tr>
<td>BaSO(_4)</td>
<td>1.5 ( \times ) 10(^{-9} )</td>
<td></td>
</tr>
<tr>
<td>Chromates</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SrCrO(_4)</td>
<td>3.6 ( \times ) 10(^{-6} )</td>
<td></td>
</tr>
<tr>
<td>Hg(_2)CrO(_4)(^a)</td>
<td>2 ( \times ) 10(^{-9} )</td>
<td></td>
</tr>
<tr>
<td>BaCrO(_4)</td>
<td>8.5 ( \times ) 10(^{-11} )</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)As Hg\(_2^+\) ion. \( K_{sp} = [\text{Hg}_2^+] [\text{X}^-]^2 \)

---

### Example 19

What is the solubility of lead sulfate, PbSO\(_4\), in water at 25°C?

**Solution**

The dissociation reaction is

\[
PbSO_4 \rightleftharpoons Pb^{2+} + SO_4^{2-}
\]

Let the unknown solubility be \( s \) moles liter\(^{-1} \). Then since each mole of dissolved PbSO\(_4\) produces 1 mole of each ion,

\[
[Pb^{2+}] = [SO_4^{2-}] = s
\]
The solubility-product equation is
\[ K_{sp} = [\text{Pb}^{2+}][\text{SO}_4^{2-}] = s^2 = 1.3 \times 10^{-8} \] (from Table 5-7)
\[ s = 1.1 \times 10^{-4} \text{ mole liter}^{-1} \]

---

**Example 20**

In Table 5-7 we see that cadmium carbonate, CdCO₃, and silver carbonate, Ag₂CO₃, have approximately the same solubility-product constants. Compare their molar solubilities in water (at 25°C).

**Solution**

For cadmium carbonate,
\[ K_{sp} = [\text{Cd}^{2+}][\text{CO}_3^{2-}] = s^2 = 5.2 \times 10^{-12} \]
\[ s = 2.3 \times 10^{-6} \text{ mole liter}^{-1} \]

For Ag₂CO₃ the expression is slightly different. If the solubility again is \( s \) moles liter\(^{-1} \), since each mole of salt produces 2 moles of Ag\(^+\) ions,
\[ [\text{Ag}^{+}] = 2s \]
\[ [\text{CO}_3^{2-}] = s \]
\[ K_{sp} = [\text{Ag}^{+}]^2[\text{CO}_3^{2-}] = (2s)^2 \times s = 4s^3 = 8.2 \times 10^{-12} \]
\[ s = 1.3 \times 10^{-4} \text{ mole liter}^{-1} \]

Although cadmium carbonate and silver carbonate have nearly the same solubility-product constants, their solubilities in moles liter\(^{-1} \) differ by a factor of 100 because the form of the solubility-product expression is different. The solubility of Ag₂CO₃ is sensitive to the square of the metal-ion concentration, because two silver ions per carbonate ion are necessary to build the solid crystal.

---

**Common-Ion Effect**

In the preceding example, the solubility of silver carbonate in pure water was calculated to be \( 1.3 \times 10^{-4} \) mole liter\(^{-1} \). Will silver carbonate be more soluble or less soluble in silver nitrate solution? Le Chatelier’s principle leads us to predict that a new, outside source of silver ions would shift the silver carbonate equilibrium reaction in the direction of less dissociation:

\[ \text{Ag}_2\text{CO}_3 \rightleftharpoons 2\text{Ag}^+ + \text{CO}_3^{2-} \] (5-54)

or that silver carbonate would be less soluble in a silver nitrate solution than in pure water. This decrease in the solubility of one salt in a solution of another salt that has a common cation or anion is called the **common-ion effect**.
What is the solubility at 25°C of calcium fluoride, CaF₂, (a) in pure water, (b) in 0.10M calcium chloride, CaCl₂, and (c) in 0.10M sodium fluoride, NaF?

**Solution**

(a) If the solubility in pure water is \( s \), then

\[
\begin{align*}
[\text{Ca}^{2+}] &= s \\
[\text{F}^-] &= 2s \\
K_{sp} &= s \times 4s^2 = 4s^3 = 3.9 \times 10^{-11} \\
s &= 2.1 \times 10^{-4} \text{ mole liter}^{-1}
\end{align*}
\]

(b) In 0.10M CaCl₂, the calcium ion concentration is the sum of the concentration of calcium ions from calcium chloride and from calcium fluoride, whose solubility we are seeking:

\[
\begin{align*}
[\text{Ca}^{2+}] &= 0.10 + s \\
[\text{F}^-] &= 2s \\
K_{sp} &= (0.10 + s)(2s)^2 = 3.9 \times 10^{-11}
\end{align*}
\]

This is a cubic equation, but a moment’s thought about the chemistry involved will eliminate the need to solve it as such. With such a small solubility-product constant, you can predict that the solubility of calcium fluoride will be very small in comparison with 0.10 mole liter⁻¹. (You already should realize from (a) and Le Chatelier’s principle that in this problem \( s \) will be less than 2.1 × 10⁻⁴ mole liter⁻¹.) If our prediction is valid, we can simplify the solubility-product equation and calculate the approximate solubility:

\[
0.10 \times (2s)^2 = 3.9 \times 10^{-11}
\]

\[
s^2 = \frac{3.9 \times 10^{-11}}{4 \times 0.10} = 9.75 \times 10^{-11}
\]

\[
s = 0.99 \times 10^{-5} = 9.9 \times 10^{-6} \text{ mole liter}^{-1}
\]

Therefore the approximation is justified. Only 4.7% as much CaF₂ will dissolve in 0.10M CaCl₂ as in pure water:

\[
\frac{9.9 \times 10^{-6}}{2.1 \times 10^{-4}} \times 100 = 4.7\%
\]

(c) In 0.10M NaF,

\[
[\text{Ca}^{2+}] = s \quad \text{and} \quad [\text{F}^-] = 0.10 + 2s
\]

since fluoride ions come from NaF as well as from CaF₂. The solubility-product equation is

\[
K_{sp} = s(2s + 0.10)^2 = 3.9 \times 10^{-11}
\]
Again, thinking about the chemical meaning will avoid the necessity of solving a cubic equation. The $2s$ term will be very small compared to $0.10$ mole liter$^{-1}$, therefore,

$$s(0.10)^2 = 3.9 \times 10^{-11}$$

$$s = 3.9 \times 10^{-9} \text{ mole liter}^{-1}$$

This approximation is even more valid than the previous one, since from the calculation

$$\frac{3.9 \times 10^{-9}}{2.1 \times 10^{-4}} \times 100 = 0.0019\%$$

only $0.0019\%$ as much CaF$_2$ will dissolve in $0.10M$ NaF as in pure water. Fluoride is more effective than calcium as a common ion because it has a second-power effect on the solubility equilibrium.

---

The common-ion method of controlling solubility often is used with solutions of sulfide ion, $S^{2-}$, because many metals form insoluble sulfides, and the sulfide ion concentration can be controlled by adjusting the pH.

### Example 22

What is the maximum possible concentration of Ni$^{2+}$ ion in water at $25^\circ$C that is saturated with $H_2S$ and maintained at pH 3.0 with $HCl$?

**Solution**

From the solubility-product equilibrium equation we predict that too much nickel ion will cause the precipitation of nickel sulfide, NiS:

$$K_{sp} = [Ni^{2+}][S^{2-}] = 3 \times 10^{-21}$$

The only new twist to this problem is finding the sulfide ion concentration from the $H_2S$ equilibrium. Hydrogen sulfide dissociates in two steps, each with an equilibrium constant:

$$H_2S \rightleftharpoons H^+ + HS^- \quad K_{a_1} = 9.1 \times 10^{-8}$$

$$HS^- \rightleftharpoons H^+ + S^{2-} \quad K_{a_2} = 1.1 \times 10^{-12}$$

$$H_2S \rightleftharpoons 2H^+ + S^{2-} \quad K_{a_{1,2}} = K_{a_1} \times K_{a_2}$$

Because the overall dissociation is the sum of two dissociation steps, the overall equilibrium constant, $K_{a_{1,2}}$, is the product of $K_{a_1}$ and $K_{a_2}$:

$$K_{a_{1,2}} = \frac{[H^+][HS^-]}{[H_2S]} \times \frac{[H^+][S^{2-}]}{[HS^-]} = \frac{[H^+]^2[S^{2-}]}{[H_2S]}$$

$$K_{a_{1,2}} = 9.1 \times 10^{-8} \times 1.1 \times 10^{-12} = 1.0 \times 10^{-19}$$
Saturated $\text{H}_2\text{S}$ is approximately 0.10$M$ at 25$^\circ$C, and the very small value of $K_{a_{\text{H}_2\text{S}}}$ means that dissociation of $\text{H}_2\text{S}$ is very slight. Hence we can write

$$[\text{H}_2\text{S}] = 0.10 \text{ mole liter}^{-1} \quad \text{and} \quad [\text{H}^+]^2[\text{S}^{2-}] = 1.0 \times 10^{-20}$$

in a saturated $\text{H}_2\text{S}$ solution. This "ion product" for saturated $\text{H}_2\text{S}$ is a useful relationship to remember.

In this problem, the pH has been adjusted to 3.0 with hydrochloric acid, so

$$[\text{H}^+] = 1.0 \times 10^{-3} \text{ mole liter}^{-1}$$

Therefore, the sulfide ion concentration can be calculated from

$$[\text{S}^{2-}] = K_{a_{\text{H}_2\text{S}}} \times \frac{[\text{H}_2\text{S}]}{[\text{H}^+]^2} = 1.0 \times 10^{-19} \times \frac{0.10}{(1.0 \times 10^{-3})^2}$$

which gives

$$[\text{S}^{2-}] = 1.0 \times 10^{-14} \text{ mole liter}^{-1}$$

Since NiS will precipitate if the solubility product is exceeded, the highest value that the nickel ion concentration can have is

$$[\text{Ni}^{2+}] = \frac{K_{\text{sp}}}{[\text{S}^{2-}]} = \frac{3 \times 10^{-21}}{1 \times 10^{-14}} = 3 \times 10^{-7} \text{ mole liter}^{-1}$$

### Separation of Compounds by Precipitation

Solubility-product constants can be used to devise methods for separating ions in solution by selective precipitation. The entire traditional qualitative-analysis scheme is based on the use of these equilibrium constants to determine the correct precipitating ions and the correct strategy.

---

**Example 23**

A solution is 0.010$M$ in barium chloride, $\text{BaCl}_2$, and 0.020$M$ in strontium chloride, $\text{SrCl}_2$. Can either $\text{Ba}^{2+}$ or $\text{Sr}^{2+}$ be precipitated selectively with concentrated sodium sulfate, $\text{Na}_2\text{SO}_4$, solution? Which ion will precipitate first? When the second ion just begins to precipitate, what is the residual concentration of the first ion, and what fraction of the original amount of the first ion is left in solution? (For simplicity, assume that the $\text{Na}_2\text{SO}_4$ solution is so concentrated that the volume change in the $\text{Ba}–\text{Sr}$ solution can be neglected.)

**Solution**

The upper limit on barium sulfate solubility is given by

$$K_{\text{sp}} = [\text{Ba}^{2+}][\text{SO}_4^{2-}] = 1.5 \times 10^{-9}$$
With 0.010 mole liter\(^{-1}\) of Ba\(^{2+}\), precipitation of barium sulfate will not occur until the sulfate ion concentration increases to

\[
[SO_4^{2-}] = \frac{1.5 \times 10^{-9}}{0.010} = 1.5 \times 10^{-7} \text{ mole liter}^{-1}
\]

Strontium sulfate will precipitate when the sulfate concentration is

\[
[SO_4^{2-}] = \frac{K_{sp(SrSO_4)}}{[Sr^{2+}]} = \frac{7.6 \times 10^{-7}}{0.020} = 3.8 \times 10^{-5} \text{ mole liter}^{-1}
\]

Therefore, barium will precipitate first. When the sulfate concentration has risen to 3.8 \times 10^{-5} mole liter\(^{-1}\) and strontium sulfate just begins to precipitate, the residual barium concentration left in solution will be

\[
[Ba^{2+}] = \frac{1.5 \times 10^{-9}}{3.8 \times 10^{-5}} = 3.9 \times 10^{-5} \text{ mole liter}^{-1}
\]

This quantity is

\[
\frac{3.9 \times 10^{-5}}{0.010} \times 100 = 0.39\%
\]

or 0.39% of the original Ba\(^{2+}\) present. Thus 99.6% of the barium has been precipitated before any strontium begins to precipitate.

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**Summary**

In this chapter we have applied the concepts of chemical equilibrium to ions in aqueous solution, especially to acid–base and precipitation reactions. We have used the equilibrium-constant expression from Chapter 4, with concentrations expressed in units of moles per liter (moles liter\(^{-1}\)). Since the concentration of water is effectively constant, especially in dilute solutions, we have incorporated all water concentration terms, [H\(_2\)O], into the equilibrium constants.

Water itself ionizes with an equilibrium or ion-product constant at room temperature of \(K_w = [H^+][OH^-] = 10^{-14}\). To avoid the inconvenience of large exponential numbers, a negative exponent notation is used, whereby \(pH = -\log_{10}[H^+]\), \(pOH = -\log_{10}[OH^-]\), and \(pK_{eq} = -\log_{10} K_{eq}\). In this notation, the dissociation of water can be represented by \(pH + pOH = pK_w = 14\). For pure water, \([H^+]\) and \([OH^-]\) must be the same, and equal to \(10^{-7}\) mole liter\(^{-1}\), so the pH and pOH each are equal to 7. The pH is a convenient measure of acidity, since in acid solutions the pH is less than 7, and in basic solutions it is greater than 7.

According to the Brønsted–Lowry theory of acids and bases, any substance that gives up a proton is an *acid*, and any substance that can combine with a proton and remove it from solution is a *base*. When an acid loses its
proton, it becomes the conjugate base. A strong acid such as HCl has a weak conjugate base, Cl\(^-\), and a weak acid such as HAc or NH\(_4^+\) has a relatively strong conjugate base, Ac\(^-\) or NH\(_3\). Any acid whose conjugate base is sufficiently weaker than H\(_2\)O (has a lesser affinity for H\(^+\)) will be dissociated completely in aqueous solution, hence it is classified as a strong acid. Acids that dissociate only partially in aqueous solution are weak acids.

Strong acids and bases are simple to deal with, since their dissociation is complete in aqueous solution. When a strong acid is added to water, the increase in hydrogen ion concentration equals the concentration of added acid. Neutralization occurs when H\(^+\) from an acid combines with OH\(^-\) from a base to form water molecules. The amount of acid present in a sample can be determined by finding out how much base of known strength is required to make the solution neutral as measured by an acid–base indicator. This is called titration, and it is a useful analytical procedure.

The equilibrium expression for a weak acid, equation 5-34, is obtained with the help of two conservation expressions: a mass-balance equation that says the total amount of acid anion is constant, and a charge-balance equation that says the solution must remain neutral as a whole. This simple expression can be solved as a quadratic equation or by the method of successive approximations, and it is valid as long as the solution is so acid that the contribution to [H\(^+\)] from the dissociation of water can be neglected. If this is not the case, then a more complete expression (Appendix 5) must be used. Acid–base indicators themselves are weak acids or weak bases whose dissociated and undissociated forms have different colors.

A buffer is a mixture of a weak acid and its salt with a strong base, or alternatively, of a weak base and its salt with a strong acid. The equilibrium between the acid and salt form of the substances shifts to counteract the effect of added acid or base, making the buffered solution resistant to pH change. The pH in such solutions can be calculated from equations 5-42 and 5-46.

Hydrolysis is the interaction of the salt of a weak acid (or weak base) with water to form undissociated acid (or base) and OH\(^-\) (or H\(^+\)) ions. What is sometimes described as a hydrolysis constant is actually nothing more than the dissociation constant for the conjugate of the weak acid or base. The base constant, \(K_b\), and the acid constant, \(K_a\), are related by \(K_aK_b = K_w\).

Some acids can release more than one proton in successive dissociations. These are called polyprotic acids. As long as the successive dissociation constants, \(K_1\), \(K_2\), and so on, differ by factors of 10\(^{-4}\) or 10\(^{-5}\), the successive dissociations can be treated as separate events.

Most of the general comments just made about solving acid–base equilibrium problems are applicable to solubility equilibria, for situations in which ions combine to form an insoluble salt. Solubility-product calculations are more useful to indicate whether precipitation will occur under certain conditions, what the upper limit on concentration of an ion in solution may be, and whether two ions can be separated in solution by selective precipitation.
Self-Study Questions

1. In what sense is water a polar molecule? How does its polarity help it to be a better solvent? For what kinds of substances is water an especially good solvent?

2. Why is water a better solvent for methanol than for methane? Why is table salt more soluble in water than in benzene?

3. What is hydration of an ion? What kinds of ions are hydrated? What is solvation, and how is it related to hydration? How does hydration affect the solubility of salts?

4. What is the ion-product constant for the dissociation of water? Why does the concentration of water not appear explicitly in the expression?

5. What is the pH scale, and why is it useful? Does a strong acid have a high pH or a low pH? Does it have a high pOH or a low pOH? If the pH of a solution is 3, what are the pOH and the hydrogen and hydroxide ion concentrations?

6. When the pH changes by two units, by what factor does the hydrogen ion concentration change? When the pH changes by one unit, by what factor does the hydroxide ion concentration change?

7. What is an acid, and what is a base, in the theories of Arrhenius and of Brönsted and Lowry? What are conjugate acids and bases? Give two examples of conjugate acid–base pairs, in one of which the acid is charged and the base is neutral, and in the other of which the acid is neutral and the base is charged.

8. What is the difference between strong and weak acids? Why is it correct to say that a strong acid is one whose acid anion is a weaker base than a water molecule? What is the leveling effect? In methanol as a solvent, will some acids that are in aqueous solution become weak acids, or will some of the acids that are weak in aqueous solution become strong acids? Explain in terms of competition for the proton.

9. How are $K_a$ and $K_b$, the acid- and base-dissociation constants, defined? Why do their product always equal $K_w$? Illustrate with an example other than the ones used in this chapter.

10. What is meant by an equivalent of an acid or a base in titration? (See Chapter 2 if you have forgotten.) How many equivalent weights of acid are there per mole of hydrochloric acid? Phosphoric acid? Sulfuric acid? How many moles of sodium hydroxide would be required to neutralize 1 mole of sulfuric acid?

11. Why is the choice of an indicator relatively uncritical in the titration of a strong acid by a strong base? Why is it more critical when a weak acid is titrated?

12. What makes some weak acids or bases suitable as indicators? What do they “indicate,” and how?

13. Is the pH of a solution of a weak base greater or smaller than the pH of a
solution of the same concentration of a strong base, assuming the same number of equivalents of base per mole? Why?

14. What are mass-balance and charge-balance equations, and how are they involved in deriving equilibrium-constant expressions? What is the physical meaning of these balance equations in terms of atoms, ions, and charge?

15. What is the method of successive approximations, and how can it be applied to solving problems involving weak acids or weak bases?

16. Will a solution of ammonium chloride be acidic, neutral, or basic? As the concentration of the solution is increased, what will happen to the pH?

17. When is the contribution from dissociation of water important in weak-acid equilibria? When may it be neglected?

18. What will be the effect on the degree of dissociation of an aqueous ammonia solution if we add some ammonium chloride? What do you think would happen to the degree of dissociation if instead we added a substance that formed a complex ion such as Cu(NH₃)₄²⁺ with ammonia molecules? How is Le Chatelier’s principle involved here?

19. How does a buffer counteract attempts to change the pH of a solution? What are the two components of a typical buffer solution?

20. Under what conditions will the pH of a buffer mixture be equal to the pKₐ of the buffer acid? How could you set up the buffer mixture so the pH was one unit less than the pKₐ?

21. What mass and charge balances are involved in deriving the general expression for equilibrium in a solution of a weak acid and its salt with a strong base? How does the general expression reduce the simpler expressions that we have used for weak acids, buffers, and hydrolysis?

22. What is hydrolysis? What is the hydrolysis constant, and how is it related to Kₐ, Kₐ', and Kₐ''?

23. What are polyprotic acids? How do their successive equilibrium dissociation constants usually compare?

24. If a dissociation has a pKₐ of 4, what will be the ratio of undissociated to dissociated forms in a neutral solution? What would this same ratio be if the pKₐ were 9 instead?

25. What is the relationship between solubility (s) and solubility-product constants (K_{sp}) for CaCO₃? For CaF₂? For Ca₃(PO₄)₂?

26. What is the common-ion effect, and how does it influence solubility equilibria?

27. How can a knowledge of solubility-product constants be used to make analytical separations of ions in solution?

28. How can pH be used to control the concentration of sulfide ion, S²⁻, in solution? As the pH is increased, does the sulfide ion concentration increase, or does it decrease? Give a physical explanation for your answer.
Problems

Calculation of pH

1. What is the pH of a 0.01 M NaOH solution?

2. What is the pH of a $1.0 \times 10^{-10} M$ HCl solution? Why is the answer not pH 10?

3. What is the pH of each of the following solutions: (a) 0.001 M HCl; (b) 0.02 M HCl; (c) 0.001 M NaOH; (d) 0.001 M Ba(OH)$_2$?

4. What is the pH of each of the following solutions: (a) 0.10 M NaOH; (b) 0.020 M HCl; (c) 0.050 M NaCl; (d) pure water?

5. What are pH and pOH in a 0.120 M solution of acetic acid?

6. What is the pH of each of the following solutions: (a) 0.10 M acetic acid; (b) 0.10 M chloroacetic acid; (c) 0.01 M chloroacetic acid; (d) 0.10 M hydrogen cyanide?

Changes in pH

7. A solution contains H$^+$, NO$_2^-$, and HNO$_2$ in equilibrium. In which direction will the pH change if each of the following is added to the original solution: (a) HCl; (b) HCN; (c) NaCN; (d) NaCl; (e) H$_2$O?

8. In which direction will the pH of pure water change if each one of the following is added to it: (a) HCN; (b) HCl; (c) NaCN; (d) NaCl; (e) NH$_4$Cl; (f) NH$_3$; (f) NH$_4$CN?

pH and $K_a$

9. If a 0.10 M acetic acid solution is 1.3% ionized, what is the pH of the solution? What is $K_a$ for the acid? Compare your answer with the value in Table 5-3.

10. If a 0.10 M HF solution is 5.75% ionized, what is the pH of the solution? What is $K_a$ for HF? Compare your value with that in Table 5-3.

pH

11. From the data in Table 5-3, calculate the dissociation constant for ammonium hydroxide. Is undissociated NH$_4$OH really present in the solution? If not, what is the reaction for the production of ammonium ion and OH$^-$? What is the pH of a 0.0100 M solution of ammonia?

12. A detergent box must bear a warning label if its contents will form a solution of pH greater than 11, because a strong base degrades protein structure. Should a box bear such a label if the H$^+$ concentration of a solution of its contents is $2.5 \times 10^{-12}$ mole liter$^{-1}$?

Weak acids

13. The ionization constant for arsenious acid, HAsO$_2$, is $6.0 \times 10^{-10}$. What is the pH of a 0.10 M solution of arsenious acid? What is the pOH of a 0.10 M solution?

14. What are the CN$^-$ ion concentration and the pOH in a 1.00 M aqueous solution of HCN?

15. What is the equilibrium concentration of NO$_2^-$ ion in a 0.25 M aqueous solution of nitrous acid? What is the pH? What is the percent ionization of HNO$_2$?

Weak bases

16. A solution of ammonia has a hydrogen
ion concentration of \( 8.0 \times 10^{-9} \) mole liter\(^{-1} \). What is the pOH of this solution?

17. Pyridine is an organic base that reacts with water as follows:
\[
C_5H_5N + H_2O \rightleftharpoons C_5H_5NH^+ + OH^- 
\]
The base-dissociation constant for this reaction, \( K_b \), is \( 1.58 \times 10^{-8} \). What is the concentration of \( C_5H_5NH^+ \) ion in a solution that was initially \( 0.10M \) in pyridine? What is the pH of the solution?

18. Hydrazine is a weak base that dissociates in water as follows:
\[
N_2H_4 + H_2O \rightleftharpoons N_2H_5^+ + OH^- 
\]
The equilibrium constant for this dissociation at 25°C is \( 2.0 \times 10^{-6} \). Write the equilibrium-constant expression for the reaction. If the initial hydrazine concentration is \( 0.010M \), what is the concentration of hydrazinium ion, \( N_2H_5^+ \)? What is the pH?

Hydrolysis

19. What is the pH of a \( 0.18M \) solution of ammonium chloride?

20. What is the pH of a \( 0.025M \) solution of sodium acetate?

21. The hypobromite ion, \( OBr^- \), is the conjugate base of the weak hypobromous acid, \( HOBr \). When \( 0.100M \) sodium hypobromite, \( NaOBr \), is dissolved in water, the pH of the solution is 10.85. Write the equation for the hydrolysis of \( NaOBr \) and the equilibrium-constant expression for the reaction. Calculate the value of the hydrolysis constant and of the acid-dissociation constant for \( HOBr \).

22. The phenolate ion, \( C_6H_5O^- \), is the anion of the weak acid phenol, \( C_6H_5OH \). The anion undergoes hydrolysis according to the equation
\[
C_6H_5O^- + H_2O \rightleftharpoons C_6H_5OH + OH^- 
\]
A 0.0100\( M \) solution of sodium phenolate has a pH of 11.0. Write the expression for the hydrolysis constant. Calculate the numerical values of the hydrolysis constant and the acid-dissociation constant for phenol.

23. The pH of a 0.100\( M \) sodium nitrite solution is 8.15. Calculate the hydrolysis constant, \( K_b \), for \( NO_2^- \). Calculate the dissociation constant for nitrous acid.

24. What is the pH of a 1.0\( M \) solution of sodium cyanide?

Buffers

25. A buffer solution is made with 0.30\( M \) sodium cyanide and 0.30\( M \) HCN. What is the pH of the buffer solution?

26. What is the pH of a buffer that is 0.20\( M \) in \( NH_3 \) and 0.40\( M \) in \( NH_4Cl \)?

27. A buffer solution is made from equal volumes of 0.10\( M \) acetic acid and 0.10\( M \) sodium acetate. What is the pH of the buffer?

28. What is the pH of a solution made from equal volumes of 0.20\( M \) propionic acid and 0.20\( M \) sodium propionate?

pH control

29. If 0.010 mole of HCl gas is dissolved in 1 liter of pure water, what is the final pH? If the same amount of HCl is dissolved instead in 1 liter of the buffer solution of the preceding problem, what is the final pH?

30. A solution is 0.10\( M \) in formic acid and 0.010\( M \) in sodium formate. What is the
pH of the solution? If 0.10 g of sodium hydroxide is added to a liter of the buffer, what is the final pH? What will the final pH be if 1.0 g of NaOH is added instead?

31. If 20 ml of a solution of 0.6M ammonia are mixed with 10 ml of a 1.8M ammonium chloride solution, what is the final pH? If 1 ml of a 1.0M HCl solution is added, what will the pH become?

32. If the buffer solution of the preceding problem had been prepared from 0.06M ammonia and 0.18M ammonium chloride, would the same HCl solution change the pH more or less than in the first situation? Why? What would the pH be before and after addition of HCl?

Titration

33. Novocain (Nvc) is a weak organic base that reacts with water as follows:

\[ \text{Nvc} + \text{H}_2\text{O} \rightleftharpoons \text{NvcH}^+ + \text{OH}^- \]

The base-dissociation constant for this reaction is \( K_b = 9.0 \times 10^{-6} \). Suppose that a 0.010M solution of Novocain is titrated with nitric acid. (a) What is the pH of the Novocain solution at the beginning of titration, before any acid has been added? (b) At the equivalence point of the titration, the solution behaves just like a solution of 0.010M NvcH\(^+\)NO\(_3^-\). What is the pH of this solution? (c) The indicator bromcresol green has a \( pK_a \) of 5.0. Is this indicator suitable for the titration?

34. If 0.10M pyridine solution (\( K_b = 1.58 \times 10^{-8} \)) is titrated with HCl, what is the pH of the solution when the ratio of equivalents of H\(^+\) added to initial equivalents of pyridine is 0.50? What is the pH when this ratio is 1.00? From the information in Figure 5-5, which indicator would be most suitable for this titration—methyl violet, methyl orange, bromthymol blue, or alizarin?

Dissociation constant

35. A student titrated a spoonful of an unknown monoprotic acid with an NaOH solution of unknown concentration. After adding 5.00 ml of base, he found the pH of the solution to be 6.0. The equivalence point came when he added 7.00 ml of additional base. Calculate the dissociation constant of the acid.

Equilibrium constants

36. Determine equilibrium constants for the following reactions, using data in this chapter:

a) \( \text{NO}_2^- + \text{HF} \rightleftharpoons \text{HNO}_2 + \text{F}^- \)

b) \( \text{CH}_3\text{COOH} + \text{F}^- \rightleftharpoons \text{HF} + \text{CH}_3\text{COO}^- \)

c) \( \text{CH}_3\text{COOH} + \text{SO}_3^- \rightleftharpoons \text{HSO}_3^- + \text{CH}_3\text{COO}^- \)

d) \( \text{NH}_3 + \text{HSO}_3^- \rightleftharpoons \text{SO}_3^{2-} + \text{NH}_4^+ \)

Arrange the Brønsted acids in these equations in order of increasing acid strength.

Polyprotic acids

37. What are the concentrations of H\(^+\), HCO\(_3^-\), CO\(_3^{2-}\), and CO\(_2(aq)\) in a saturated solution of carbonic acid (0.034M in CO\(_2\))? What is the pH of this solution?

38. What are the concentrations of H\(^+\), HSO\(_3^-\), SO\(_3^{2-}\), and H\(_2\)SO\(_4\) in a 0.30M solution of sulfuric acid? What is the pH?

39. What are the concentrations of H\(^+\), HSO\(_3^-\), SO\(_3^{2-}\), and H\(_2\)SO\(_3\) in a 0.050M solution of SO\(_2\)?
40. What are the concentrations of $H^+$, $H_2AsO_4^-$, $HAsO_4^{2-}$, $AsO_4^{3-}$, and $H_3AsO_4$ in a 0.30$M$ solution of arsenic acid?

$K_{sp}$ calculation

41. The solubility of silver phosphate, $Ag_3PO_4$, in water is 0.0067 g liter$^{-1}$ at 20°C. What is the solubility product, $K_{sp}$, for this salt? What is the solubility of silver phosphate, in moles liter$^{-1}$, in a solution containing a total of 0.10 mole liter$^{-1}$ of Ag$^+$?

42. If a solution containing 0.16 mole liter$^{-1}$ of Pb$^{2+}$ is made 0.10 $M$ in chloride ion, 99.0% of the Pb$^{2+}$ is removed as PbCl$_2$. What is $K_{sp}$ for PbCl$_2$?

Solubilities

43. With data in Table 5-7, calculate the solubility in moles liter$^{-1}$ of MgF$_2$ in pure water. What is the solubility in 0.050$M$ NaF?

44. What is the solubility of CoS in pure water, in moles liter$^{-1}$? What is the solubility of CoS in 0.10$M$ sodium sulfide solution?

Common-ion effect

45. What is the silver ion concentration in a solution of silver chromate in pure water? In 0.10$M$ chromate solution?

46. Calculate the calcium ion concentration in a saturated solution of calcium fluoride. What will the calcium ion concentration be if the solution is also 0.05$M$ in NaF?

Precipitation

47. A solution is made 0.10$M$ in Mg$^{2+}$, 0.10$M$ in NH$_3$, and 1.0$M$ in NH$_4$Cl. Will Mg(OH)$_2$ precipitate?

48. How many grams of ammonium chloride must be added to 100 ml of 0.050$M$ ammonium hydroxide to prevent the precipitation of ferrous hydroxide, Fe(OH)$_2$, when the NH$_4$Cl–NH$_4$OH mixture is added to 100 ml of 0.020$M$ FeCl$_2$? Assume that the addition of solid NH$_4$Cl produces no volume change.

pH and precipitation control

49. The $K_{sp}$ of calcium phosphate, Ca$_3$(PO$_4$)$_2$, is $1.3 \times 10^{-32}$, and the third ionization constant of phosphoric acid is $2.2 \times 10^{-13}$. Suppose that 0.31 g of calcium phosphate is added to 100 ml of water, and the pH of the solution is adjusted until all of the calcium phosphate dissolves. What is this pH? (Assume that HPO$_4^{2-}$ is the only other species formed in the solution, and that CaHPO$_4$ is soluble.)

50. In the precipitation of metal sulfides, selective precipitation can be achieved by adjusting the hydrogen ion concentration. At what pH does ZnS begin to precipitate from a 0.077$M$ solution of H$_2$S containing 0.08$M$ Zn$^{2+}$? (Necessary data are in the tables in this chapter.)

Solubility and pH

51. What is the solubility of AgOH in a buffer at pH 13?

52. In a water solution saturated with H$_2$S, the “ion product” for H$_2$S is as given in Example 22. Calculate the solubility of FeS at pH 9 and at pH 2. Can you see how its behavior might be useful in analytical separations?

53. Calculate the solubility of Mg(OH)$_2$ in aqueous solution at pH 2 and pH 12.
How is this behavior useful in chemical separations?

54. Frequently, communities partially soften their water by adding slaked lime, Ca(OH)$_2$, to the water supply. The slaked lime reacts with HCO$_3^-$,

$$\text{Ca(OH)}_2(s) + 2\text{HCO}_3^- \rightarrow \text{CaCO}_3(s) + \text{CO}_3^{2-} + 2\text{H}_2\text{O}(l)$$

to produce a mole of CO$_3^{2-}$, which further reacts with Ca$^{2+}$ originally in the water to precipitate CaCO$_3$. Thus Ca$^{2+}$ ion is added to remove Ca$^{2+}$ ion. A malfunctioning water-softening plant once delivered saturated Ca(OH)$_2$ solution to the home owners' taps in Charleston, Illinois. Calculate the pH of a saturated solution of Ca(OH)$_2$ at 0°C. Is it unsafe for human consumption? (See Problem 12.) The solubility of Ca(OH)$_2$ can be found in a handbook.

Precipitation

55. Three suggestions are made for ways to remove silver ions from solution: (a) Make the solution 0.010M in NaI. (b) Buffer the solution at pH 13. (c) Make the solution 0.0010M in Na$_2$S. What will be the equilibrium silver ion concentration in each case? Which course of action is most effective in removing Ag$^+$ ions?

Suggested Reading