

# Chapter 9

## Aqueous Solutions and Chemical Equilibria

At equilibrium, the rate of a forward process or reaction and that of the reverse process are equal.

## 9A The chemical composition of aqueous solutions

### *Classifying Solutions of Electrolytes*

Electrolytes form ions when dissolved in solvent and thus produce solutions that conduct electricity.

Strong electrolytes ionize almost completely in a solvent, but weak electrolytes ionize only partially.

**TABLE 9-1**

#### Classification of Electrolytes

##### **Strong**

1. Inorganic acids such as  $\text{HNO}_3$ ,  $\text{HClO}_4$ ,  $\text{H}_2\text{SO}_4^*$ ,  $\text{HCl}$ ,  $\text{HI}$ ,  $\text{HBr}$ ,  $\text{HClO}_3$ ,  $\text{HBrO}_3$
2. Alkali and alkaline-earth hydroxides
3. Most salts

##### **Weak**

1. Many inorganic acids, including  $\text{H}_2\text{CO}_3$ ,  $\text{H}_3\text{BO}_3$ ,  $\text{H}_3\text{PO}_4$ ,  $\text{H}_2\text{S}$ ,  $\text{H}_2\text{SO}_3$
2. Most organic acids
3. Ammonia and most organic bases
4. Halides, cyanides, and thiocyanates of Hg, Zn, and Cd

\* $\text{H}_2\text{SO}_4$  is completely dissociated into  $\text{HSO}_4^-$  and  $\text{H}_3\text{O}^+$  ions and for this reason is classified as a strong electrolyte. Note, however, that the  $\text{HSO}_4^-$  ion is a weak electrolyte and is only partially dissociated into  $\text{SO}_4^{2-}$  and  $\text{H}_3\text{O}^+$ .

Among the strong electrolytes listed are acids, bases, and salts.

A salt is produced in the reaction of an acid with a base.

Ex., NaCl, Na<sub>2</sub>SO<sub>4</sub>, and NaOOCCH<sub>3</sub> (sodium acetate).

### *Acids and bases*

According to the Brønsted-Lowry theory, an acid is a proton donor, and a base is a proton acceptor. For a molecule to behave as an acid, it must encounter a proton acceptor (or base) and vice versa.

### *Conjugate Acids and Bases*

A conjugate base is formed when an acid loses a proton.

For example, acetate ion is the conjugate base of acetic acid.

A conjugate acid is formed when a base accepts a proton.



Acid<sub>1</sub> and base<sub>1</sub> act as a conjugate acid/base pair, or just a conjugate pair.

Similarly, every base accepts a proton to produce a conjugate acid. When these two processes are combined, the result is an acid/base, or neutralization reaction.

This reaction proceeds to an extent that depends on the relative tendencies of the two bases to accept a proton (or the two acids to donate a proton).

In an aqueous solution of ammonia, water can donate a proton and acts as an acid with respect to the solute  $\text{NH}_3$ .



Ammonia (base1) reacts with water (acid2) to give the conjugate acid ammonium ion (acid1) and hydroxide ion (base2) of the acid water.

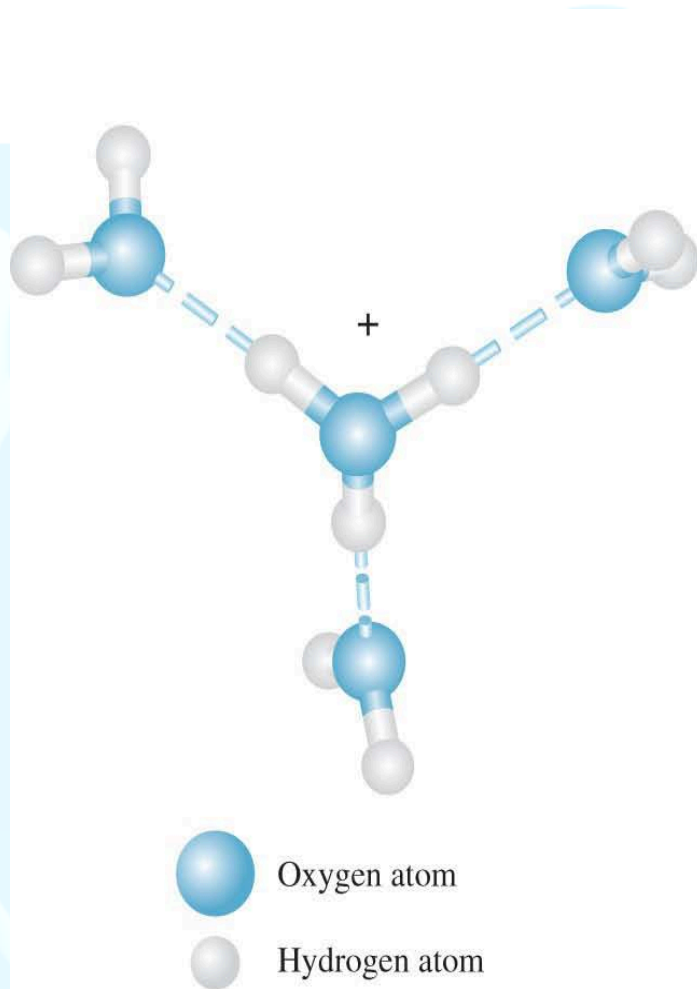
On the other hand, water acts as a proton acceptor, or base, in an aqueous solution of nitrous acid.



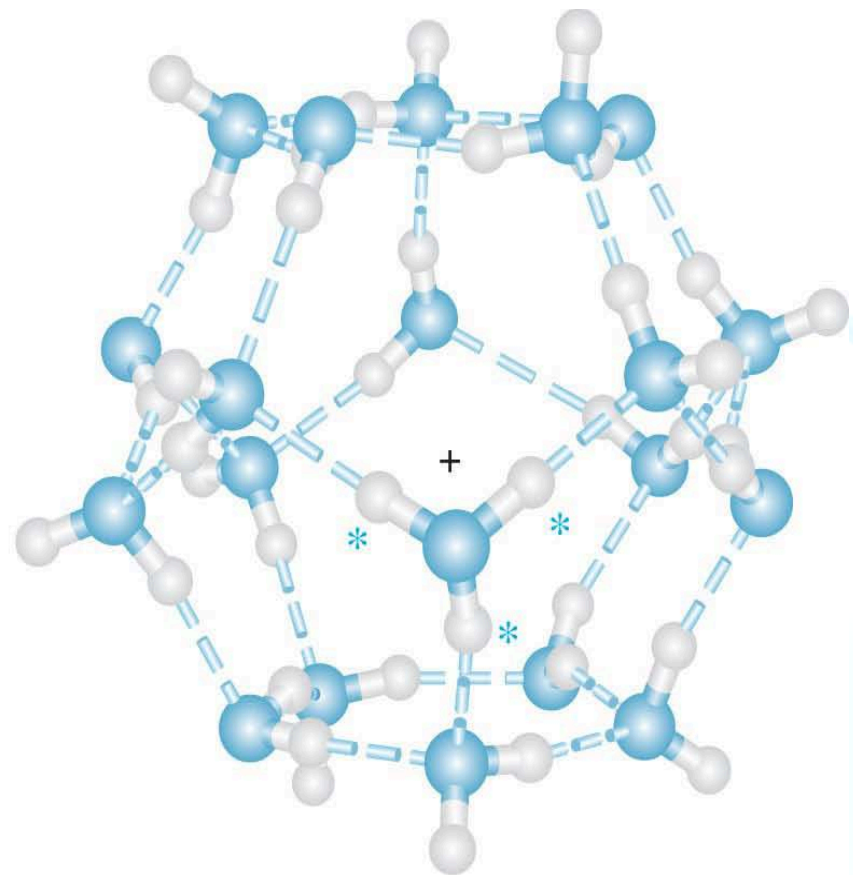
The conjugate base of the acid  $\text{HNO}_2$  is nitrite ion.

The conjugate acid of water is the hydrated proton written as  $\text{H}_3\text{O}_1$ .

This species is called the hydronium ion, and it consists of a proton covalently bonded to a single water molecule.



(a)



(b)

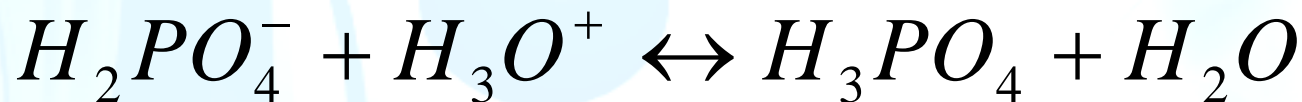
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Figure 9-1 Possible structures for the hydronium ion. Higher hydrates such as  $\text{H}_5\text{O}_{21}$ ,  $\text{H}_9\text{O}_{41}$ , having a dodecahedral cage structure may also appear in aqueous solutions of protons.

## Amphiprotic species

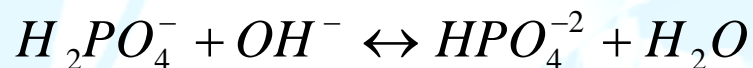
Species that have both acidic and basic properties are amphiprotic.

Ex., dihydrogen phosphate ion,  $H_2PO_4^-$ , which behaves as a base in the presence of a proton donor such as  $H_3O^+$ .



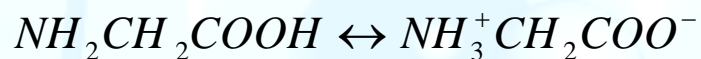
Here,  $H_3PO_4$  is the conjugate acid of the original base.

- In the presence of a proton acceptor, such as hydroxide ion, however,  $H_2PO_4^-$  behaves as an acid and donates a proton to form the conjugate base  $HPO_4^{2-}$ .



The simple amino acids are an important class of amphiprotic compounds that contain both a weak acid and a weak base functional group.

When dissolved in water, an amino acid, such as glycine, undergoes a kind of internal acid/base reaction to produce a zwitterion—a species that has both a positive and a negative charge.



Water is the classic example of an amphiprotic solvent.

Common amphiprotic solvents include methanol, ethanol, and anhydrous acetic acid.



## Autoprotolysis

Autoprotolysis (also called autoionization) is the spontaneous reaction of molecules of a substance to give a pair of ions.

The hydronium and hydroxide ion concentrations in pure water are only about  $10^{-7}$  M.

## Strengths of Acids and Bases

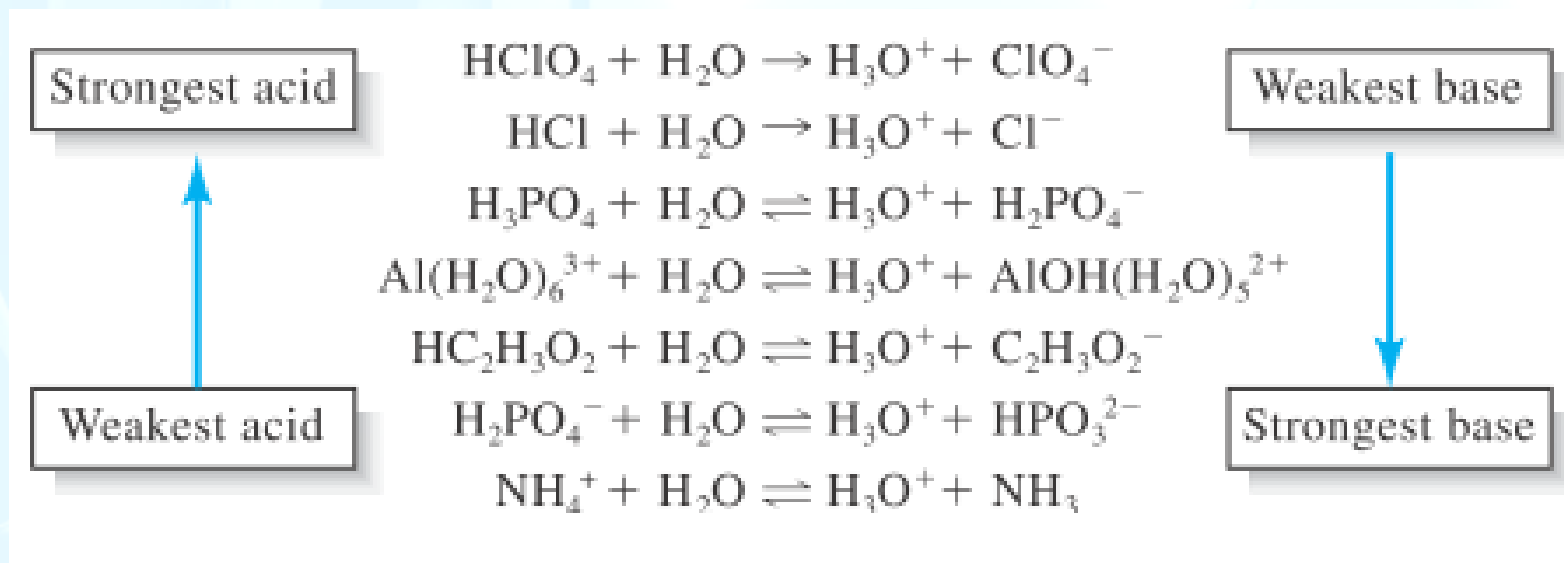


Figure 9-2 Dissociation reactions and relative strengths of some common acids and their conjugate bases.

- The common strong acids include HCl, HBr, HI, HClO<sub>4</sub>, HNO<sub>3</sub>, the first proton in H<sub>2</sub>SO<sub>4</sub>, and the organic sulfonic acid RSO<sub>3</sub>H.

- The common strong bases include NaOH, KOH, Ba(OH)<sub>2</sub>, and the quaternary ammonium hydroxide R<sub>4</sub>NOH, where R is an alkyl group such as CH<sub>3</sub> or C<sub>2</sub>H<sub>5</sub>.

-The tendency of a solvent to accept or donate protons determines the strength of a solute acid or base dissolved in it. For example, perchloric and hydrochloric acids are strong acids in water. If anhydrous acetic acid, a weaker proton acceptor than water, is substituted *as the solvent, neither of these acids undergoes complete dissociation*. Instead, equilibria such as the following are established:



- Perchloric acid is, however, about 5000 times stronger than hydrochloric acid in this solvent. Acetic acid thus acts as a **differentiating solvent toward the two acids by** revealing the inherent differences in their acidities.

-In a differentiating solvent, such as acetic acid, various acids dissociate to different degrees and have different strengths.

- Water, on the other hand, is a **leveling solvent** for perchloric, hydrochloric, and nitric acids because all three are completely ionized in this solvent and show no differences in strength.

## 9B Chemical equilibrium

- Many reactions never result in complete conversion of reactants to products. They proceed to a state of chemical equilibrium in which the ratio of concentrations of reactants and products is constant.
- Equilibrium-constant expressions are algebraic equations that describe the concentration relationships among reactants and products at equilibrium.

### *The Equilibrium State*

- The final position of a chemical equilibrium is independent of the route to the equilibrium state.
- This relationship can be altered by applying stressors such as changes in temperature, in pressure, or in total concentration of a reactant or a product.

These effects can be predicted qualitatively by the ***Le Châtelier's principle***.

This principle states that the position of chemical equilibrium always shifts in a direction that tends to relieve the effect of an applied stress.

Ex., an increase in temperature of a system alters the concentration relationship in the direction that tends to absorb heat.

The **mass-action effect** is a shift in the position of an equilibrium caused by adding one of the reactants or products to a system.

Equilibrium is a dynamic process.

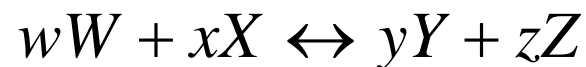
At equilibrium, the amounts of reactants and products are constant because the rates of the forward and reverse processes are exactly the same.

Chemical thermodynamics is a branch of chemistry that concerns the flow of heat and energy in chemical reactions. The position of a chemical equilibrium is related to these energy changes.

## Equilibrium-Constant Expressions

- The influence of concentration or pressure on the position of a chemical equilibrium is described in quantitative terms by means of an equilibrium-constant expression.
- They allow us to predict the direction and completeness of chemical reactions.
- An equilibrium-constant expression yields no information concerning the rate of a reaction.
- Some reactions have highly favorable equilibrium constants but are of little analytical use because they are slow. This limitation can often be overcome by the use of a catalyst.

w moles of W react with x moles of X to form y moles of Y and z moles of Z.



The equilibrium-constant expression becomes

$$K = \frac{[Y]^y [Z]^z}{[W]^w [X]^x}$$

The square-bracketed terms are:

1. molar concentrations if they represent dissolved solutes.
2. partial pressures in atmospheres if they are gas-phase reactants or products.  $[Z]^z$  is replaced with  $p_z$  (partial pressure of Z in atmosphere).

No term for Z is included in the equation if this species is a pure solid, a pure liquid, or the solvent of a dilute solution.

$$K = \frac{[Y]^y}{[W]^w [X]^x}$$

- The constant  $K$  is a temperature-dependent numerical quantity called the equilibrium constant.
- By convention, the concentrations of the products, as the equation is written, are always placed in the numerator and the concentrations of the reactants are always in the denominator.
- The exact equilibrium-constant expression takes the form:

$$K = \frac{a_Y^y a_Z^z}{a_W^w a_X^x}$$

where  $a_Y$ ,  $a_Z$ ,  $a_W$ , and  $a_X$  are the activities of species Y, Z, W, and X.

# Types of Equilibrium Constants in Analytical Chemistry

**TABLE 9-2**

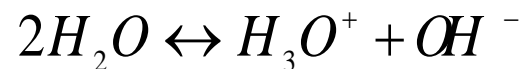
Equilibria and Equilibrium Constants Important in Analytical Chemistry

Type of Equilibrium	Name and Symbol of Equilibrium-Constant	Typical Example	Equilibrium-Constant Expression
Dissociation of water Heterogeneous equilibrium between a slightly soluble substance and its ions in a saturated solution	Ion-product constant, $K_w$ Solubility product, $K_{sp}$	$2\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-$ $\text{BaSO}_4(s) \rightleftharpoons \text{Ba}^{2+} + \text{SO}_4^{2-}$	$K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$ $K_{sp} = [\text{Ba}^{2+}][\text{SO}_4^{2-}]$
Dissociation of a weak acid or base	Dissociation constant, $K_a$ or $K_b$	$\text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{CH}_3\text{COO}^-$ $\text{CH}_3\text{COO}^- + \text{H}_2\text{O} \rightleftharpoons \text{OH}^- + \text{CH}_3\text{COOH}$	$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$ $K_b = \frac{[\text{OH}^-][\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]}$
Formation of a complex ion	Formation constant, $\beta_n$	$\text{Ni}^{2+} + 4\text{CN}^- \rightleftharpoons \text{Ni}(\text{CN})_4^{2-}$	$\beta_4 = \frac{[\text{Ni}(\text{CN})_4^{2-}]}{[\text{Ni}^{2+}][\text{CN}^-]^4}$
Oxidation/reduction equilibrium	$K_{\text{redox}}$	$\text{MnO}_4^- + 5\text{Fe}^{2+} + 8\text{H}^+ \rightleftharpoons \text{Mn}^{2+} + 5\text{Fe}^{3+} + 4\text{H}_2\text{O}$	$K_{\text{redox}} = \frac{[\text{Mn}^{2+}][\text{Fe}^{3+}]^5}{[\text{MnO}_4^-][\text{Fe}^{2+}]^5[\text{H}^+]^8}$
Distribution equilibrium for a solute between immiscible solvents	$K_d$	$\text{I}_2(aq) \rightleftharpoons \text{I}_2(org)$	$K_d = \frac{[\text{I}_2]_{org}}{[\text{I}_2]_{aq}}$



## 9B-4 Applying the Ion-Product Constant for Water

➤ Aqueous solutions contain small concentrations of hydronium and hydroxide ions as a result of the dissociation reaction.



➤ The dissociation constant can be written as

$$K = \frac{[H_3O^+][OH^-]}{[H_2O]^2}$$

➤ The concentration of water in dilute aqueous solutions is enormous, however, when compared with the concentration of hydronium and hydroxide ions. As a result,  $[H_2O]^2$  can be considered as constant and we write

$$K[H_2O]^2 = K_w = [H_3O^+][OH^-]$$

the new constant  $K_w$  is called the ion-product constant for water.

➤ *Negative logarithm of the equation gives*  $-\log K_w = -\log[H_3O^+] - \log[OH^-]$

➤ *By definition of p function, we have*

$$pK_w = pH + pOH$$

**TABLE 9-3**Variation of  $K_w$  with Temperature

Temperature, °C	$K_w$
0	$0.114 \times 10^{-14}$
25	$1.01 \times 10^{-14}$
50	$5.47 \times 10^{-14}$
75	$19.9 \times 10^{-14}$
100	$49 \times 10^{-14}$

At 25°C, the ion-product constant for water is  $1.008 \times 10^{-14}$ . For convenience, we use the approximation that at room temperature  $K_w \cong 1.00 \times 10^{-14}$ .

**Table 9-3 shows** how  $K_w$  depends on temperature. *The ion-product constant for water permits us to easily find the hydronium and hydroxide ion concentrations of aqueous solutions.*

**EXAMPLE 9-1**

Calculate the hydronium and hydroxide ion concentrations of pure water at 25°C and 100°C.

**Solution**

Because  $\text{OH}^-$  and  $\text{H}_3\text{O}^+$  are formed only from the dissociation of water, their concentrations must be equal:

$$[\text{H}_3\text{O}^+] = [\text{OH}^-]$$

We substitute this equality into Equation 9-11 to give

$$\begin{aligned} [\text{H}_3\text{O}^+]^2 &= [\text{OH}^-]^2 = K_w \\ [\text{H}_3\text{O}^+] &= [\text{OH}^-] = \sqrt{K_w} \end{aligned}$$

At 25°C,

$$[\text{H}_3\text{O}^+] = [\text{OH}^-] = \sqrt{1.00 \times 10^{-14}} = 1.00 \times 10^{-7} \text{ M}$$

At 100°C, from Table 9-3,

### EXAMPLE 9-2

Calculate the hydronium and hydroxide ion concentrations and the pH and pOH of 0.200 M aqueous NaOH at 25°C.

#### Solution

Sodium hydroxide is a strong electrolyte, and its contribution to the hydroxide ion concentration in this solution is 0.200 mol/L. As in Example 9-1, hydroxide ions and hydronium ions are formed in equal amounts from the dissociation of water. Therefore, we write

$$[\text{OH}^-] = 0.200 + [\text{H}_3\text{O}^+]$$

where  $[\text{H}_3\text{O}^+]$  is equal to the hydroxide ion concentration from the dissociation of water. The concentration of  $\text{OH}^-$  from the water is insignificant, however, compared with 0.200, so we can write

$$[\text{OH}^-] \approx 0.200$$

$$\text{pOH} = -\log 0.200 = 0.699$$

Equation 9-11 is then used to calculate the hydronium ion concentration:

$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.00 \times 10^{-14}}{0.200} = 5.00 \times 10^{-14} \text{ M}$$

$$\text{pH} = -\log 5.00 \times 10^{-14} = 13.301$$

Note that the approximation

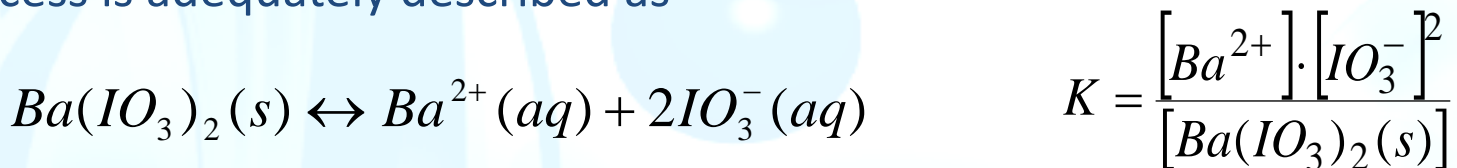
$$[\text{OH}^-] = 0.200 + 5.00 \times 10^{-14} \approx 0.200 \text{ M}$$

causes no significant error in our answer.

## Using Solubility-Product Constants

➤ Most sparingly soluble salts are completely dissociated in saturated aqueous solution, which means that the very small amount that does go into solution dissociates completely.

➤ When an excess of barium iodate is equilibrated with water, the dissociation process is adequately described as



➤ “An excess of barium iodate is equilibrated with water” means that more solid barium iodate is added to a portion of water than would dissolve at the temperature of the experiment.

➤ Some solid  $BaIO_3$  is in contact with the saturated solution. The concentration of a compound in its solid state is, however, constant. In other words, the number of moles of  $Ba(IO_3)_2$  divided by the *volume of the solid  $Ba(IO_3)_2$*  is *constant* no matter how much excess solid is present. Therefore, the previous equation can be rewritten in the form

$$K[Ba(IO_3)_2(s)] = K_{sp} = [Ba^{2+}][IO_3^-]^2 \qquad \text{solubility-product constant}$$

The equation shows that the position of this equilibrium is independent of the amount of  $Ba(IO_3)_2$  as long as some solid is present.

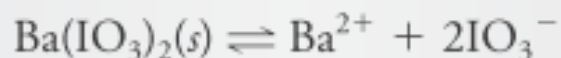
## The Solubility of a Precipitate in Pure Water

### EXAMPLE 9-3

What mass (in grams) of  $\text{Ba}(\text{IO}_3)_2$  (487 g/mol) can be dissolved in 500 mL of water at 25°C?

#### Solution

The solubility-product constant for  $\text{Ba}(\text{IO}_3)_2$  is  $1.57 \times 10^{-9}$  (see Appendix 2). The equilibrium between the solid and its ions in solution is described by the equation



and so

$$K_{\text{sp}} = [\text{Ba}^{2+}][\text{IO}_3^-]^2 = 1.57 \times 10^{-9}$$

The equation describing the equilibrium reveals that 1 mol of  $\text{Ba}^{2+}$  is formed for each mole of  $\text{Ba}(\text{IO}_3)_2$  that dissolves. Therefore,

$$\text{molar solubility of } \text{Ba}(\text{IO}_3)_2 = [\text{Ba}^{2+}]$$

Since two moles of iodate are produced for each mole of barium ion, the iodate concentration is twice the barium ion concentration:

$$[\text{IO}_3^-] = 2[\text{Ba}^{2+}]$$

Substituting this last equation into the equilibrium-constant expression gives

$$[\text{Ba}^{2+}](2[\text{Ba}^{2+}])^2 = 4[\text{Ba}^{2+}]^3 = 1.57 \times 10^{-9}$$

$$[\text{Ba}^{2+}] = \left( \frac{1.57 \times 10^{-9}}{4} \right)^{1/3} = 7.32 \times 10^{-4} \text{ M}$$

Since 1 mol  $\text{Ba}^{2+}$  is produced for every mole of  $\text{Ba}(\text{IO}_3)_2$ ,

$$\text{solubility} = 7.32 \times 10^{-4} \text{ M}$$

To compute the number of millimoles of  $\text{Ba}(\text{IO}_3)_2$  dissolved in 500 mL of solution, we write

$$\text{no. mmol Ba}(\text{IO}_3)_2 = 7.32 \times 10^{-4} \frac{\text{mmol Ba}(\text{IO}_3)_2}{\text{mL}} \times 500 \text{ mL}$$

The mass of  $\text{Ba}(\text{IO}_3)_2$  in 500 mL is given by

$$\text{mass Ba}(\text{IO}_3)_2 =$$

$$\begin{aligned} & (7.32 \times 10^{-4} \times 500) \frac{\text{mmol Ba}(\text{IO}_3)_2}{\text{mL}} \times 0.487 \frac{\text{g Ba}(\text{IO}_3)_2}{\text{mmol Ba}(\text{IO}_3)_2} \\ & = 0.178 \text{ g} \end{aligned}$$

## *The Effect of a Common Ion on the Solubility of a Precipitate*

The **common-ion effect** is a mass-action effect predicted from Le Châtelier's principle and is demonstrated by the following examples.

### EXAMPLE 9-4

Calculate the molar solubility of  $\text{Ba}(\text{IO}_3)_2$  in a solution that is 0.0200 M in  $\text{Ba}(\text{NO}_3)_2$ .

#### Solution

The solubility is not equal to  $[\text{Ba}^{2+}]$  in this case because  $\text{Ba}(\text{NO}_3)_2$  is also a source of barium ions. We know, however, that the solubility is related to  $[\text{IO}_3^-]$ :

$$\text{molar solubility of } \text{Ba}(\text{IO}_3)_2 = \frac{1}{2}[\text{IO}_3^-]$$

There are two sources of barium ions:  $\text{Ba}(\text{NO}_3)_2$  and  $\text{Ba}(\text{IO}_3)_2$ . The contribution from the nitrate is 0.0200 M, and that from the iodate is equal to the molar solubility, or  $\frac{1}{2}[\text{IO}_3^-]$ . Thus,

$$[\text{Ba}^{2+}] = 0.0200 + \frac{1}{2}[\text{IO}_3^-]$$

By substituting these quantities into the solubility-product expression, we find that

$$\left(0.0200 + \frac{1}{2}[\text{IO}_3^-]\right)[\text{IO}_3^-]^2 = 1.57 \times 10^{-9}$$

The solubility of an ionic precipitate decreases when a soluble compound containing one of the ions of the precipitate is added to the solution. This behavior is called the common-ion effect.

Since this is a cubic equation, we would like to make an assumption that would simplify the algebra required to find  $[\text{IO}_3^-]$ . The small numerical value of  $K_{\text{sp}}$  suggests that the solubility of  $\text{Ba}(\text{IO}_3)_2$  is quite small, and this finding is confirmed by the result obtained in Example 9-3. Also, barium ion from  $\text{Ba}(\text{NO}_3)_2$  will further suppress the limited solubility of  $\text{Ba}(\text{IO}_3)_2$ . Therefore, it seems reasonable to assume that 0.0200 is large with respect to  $\frac{1}{2}[\text{IO}_3^-]$  in order to find a provisional answer to the problem. That is, we assume that  $\frac{1}{2}[\text{IO}_3^-] \ll 0.0200$ , so

$$[\text{Ba}^{2+}] = 0.0200 + \frac{1}{2}[\text{IO}_3^-] \approx 0.0200 \text{ M}$$

The original equation then simplifies to

$$\begin{aligned} 0.0200 [\text{IO}_3^-]^2 &= 1.57 \times 10^{-9} \\ [\text{IO}_3^-] &= \sqrt{1.57 \times 10^{-9}/0.0200} = \sqrt{7.85 \times 10^{-8}} = 2.80 \times 10^{-4} \text{ M} \end{aligned}$$

The assumption that  $(0.0200 + \frac{1}{2} \times 2.80 \times 10^{-4}) \approx 0.0200$  causes minimal error because the second term, representing the amount of  $\text{Ba}^{2+}$  arising from the dissociation of  $\text{Ba}(\text{IO}_3)_2$ , is only about 0.7% of 0.0200. Usually, we consider an assumption of this type to be satisfactory if the discrepancy is less than 10%.<sup>1</sup> Finally, then,

$$\text{solubility of } \text{Ba}(\text{IO}_3)_2 = \frac{1}{2}[\text{IO}_3^-] = \frac{1}{2} \times 2.80 \times 10^{-4} = 1.40 \times 10^{-4} \text{ M}$$

If we compare this result with the solubility of barium iodate in pure water (Example 9-3), we see that the presence of a small concentration of the common ion has decreased the molar solubility of  $\text{Ba}(\text{IO}_3)_2$  by a factor of about 5.



### EXAMPLE 9-5

Calculate the solubility of  $\text{Ba}(\text{IO}_3)_2$  in a solution prepared by mixing 200 mL of 0.0100 M  $\text{Ba}(\text{NO}_3)_2$  with 100 mL of 0.100 M  $\text{NaIO}_3$ .

#### Solution

First, establish whether either reactant is present in excess at equilibrium. The amounts taken are

$$\text{no. mmol Ba}^{2+} = 200 \text{ mL} \times 0.0100 \text{ mmol/mL} = 2.00$$

$$\text{no. mmol IO}_3^- = 100 \text{ mL} \times 0.100 \text{ mmol/mL} = 10.0$$

If the formation of  $\text{Ba}(\text{IO}_3)_2$  is complete,

$$\text{no. mmol excess NaIO}_3 = 10.0 - 2 \times 2.00 = 6.0$$

$$[\text{IO}_3^-] = \frac{6.0 \text{ mmol}}{200 \text{ mL} + 100 \text{ mL}} = \frac{6.0 \text{ mmol}}{300 \text{ mL}} = 0.0200 \text{ M}$$

As in Example 9-3,

$$\text{molar solubility of Ba}(\text{IO}_3)_2 = [\text{Ba}^{2+}]$$

In this case, however,

$$[\text{IO}_3^-] = 0.0200 + 2[\text{Ba}^{2+}]$$

where  $2[\text{Ba}^{2+}]$  represents the iodate contributed by the sparingly soluble  $\text{Ba}(\text{IO}_3)_2$ . We find a provisional answer after making the assumption that  $[\text{IO}_3^-] \approx 0.0200$ . Therefore,

$$\text{solubility of } \text{Ba}(\text{IO}_3)_2 = [\text{Ba}^{2+}] = \frac{K_{\text{sp}}}{[\text{IO}_3^-]^2} = \frac{1.57 \times 10^{-9}}{(0.0200)^2} = 3.93 \times 10^{-6} \text{ M}$$

Since the provisional answer is nearly four orders of magnitude less than 0.0200 M, our approximation is justified, and the solution does not need further refinement.

The uncertainty in  $[\text{IO}_3^-]$  is 0.1 part in 6.0 or 1 part in 60. thus, 0.0200 (1/60) 5 0.0003, and we round to 0.0200 M.

A 0.02 M excess of  $\text{Ba}^{+2}$  decreases the solubility of  $\text{Ba}(\text{IO}_3)^-$  by a factor of about 5; this same excess of  $\text{IO}_3^-$  lowers the solubility by a factor of about 200.

## Using Acid/Base Dissociation Constants

When a weak acid or a weak base is dissolved in water, partial dissociation occurs.



$K_a$  is the acid dissociation constant for nitrous acid.

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{NO}_2^-]}{[\text{HNO}_2]}$$

In an analogous way, the base dissociation constant for ammonia is

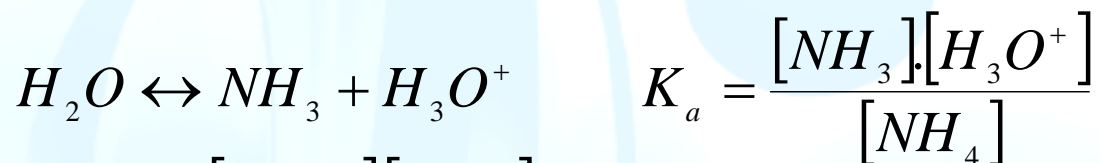
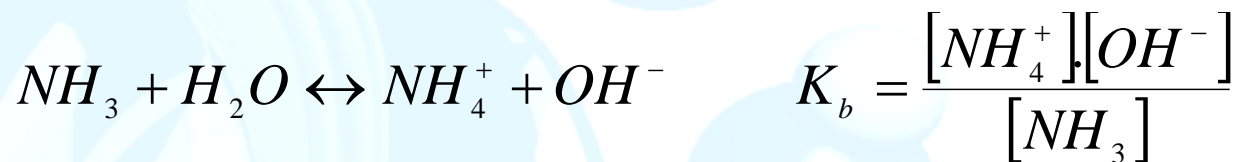


$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

For both,  $[\text{H}_2\text{O}]$  does not appear in the denominator because the concentration of water is very large relative to the concentration of the weak acid or base that the dissociation does not alter  $[\text{H}_2\text{O}]$  appreciably.

## Dissociation Constants for Conjugate Acid/Base Pairs

Consider the base dissociation-constant expression for ammonia and the acid dissociation-constant expression for its conjugate acid, ammonium ion:



$$K_a K_b = [H_3O^+][OH^-]$$

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

$$K_w = K_a K_b$$

### EXAMPLE 9-6

What is  $K_b$  for the equilibrium  $CN^- + H_2O \rightleftharpoons HCN + OH^-$

### Solution

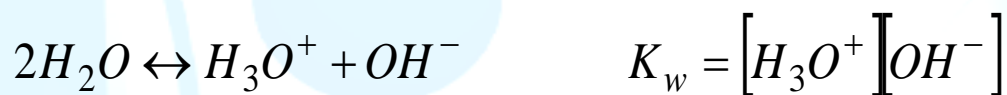
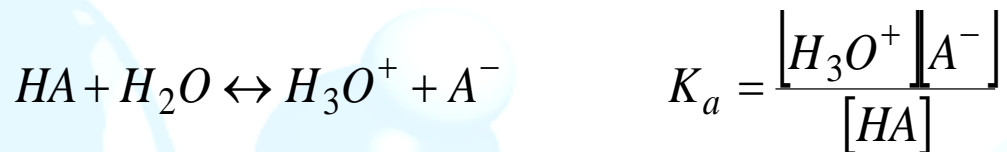
Appendix 3 lists a  $K_a$  value of  $6.2 \times 10^{-10}$  for HCN. Thus,

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

$$K_b = \frac{1.00 \times 10^{-14}}{6.2 \times 10^{-10}} = 1.61 \times 10^{-5}$$

## Hydronium Ion Concentration of Solutions of Weak Acids

When the weak acid HA is dissolved in water, two equilibria produce hydronium ions:



Normally, the hydronium ions produced from the first reaction suppress the dissociation of water to such an extent that the contribution of hydronium ions from the second equilibrium is negligible. Under these circumstances;

- one  $H_3O^+$  ion is formed for each  $A^-$  ion, and we write

$$[A^-] \approx [H_3O^+]$$

The sum of the molar concentrations of the weak acid and its conjugate base must equal the analytical concentration of the acid  $c_{HA}$

Thus, we get the mass-balance equation

$$c_{HA} = [A^-] + [HA^-]$$

Substituting  $[H_3O^+]$  for  $[A^-]$  yields

$$c_{HA} = [H_3O^+] + [HA]$$

Which rearranges to

$$[HA] = c_{HA} - [H_3O^+]$$

Thus, the equilibrium-constant expression becomes

$$K_a = \frac{[H_3O^+]^2}{c_{HA} - [H_3O^+]} \quad (\text{Eqn...9-18})$$

Which rearranges to

$$[H_3O^+]^2 + K_a[H_3O^+] - K_a c_{HA} = 0$$

The positive solution to this quadratic equation is 
$$[H_3O^+] = \frac{-K_a + \sqrt{K_a^2 + 4 \cdot K_a \cdot c_{HA}}}{2}$$

This can be simplified by making the additional assumption that dissociation does not appreciably decrease the molar concentration of HA.

Thus, if  $[H_3O^+] \ll c_{HA}$ ,  $c_{HA} - [H_3O^+] \approx c_{HA}$ , and Equation 9-18 reduces to

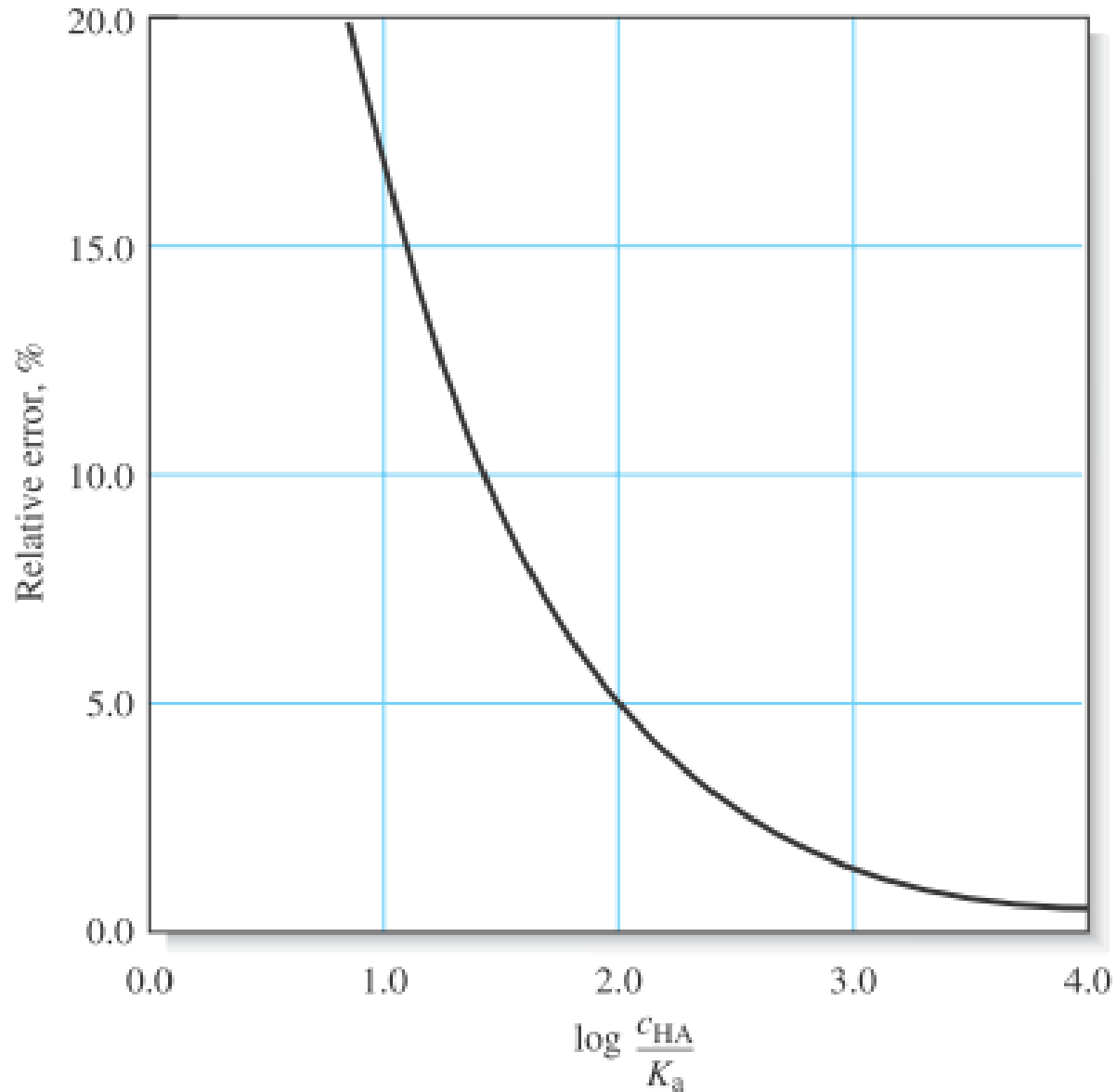
$$K_a = \frac{[H_3O^+]^2}{c_{HA}} \quad [H_3O^+] = \sqrt{K_a c_{HA}}$$

**TABLE 9-4**

Error Introduced by Assuming  $H_3O^+$  Concentration Is Small Relative to  $c_{HA}$  in Equation 9-16

$K_a$	$c_{HA}$	$[H_3O^+]$ Using Assumption	$\frac{c_{HA}}{K_a}$	$[H_3O^+]$ Using More Exact Equation	Percent Error
$1.00 \times 10^{-2}$	$1.00 \times 10^{-3}$	$3.16 \times 10^{-3}$	$10^{-1}$	$0.92 \times 10^{-3}$	244
	$1.00 \times 10^{-2}$	$1.00 \times 10^{-2}$	$10^0$	$0.62 \times 10^{-2}$	61
	$1.00 \times 10^{-1}$	$3.16 \times 10^{-2}$	$10^1$	$2.70 \times 10^{-2}$	17
$1.00 \times 10^{-4}$	$1.00 \times 10^{-4}$	$1.00 \times 10^{-4}$	$10^0$	$0.62 \times 10^{-4}$	61
	$1.00 \times 10^{-3}$	$3.16 \times 10^{-4}$	$10^1$	$2.70 \times 10^{-4}$	17
	$1.00 \times 10^{-2}$	$1.00 \times 10^{-3}$	$10^2$	$0.95 \times 10^{-3}$	5.3
	$1.00 \times 10^{-1}$	$3.16 \times 10^{-3}$	$10^3$	$3.11 \times 10^{-3}$	1.6
$1.00 \times 10^{-6}$	$1.00 \times 10^{-5}$	$3.16 \times 10^{-6}$	$10^1$	$2.70 \times 10^{-6}$	17
	$1.00 \times 10^{-4}$	$1.00 \times 10^{-5}$	$10^2$	$0.95 \times 10^{-5}$	5.3
	$1.00 \times 10^{-3}$	$3.16 \times 10^{-5}$	$10^3$	$3.11 \times 10^{-5}$	1.6
	$1.00 \times 10^{-2}$	$1.00 \times 10^{-4}$	$10^4$	$9.95 \times 10^{-5}$	0.5
	$1.00 \times 10^{-1}$	$3.16 \times 10^{-4}$	$10^5$	$3.16 \times 10^{-4}$	0.0

Figure 9-3 Relative error resulting from the assumption that  $[H_3O^+] \ll c_{HA}$





### EXAMPLE 9-7

Calculate the hydronium ion concentration in 0.120 M nitrous acid.

#### Solution

The principal equilibrium is



for which (see Appendix 2)

$$K_a = 7.1 \times 10^{-4} = \frac{[\text{H}_3\text{O}^+][\text{NO}_2^-]}{[\text{HNO}_2]}$$

Substitution into Equations 9-15 and 9-17 gives

$$\begin{aligned}[\text{NO}_2^-] &= [\text{H}_3\text{O}^+] \\ [\text{HNO}_2] &= 0.120 - [\text{H}_3\text{O}^+]\end{aligned}$$

When these relationships are introduced into the expression for  $K_a$ , we obtain

$$K_a = \frac{[\text{H}_3\text{O}^+]^2}{0.120 - [\text{H}_3\text{O}^+]} = 7.1 \times 10^{-4}$$

If we now assume that  $[\text{H}_3\text{O}^+] \ll 0.120$ , we find

$$\frac{[\text{H}_3\text{O}^+]^2}{0.120} = 7.1 \times 10^{-4}$$

$$[\text{H}_3\text{O}^+] = \sqrt{0.120 \times 7.1 \times 10^{-4}} = 9.2 \times 10^{-3} \text{ M}$$

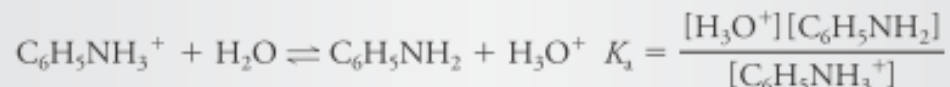
We now examine the assumption that  $0.120 - 0.0092 \approx 0.120$  and see that the error is about 8%. The relative error in  $[\text{H}_3\text{O}^+]$  is actually smaller than this figure, however, as we can see by calculating  $\log(c_{\text{HA}}/K_a) = 2.2$ , which from Figure 9-3, suggests an error of about 4%. If a more accurate figure is needed, the quadratic equation gives an answer of  $8.9 \times 10^{-3} \text{ M}$  for the hydronium ion concentration.

### EXAMPLE 9-8

Calculate the hydronium ion concentration in a solution that is  $2.0 \times 10^{-4}$  M in aniline hydrochloride,  $\text{C}_6\text{H}_5\text{NH}_3\text{Cl}$ .

#### Solution

In aqueous solution, dissociation of the salt to  $\text{Cl}^-$  and  $\text{C}_6\text{H}_5\text{NH}_3^+$  is complete. The weak acid  $\text{C}_6\text{H}_5\text{NH}_3^+$  dissociates as follows:



If we look in Appendix 3, we find that the  $K_a$  for  $\text{C}_6\text{H}_5\text{NH}_3^+$  is  $2.51 \times 10^{-5}$ . Proceeding as in Example 9-7, we have

$$\begin{aligned}[\text{H}_3\text{O}^+] &= [\text{C}_6\text{H}_5\text{NH}_2] \\ [\text{C}_6\text{H}_5\text{NH}_3^+] &= 2.0 \times 10^{-4} - [\text{H}_3\text{O}^+]\end{aligned}$$

Assume that  $[\text{H}_3\text{O}^+] \ll 2.0 \times 10^{-4}$ , and substitute the simplified value for  $[\text{C}_6\text{H}_5\text{NH}_3^+]$  into the dissociation-constant expression to obtain (see Equation 9-21)

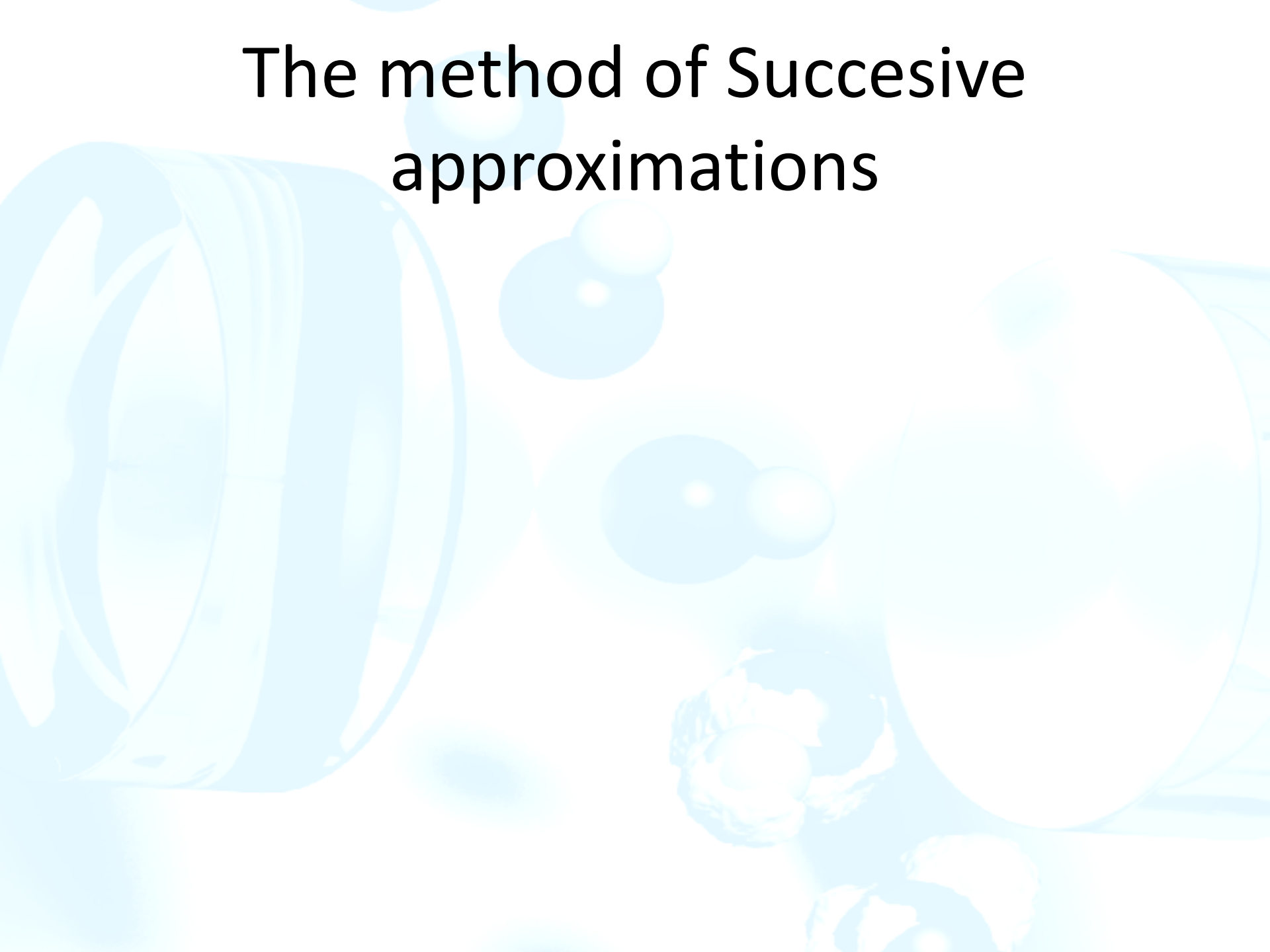
$$\begin{aligned}\frac{[\text{H}_3\text{O}^+]^2}{2.0 \times 10^{-4}} &= 2.51 \times 10^{-5} \\ [\text{H}_3\text{O}^+] &= \sqrt{5.02 \times 10^{-9}} = 7.09 \times 10^{-5} \text{ M}\end{aligned}$$

If we compare  $7.09 \times 10^{-5}$  with  $2.0 \times 10^{-4}$ , we see that a significant error has been introduced by the assumption that  $[\text{H}_3\text{O}^+] \ll c_{\text{C}_6\text{H}_5\text{NH}_3^+}$  (Figure 9-3 indicates that this error is about 20%.) Thus, unless only an approximate value for  $[\text{H}_3\text{O}^+]$  is needed, it is necessary to use the more accurate expression (Equation 9-19)

$$\frac{[\text{H}_3\text{O}^+]^2}{2.0 \times 10^{-4} - [\text{H}_3\text{O}^+]} = 2.51 \times 10^{-5}$$

$$\begin{aligned}[\text{H}_3\text{O}^+]^2 + 2.51 \times 10^{-5}[\text{H}_3\text{O}^+] - 5.02 \times 10^{-9} &= 0 \\ [\text{H}_3\text{O}^+] &= \frac{-2.51 \times 10^{-5} + \sqrt{(2.54 \times 10^{-5})^2 + 4 \times 5.02 \times 10^{-9}}}{2} \\ &= 5.94 \times 10^{-5} \text{ M}\end{aligned}$$

# The method of Successive approximations



## *Hydronium Ion Concentration of Solutions of Weak Bases*

Aqueous ammonia is basic as a result of the reaction



The equilibrium constant of the reaction is

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

### EXAMPLE 9-9

Calculate the hydroxide ion concentration of a 0.0750 M  $\text{NH}_3$  solution.

#### Solution

The predominant equilibrium is



As we showed on page 211,

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{1.00 \times 10^{-14}}{5.70 \times 10^{-10}} = 1.75 \times 10^{-5}$$

The chemical equation shows that  $[\text{NH}_4^+] = [\text{OH}^-]$

Both  $\text{NH}_4^+$  and  $\text{NH}_3$  come from the 0.0750 M solution. Thus,

$$[\text{NH}_4^+] + [\text{NH}_3] = c_{\text{NH}_3} = 0.0750 \text{ M}$$

If we substitute  $[\text{OH}^-]$  for  $[\text{NH}_4^+]$  in the second of these equations and rearrange, we find that

$$[\text{NH}_3] = 0.0750 - [\text{OH}^-]$$

By substituting these quantities into the dissociation-constant, we have

$$\frac{[\text{OH}^-]^2}{7.50 \times 10^{-2} - [\text{OH}^-]} = 1.75 \times 10^{-5}$$

which is analogous to Equation 9-17 for weak acids. If we assume that  $[\text{OH}^-] \ll 7.50 \times 10^{-2}$ , this equation simplifies to

$$\begin{aligned} [\text{OH}^-]^2 &\approx 7.50 \times 10^{-2} \times 1.75 \times 10^{-5} \\ [\text{OH}^-] &= 1.15 \times 10^{-3} \text{ M} \end{aligned}$$

Comparing the calculated value for  $[\text{OH}^-]$  with  $7.50 \times 10^{-2}$ , we see that the error in  $[\text{OH}^-]$  is less than 2%. If necessary, a better value for  $[\text{OH}^-]$  can be obtained by solving the quadratic equation.

### EXAMPLE 9-10

Calculate the hydroxide ion concentration in a 0.0100 M sodium hypochlorite solution.

#### Solution

The equilibrium between  $\text{OCl}^-$  and water is



for which

$$K_b = \frac{[\text{HOCl}][\text{OH}^-]}{[\text{OCl}^-]}$$

The acid dissociation constant for HOCl from Appendix 3 is  $3.0 \times 10^{-8}$ . Therefore, we rearrange Equation 9-14 and write

$$K_b = \frac{K_w}{K_a} = \frac{1.00 \times 10^{-14}}{3.0 \times 10^{-8}} = 3.33 \times 10^{-7}$$

Proceeding as in Example 9-9, we have

$$\begin{aligned}[\text{OH}^-] &= [\text{HOCl}] \\ [\text{OCl}^-] + [\text{HOCl}] &= 0.0100 \\ [\text{OCl}^-] &= 0.0100 - [\text{OH}^-] \approx 0.0100\end{aligned}$$

In this case, we have assumed that  $[\text{OH}^-] \ll 0.0100$ . We substitute this value into the equilibrium constant expression and calculate

$$\begin{aligned}\frac{[\text{OH}^-]^2}{0.0100} &= 3.33 \times 10^{-7} \\ [\text{OH}^-] &= 5.8 \times 10^{-5} \text{ M}\end{aligned}$$

Verify for yourself that the error resulting from the approximation is small.

## 9C Buffer solutions

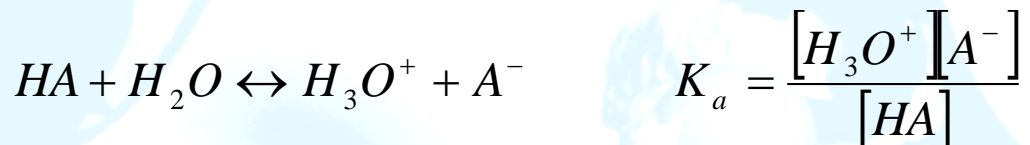
A buffer solution resists changes in pH when it is diluted or when acids or bases are added to it.

Buffer solutions are prepared from a conjugate acid/base pair.

Buffers are used in chemical applications whenever it is important to maintain the pH of a solution at a constant and predetermined level.

### *Calculating the pH of Buffer Solutions*

A solution containing a weak acid, HA, and its conjugate base, A<sup>-</sup>, may be acidic, neutral, or basic, depending on the positions of two competitive equilibria:





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

These two equilibrium-constant expressions show that the relative concentrations of the hydronium and hydroxide ions depend not only on the magnitudes of  $K_a$  and  $K_b$  but also on the ratio between the concentrations of the acid and its conjugate base.

The equilibrium concentrations of HA and NaA are expressed in terms of their analytical concentrations,  $c_{HA}$  and  $c_{NaA}$ .

$$[HA] = c_{HA} - [H_3O^{+}] + [OH^{-}]$$

$$[A^{-}] = c_{NaA} + [H_3O^{+}] - [OH^{-}]$$

$$[HA] \approx c_{HA}$$

$$[A^{-}] \approx c_{NaA}$$



The dissociation-constant expression can then be expressed as:

$$[H_3O^+] = K_a \frac{c_{HA}}{c_{NaA}}$$

The hydronium ion concentration of a solution containing a weak acid and its conjugate base depends only on the ratio of the molar concentrations of these two solutes.

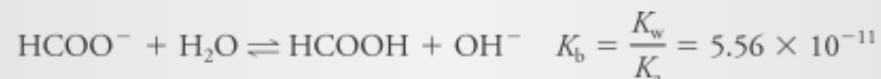
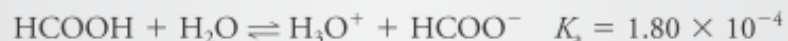
Furthermore, this ratio is independent of dilution because the concentration of each component changes proportionally when the volume changes.

### EXAMPLE 9-11

What is the pH of a solution that is 0.400 M in formic acid and 1.00 M in sodium formate?

#### Solution

The pH of this solution is affected by the  $K_a$  of formic acid and the  $K_b$  of formate ion.



Because the  $K_a$  for formic acid is orders of magnitude larger than the  $K_b$  for formate, the solution is acidic, and  $K_a$  determines the  $\text{H}_3\text{O}^+$  concentration. We can thus write

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{HCOO}^-]}{[\text{HCOOH}]} = 1.80 \times 10^{-4}$$

$$[\text{HCOO}^-] \approx c_{\text{HCOO}^-} = 1.00 \text{ M}$$

$$[\text{HCOOH}] \approx c_{\text{HCOOH}} = 0.400 \text{ M}$$

By substituting these expressions into Equation 9-29 and rearranging, we have

$$[\text{H}_3\text{O}^+] = 1.80 \times 10^{-4} \times \frac{0.400}{1.00} = 7.20 \times 10^{-5} \text{ M}$$

Notice that our assumptions that  $[\text{H}_3\text{O}^+] \ll c_{\text{HCOOH}}$  and that  $[\text{H}_3\text{O}^+] \ll c_{\text{HCOO}^-}$  are valid. Therefore,

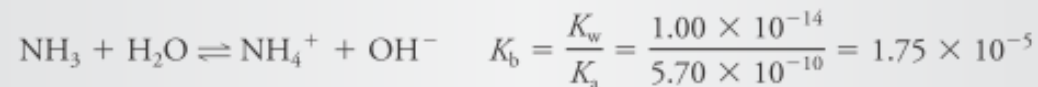
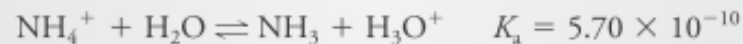
$$\text{pH} = -\log(7.20 \times 10^{-5}) = 4.14$$

### EXAMPLE 9-12

Calculate the pH of a solution that is 0.200 M in  $\text{NH}_3$  and 0.300 M in  $\text{NH}_4\text{Cl}$ .

#### Solution

In Appendix 3, we find that the acid dissociation constant  $K_a$  for  $\text{NH}_4^+$  is  $5.70 \times 10^{-10}$ . The equilibria we must consider are



Using the arguments that led to Equations 9-25 and 9-26, we find that

$$[\text{NH}_4^+] = c_{\text{NH}_4\text{Cl}} + [\text{OH}^-] - [\text{H}_3\text{O}^+] \approx c_{\text{NH}_4\text{Cl}} + [\text{OH}^-]$$

$$[\text{NH}_3] = c_{\text{NH}_3} + [\text{H}_3\text{O}^+] - [\text{OH}^-] \approx c_{\text{NH}_3} - [\text{OH}^-]$$

Because  $K_b$  is several orders of magnitude larger than  $K_a$ , we have assumed that the solution is basic and that  $[\text{OH}^-]$  is much larger than  $[\text{H}_3\text{O}^+]$ . Thus, we have neglected the concentration of  $\text{H}_3\text{O}^+$  in these approximations.

We also assume that  $[\text{OH}^-]$  is much smaller than  $c_{\text{NH}_4\text{Cl}}$  and  $c_{\text{NH}_3}$ , so that

$$[\text{NH}_4^+] \approx c_{\text{NH}_4\text{Cl}} = 0.300 \text{ M}$$

$$[\text{NH}_3] \approx c_{\text{NH}_3} = 0.200 \text{ M}$$

When we substitute these expressions into the acid dissociation constant for  $\text{NH}_4^+$ , we have a relationship similar to Equation 9-29. That is,

$$\begin{aligned}[\text{H}_3\text{O}^+] &= \frac{K_a \times [\text{NH}_4^+]}{[\text{NH}_3]} = \frac{5.70 \times 10^{-10} \times c_{\text{NH}_4\text{Cl}}}{c_{\text{NH}_3}} \\ &= \frac{5.70 \times 10^{-10} \times 0.300}{0.200} = 8.55 \times 10^{-10} \text{ M}\end{aligned}$$

To check the validity of our approximations, we calculate  $[\text{OH}^-]$ . Thus,

$$[\text{OH}^-] = \frac{1.00 \times 10^{-14}}{8.55 \times 10^{-10}} = 1.17 \times 10^{-5} \text{ M}$$

which is far smaller than  $c_{\text{NH}_4\text{Cl}}$  or  $c_{\text{NH}_3}$ . Finally, we write

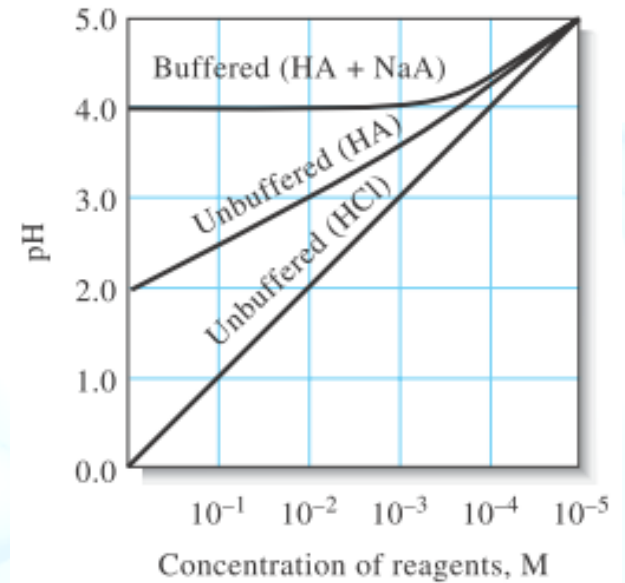
$$\text{pH} = -\log(8.55 \times 10^{-10}) = 9.07$$

## Properties of Buffer Solutions

*Figure 9-4 The effect of dilution of the pH of buffered and unbuffered solutions.*

### *The Effect of Added Acids and Bases*

Buffers do not maintain pH at an absolutely constant value, but changes in pH are relatively small when small amounts of acid or base are added.

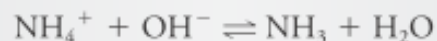


### EXAMPLE 9-13

Calculate the pH change that takes place when a 100-mL portion of (a) 0.0500 M NaOH and (b) 0.0500 M HCl is added to 400 mL of the buffer solution that was described in Example 9-12.

#### Solution

(a) Adding NaOH converts part of the  $\text{NH}_4^+$  in the buffer to  $\text{NH}_3$ :



The analytical concentrations of  $\text{NH}_3$  and  $\text{NH}_4\text{Cl}$  then become

$$c_{\text{NH}_3} = \frac{400 \times 0.200 + 100 \times 0.0500}{500} = \frac{85.0}{500} = 0.170 \text{ M}$$

$$c_{\text{NH}_4\text{Cl}} = \frac{400 \times 0.300 - 100 \times 0.0500}{500} = \frac{115}{500} = 0.230 \text{ M}$$

When substituted into the acid dissociation-constant expression for  $\text{NH}_4^+$ , these values yield

$$[\text{H}_3\text{O}^+] = 5.70 \times 10^{-10} \times \frac{0.230}{0.170} = 7.71 \times 10^{-10} \text{ M}$$

$$\text{pH} = -\log 7.71 \times 10^{-10} = 9.11$$

and the change in pH is

$$\Delta\text{pH} = 9.11 - 9.07 = 0.04$$

(b) Adding HCl converts part of the  $\text{NH}_3$  to  $\text{NH}_4^+$ . Thus,



$$c_{\text{NH}_3} = \frac{400 \times 0.200 - 100 \times 0.0500}{500} = \frac{75}{500} = 0.150 \text{ M}$$

$$c_{\text{NH}_4^+} = \frac{400 \times 0.300 + 100 \times 0.0500}{500} = \frac{125}{500} = 0.250 \text{ M}$$

$$[\text{H}_3\text{O}^+] = 5.70 \times 10^{-10} \times \frac{0.250}{0.150} = 9.50 \times 10^{-10}$$

$$\text{pH} = -\log 9.50 \times 10^{-10} = 9.02$$

$$\Delta\text{pH} = 9.02 - 9.07 = -0.05$$

### *The Composition of Buffer Solutions as a Function of pH: Alpha Values*

The composition of buffer solutions can be visualized by plotting the relative equilibrium concentrations of the two components of a conjugate acid/base as a function of the pH of the solution.

These relative concentrations are called alpha values.

If  $c_T$  is the sum of the analytical concentrations of acetic acid and sodium acetate in a typical buffer solution, we can write:

$$c_T = c_{\text{HOAc}} + c_{\text{NaOAc}}$$

$\alpha_0$  the fraction of the total concentration of acid that is undissociated is

$$\alpha_0 = \frac{[HOAc]}{c_T}$$

$\alpha_1$ , the fraction dissociated is

$$\alpha_1 = \frac{[OAc^-]}{c_T}$$

Alpha values are unitless ratios whose sum must equal unity. These values depend only on  $[H_3O^+]$  and  $K_a$ .

$$\alpha_0 + \alpha_1 = 1$$

$$[OAc^-] = \frac{K_a [HOAc]}{[H_3O^+]}$$

$$c_T = [HOAc] + [OAc^-]$$

$$c_T = [HOAc] + \frac{K_a [HOAc]}{[H_3O^+]} = [HOAc] \left( \frac{[H_3O^+] + K_a}{[H_3O^+]} \right)$$



The re-arranged equation becomes

$$\frac{[HOAc]}{c_T} = \frac{[H_3O^+]}{[H_3O^+] + K_a}$$

$[HOAc]/c_T = \alpha_0$  Thus,

$$\alpha_0 = \frac{[HOAc]}{c_T} = \frac{[H_3O^+]}{[H_3O^+] + K_a}$$

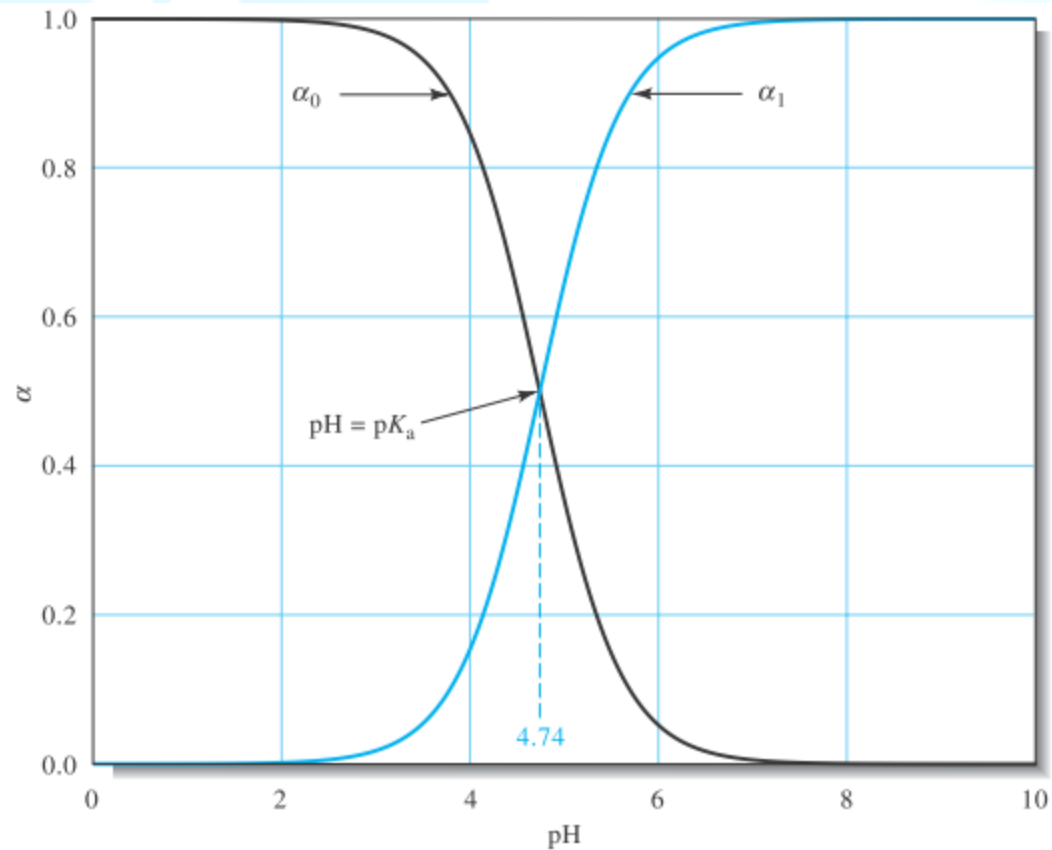
Similarly,

$$\alpha_1 = \frac{[OAc^-]}{c_T} = \frac{K_a}{[H_3O^+] + K_a}$$

Figure 9-5 Graph shows the variation in  $\alpha$  with pH.

Note that most of the transition between  $\alpha_0$  and  $\alpha_1$  occurs within  $\pm 1$  pH unit of the crossover point of the two curves.

The crossover point where  $\alpha_0 = \alpha_1 = 0.5$  occurs when  $\text{pH} = \text{p}K_{\text{HOAc}} = 4.74$ .



The buffer capacity,  $\beta$ , of a solution is defined as the number of moles of a strong acid or a strong base that causes 1.00 L of the buffer to undergo a 1.00-unit change in pH.

Mathematically,

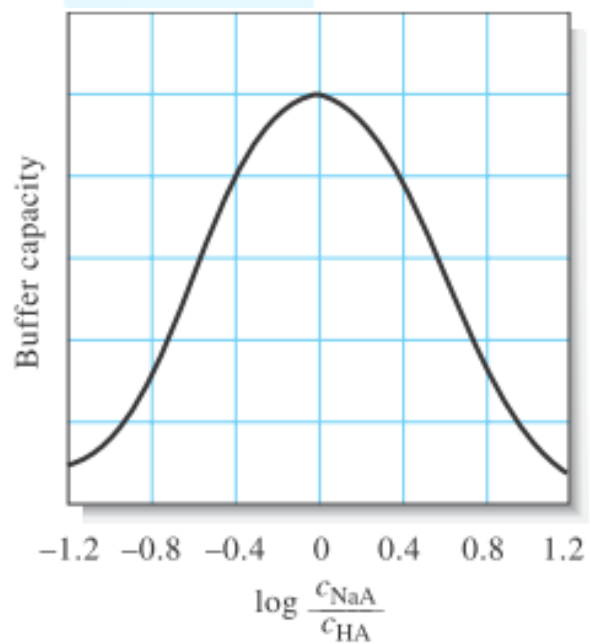
$$\beta = \frac{dc_b}{dpH} = -\frac{dc_a}{dpH}$$

where  $dc_b$  is the number of moles per liter of strong base, and  $dc_a$  is the number of moles per liter of strong acid added to the buffer.

Since adding strong acid to a buffer causes the pH to decrease,  $dc_a/dpH$  is negative, and buffer capacity is always positive.

The  $pK_a$  of the acid chosen for a given application should lie within  $\pm 1$  unit of the desired pH for the buffer to have a reasonable capacity.

Figure 9-6 Buffer capacity as a function of the logarithm of the ratio  $c_{\text{NaA}}/c_{\text{HA}}$ .



## Preparation of Buffers

### EXAMPLE 9-14

Describe how you might prepare approximately 500.0 mL of a pH 4.5 buffer solution from 1.0 M acetic acid (HOAc) and sodium acetate (NaOAc).

#### Solution

It is reasonable to assume there is little volume change if we add solid sodium acetate to the acetic acid solution. We then calculate the mass of NaOAc to add to 500.0 mL of 1.0 M HOAc. The  $\text{H}_3\text{O}^+$  concentration should be

$$[\text{H}_3\text{O}^+] = 10^{-4.5} = 3.16 \times 10^{-5} \text{ M}$$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{OAc}^-]}{[\text{HOAc}]} = 1.75 \times 10^{-5}$$

$$\frac{[\text{OAc}^-]}{[\text{HOAc}]} = \frac{1.75 \times 10^{-5}}{3.16 \times 10^{-5}} = \frac{1.75 \times 10^{-5}}{3.16 \times 10^{-5}} = 0.5534$$

The acetate concentration should be

$$[\text{OAc}^-] = 0.5534 \times 1.0 \text{ M} = 0.5534 \text{ M}$$

The mass of NaOAc needed is then

$$\begin{aligned} \text{mass NaOAc} &= \frac{0.5534 \text{ mol NaOAc}}{\cancel{\text{L}}} \times 0.500 \cancel{\text{ L}} \times \frac{82.034 \text{ g NaOAc}}{\cancel{\text{mol NaOAc}}} \\ &= 22.7 \text{ g NaOAc} \end{aligned}$$

After dissolving this quantity of NaOAc in the acetic acid solution, we would check the pH with a pH meter and, if necessary, adjust it slightly by adding a small amount of acid or base.

- Suggested problems to solve from Ch:9
- 9.1, to 9.30
- You are advised to solve each question at the ends of the chapter 9.