Analytical chemistry

1- Qualitative analysis: Is concerned with the identification of ions, molecules, elements, and compounds present in the sample.

2- Quantitative analysis: Is concerned with the determination of the quantity of one or more compounds of the sample.

The mathematical (quantitative) calculations of analytical chemistry are based on the experimental data obtained with accurate measurements of various physical parameters such as mass, volume, electrode potential, light absorbance, and so forth.

The treatment of data is mainly done on the basis of simple stoichiometric relations and chemical equilibrium constants.

a- Volumetric analysis: Is that type of quantitative analysis based on the measurement of the volume of the standard reagent to find the quantity of substance.

b- Is that type of quantitative analysis based on the measurement of the weight of a precipitate to find the quantity of substance.

c- Instrumental analysis: The quantity of the component is calculated from measurement of the physical property which is related to the mass or the concentration of the component.

Materials

1- Solids: Has a shape but does not easy to measure a volume.

2- Liquids: has no shape but can be easy to measure the volume.

3- Gases: has no shape but difficult to measure the volume.

Material

1- Solids: Has a shape but does not easy to measure a volume.

2- Liquids: has no shape but can be easy to measure the volume.

3- Gases: has no shape but difficult to measure the volume.

A stoichiometric balance chemical equation which is represent the reaction between analyte with the standard material Q.

WHAT ARE THE BASES OF QUANTITATIVE ANALYSIS?

Gas analysis: Each mole of gas in (S.T.P) occupied 22.4 liter

\[
\text{V(\text{STP})} \text{ No.of mmols} = \frac{\text{22.4}}{n}
\]

\[
\text{V(\text{STP})} \text{ No.of mequivalents} = \frac{\text{22.4}}{n}
\]

\[\text{Mwt} \quad \text{Eqwt} = \frac{\text{Mwt}}{2}\]

(n) is a howls number

1- Acid Base reaction

Examples

\[\text{H}_2\text{SO}_4 \quad n = 2 \quad [\text{H}^+] \quad \text{M}\]

\[\text{Mwt} \quad \text{Eqwt} = \frac{\text{Mwt}}{2}\]
HCl

\[
\text{Mwt} \\
\text{Eqwt} = \frac{\text{Mwt}}{1}
\]

H\textsubscript{3}PO\textsubscript{4}

\[
\text{Mwt} \\
\text{Eqwt} = \frac{\text{Mwt}}{3}
\]

2- Complex formation and precipitation reactions : (n) = no. of cations x its valiancy

\[
\text{BaSO}_4 \\
\text{Mwt} \\
\text{Eqwt} = \frac{\text{Mwt}}{4}
\]

KAl ( SO\textsubscript{4})\textsubscript{2}

\[
\text{Mwt} \\
\text{Eqwt} = \frac{\text{Mwt}}{2}
\]

\begin{align*}
n &= \text{cation } K (1) \times (+1) = 1 \\
n &= \text{cation } Al (1) + (+3) = 3 \\
n &= 4
\end{align*}

Fe\textsuperscript{+3} + SCN\textsuperscript{-} → FeSCN\textsuperscript{+2}  \quad \text{Complex formation reaction}

\begin{align*}
n &= 1 \times (+3) = 3
\end{align*}

3- Oxidation reduction reactions . \quad n= \text{numbers of electrons participate in oxidation reduction processes Redox)

As oxidizing agent KMnO\textsubscript{4}

\[
\text{KMnO}_4 \rightarrow K^+ + \text{MnO}_4^{-}
\]

a- in acid media

\[
\text{MnO}_4^{-} + 8H^+ + 5e \leftrightarrow \text{Mn}^{+2} + 4H_2O \quad n = 5e
\]

\[
\text{Mn}^{+7} \rightarrow \text{Mn}^{+2}
\]

b- Dissolve in neutral media

\[
\text{MnO}_4^{-} + 4H^+ + 3e \leftrightarrow \text{MnO}_2 + 2H_2O \quad n = 3e
\]

\[
\text{Mwt} \\
\text{Eqwt} = \frac{\text{Mwt}}{5}
\]
\[
\begin{align*}
\text{Mn}^{7+} & \rightarrow \text{Mn}^{4+} \\
c- \text{Dissolve in alkaline media} & \\
\text{MnO}_4^- + \text{1e} \leftrightarrow \text{MnO}_4^{2-} & \quad n = 1e \\
\text{Mn}^{7+} & \rightarrow \text{Mn}^{1+} \\
\end{align*}
\]

Example for gas analysis

\[
\begin{align*}
\text{CaCO}_3 \downarrow & \rightarrow \text{CaO} \downarrow + \text{CO}_2 \uparrow \\
(\text{solid}) & \quad \text{heat} \quad (\text{solid}) \quad \text{(gas)}
\end{align*}
\]

1- The above equation is balance.
2- We measure the volume of CO\(_2\) gas in (STP).
3- We applied equation (1) to fined the number of equivalent of CO\(_2\) gas

\[
\text{No.of meqt of CaCO}_3 = \text{no. of meqt CO}_2
\]

\[
n = 2 \quad \text{due to Ca}^{2+}
\]

Q \ The analyst prefer liquid analysis over gas analysis?

- The gas analysis has disadvantages
  1- It needs high quality equipments
  2- It need a proficiently and have a good experience to carry out of its analysis

Solutions

That solution contain one or more solute present in solvent

Type of solutions

1- Depend on the particle size of solute in solvent
   a- True solutions
   b- Suspended solutions
   c- Colloidal solutions
2- Depend on the concentration of solute in solvent
   a- Unsaturated solution
   b- Saturated solutions
   c- super saturated solutions

Type one

1- True solution: - Is that solution pass through filter paper and does not precipitate when its left with parent solution at a period time
   (Dissolve NaCl in water)

2- Suspended solution: - Is that solution does not pass through filter paper and precipitate when its left with parent solution
3- Colloidal solution :- Is that solution are pass through filter paper and does not precipitate when its left with parent solution at a period time

----------------------------

Type two

1- Unsaturated solution: - Is that solution, the solvent that ability to dissolve other amount of solute
2- Saturated solution :- Is that solution , the solute in dynamic equilibrium with solvent
3- Super saturated solution;- Is that solution , the solvent does not able to dissolve a large amount of solute the precipitation is formed

# The solvent can be dissolved a large amount of solute when increase the temperature of the solution (the solution is saturated )

Classifying Solutions of Electrolytes

Most of the solutes we will discuss are electrolytes, which form ions when dissolved in water (or certain other solvents) and thus produce solutions that conduct Electricity. 1-Strong electrolytes ionize essentially completely in a solvent, whereas 2-weak electrolytes ionize only partially. This mean that a solution of a weak electrolyte Will not conduct electricity as well as a solution containing an equal concentration of a strong electrolyte.

Chemical Equilibrium

Most analytical techniques require the state of chemical equilibrium. At equilibrium, the rate of a forward process or reaction and that of the reverse process are equal. Calcium carbonate dissolves in the water according to the chemical Equilibrium

CaC0_3 (s) + CO_2 (g) + H_2O (l) ↔ Ca^{2+} (aq) + 2HC0_3

THE CHEMICAL COMPOSITION OF AQUEOUS SOLUTIONS

Water is the most plentiful solvent available on Earth, is easily purified, and is not toxic. It therefore finds widespread use as a medium for carrying out chemical Analysis..

\[
K_{eq} = \frac{[C]^c[D]^d}{[A]^a[B]^b}
\]

\[
K_P = \frac{P_{C}^cP_{D}^d}{P_{A}^aP_{B}^b}
\]

If the products and reactant in the gas form

\[
N_2 (g) + 3H_2(g) ↔ 2NH_3(g)
\]

\[
K_P = \frac{P_{(NH3)}^2}{P_{(N2)}P_{(H2)}^3}
\]

Explain the relation between $K_{eq}$ (use molar concentration) and $K_P$ (use partial pressure)
PV = nRT  it’s a general law of gas  \( \text{(4)} \)

\[ P = \text{partial pressure}, \ V = \text{volume of gas}, \ R = \text{gas constant}, \ T = \text{temperature}, \ n = \text{number of moles} \]

\[ C = \text{molar concentration} \]

Then \[ P = C \text{ RT} \ \text{(6)} \]

\[ \frac{P}{C} = \frac{\text{RT}}{V} \ \text{(5)} \]

Substitutions the \( P \) value in equation (6) into equation (2) yield

\[ \frac{\text{RT}}{V} = \frac{n}{V} \]

\[ K_P = \frac{(C_C \text{ RT})^c (C_D \text{ RT})^d}{(C_A \text{ RT})^a (C_B \text{ RT})^b} \ \text{(8)} \]

\[ K_P = \frac{(C_C)^c (C_D)^d (\text{RT})^c (\text{RT})^d}{(C_A)^a (C_B)^b (\text{RT})^a (\text{RT})^b} \ \text{(9)} \]

\[ K_P = \frac{(C_C)^c (C_D)^d (\text{RT})^{(c+d)}}{(C_A)^a (C_B)^b (\text{RT})^{(a+b)}} \ \text{(10)} \]

\[ K_P = K_{eq} (\text{RT})^{(c+d)-(a+b)} \]

**Equilibrium involving precipitates and their ions**

Solubility product - Solubility

The general equation :-

\[ M_{m}X_{x} \leftrightarrow mM^{a} + xX^{b} \ \text{(1)} \]

Which describe the ionization of the slightly soluble ionic solid \( M_{m}X_{x} \) in the saturated solution ( solid in contact with the solution ), is characterized by an equilibrium constant , i.e ,
Or, since the concentration of $M_mX_x$ is constant

$$K_{[M_mX_x]} = K_{sp} = [M^{a+}]^m [X^{-b}]^x$$ ------ (4) 

The constant $K_{sp}$ is the solubility product constant.

If $S$ the molar solubility (in mole per liter) of the substance $M_mX_x$, we have

$$[M^{a+}] = mS \quad \text{and} \quad [X^{-b}] = xS$$ substituting these values in equation (4)

$$K_{sp} = (mS)^m (xS)^x = m^m x^x S^{m+x}$$ ------ (5)

For the calculation of $S$ from $K_{sp}$, equation (5) is used in the form

$$S = \sqrt{(K_{sp} / m^m x^x)}$$ ------ (6)

For example, for a saturated solution of $Ca_3(PO_4)_2$, we have $[Ca^{2+}] = 3S$ and $[PO_4^{3-}] = 2S$. Hence

$$K_{sp} = 3^3.2^2.3^{3+2} = 108S^5$$

From which

$$S = \sqrt[5]{(K_{sp} / 108)}$$

When the ion product $I.P$, of the dissolved substance exceeds the constant $K_{sp}$, a precipitate is formed in the general case of the slightly soluble substance $M_mX_x$, precipitation takes place only if

$$I.P = [M^{a+}]^m [X^{-b}]^x > K_{sp}$$

If $I.P = K_{sp}$, the solution is saturated, but no precipitate takes place. If $I.P < K_{sp}$, the solution is unsaturated, and there is a precipitate, it is dissolves, until $I.P = K_{sp}$

**Applying Solubility-Product Constants**

Most, but not all sparingly soluble salts are essentially completely dissociated in saturated aqueous solution. For example, when an excess of barium iodate is equilibrated with water, the dissociation process is adequately described by the equation

$$Ba(IO_3)_2(s) \leftrightarrow Ba^{2+}(aq) + 2IO_3^-(aq)$$

$$K_{sp} = [Ba^{2+}] [IO_3^-]^2$$

**EXAMPLE**

How many grams of $Ba(IO_3)_2$ (487 g/mol) can be dissolved in 500 mL of water at 25°C?

The solubility-product constant for $Ba(IO_3)_2$ is $1.57 \times 10^{-9}$.

The equilibrium between the solid and its ions in solution is described by the equation
Ba(IO$_3$)$_2$ (s) $\leftrightarrow$ Ba$^{2+}$(aq) + 2IO$_3^-$ (aq)  

and so 

K$_{sp}$ = [Ba$^{2+}$] [ IO$_3^-$]$^2$ = 1.57 X 10$^{-9}$  

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

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

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

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

Substituting this last equation into the equilibrium-constant expression gives 

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

EXAMPLE 9-3

How many grams of Ba(IO$_3$)$_2$ (487 g/mol) can be dissolved in 500 mL of water at 25°C?

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

Ba(IO$_3$)$_2$(s) $\leftrightarrow$ Ba$^{2+}$ + 2IO$_3^-$

and so

K$_{sp}$ = [Ba$^{2+}$][IO$_3^-$]$^2$ = 1.57 X 10$^{-9}$

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

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

(continued)
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 Ba\(^{2+}\) is produced for every mole of Ba(IO\(_3\))\(_2\),

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

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

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

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

\[ \text{mass Ba(IO}_3)_2 =
\begin{align*}
(7.32 \times 10^{-4} \times 500) \text{ mmol-Ba(IO}_3)_2 \times 0.487 \frac{\text{g Ba(IO}_3)_2}{\text{mmol-Ba(IO}_3)_2} \\
= 0.178 \text{ g}
\end{align*} \]
There are two sources of barium ions: Ba(NO₃)₂ and Ba(IO₃)₂. The contribution from the former is 0.0200 M, and that from the latter is equal to the molar solubility, or \( \frac{1}{2} [\text{IO}_3^-] \). Thus,

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

Substitution of these quantities into the solubility-product expression yields

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

Since the exact solution for [IO₃⁻] requires solving a cubic equation, we seek an approximation that simplifies the algebra. The small numerical value of \( K_{sp} \) suggests that the solubility of Ba(IO₃)₂ is not large, and this is confirmed by the result obtained in Example 9-3. Moreover, barium ion from Ba(NO₃)₂ will further repress the limited solubility of Ba(IO₃)₂. Thus, it is reasonable to seek a provisional answer to the problem by assuming that 0.0200 is large with respect to \( \frac{1}{2} [\text{IO}_3^-] \). That is, \( \frac{1}{2} [\text{IO}_3^-] \ll 0.0200 \), and

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

The original equation then simplifies to

\[
0.0200 [\text{IO}_3^-]^2 = 1.57 \times 10^{-9}
\]

\[
[\text{IO}_3^-] = \sqrt{\frac{1.57 \times 10^{-9}}{0.0200}} = \sqrt{7.85 \times 10^{-8}} = 2.80 \times 10^{-4} \text{ M}
\]

The assumption that \( (0.0200 + \frac{1}{2} \times 2.80 \times 10^{-4}) \approx 0.0200 \) does not appear to cause serious error because the second term, representing the amount of Ba²⁺ arising from the dissociation of Ba(IO₃)₂, is only about 0.7% of 0.0200. Ordinarily, we consider an assumption of this type to be satisfactory if the discrepancy is less than 10%. Finally, then,

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

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 lowered the molar solubility of Ba(IO₃)₂ by a factor of about 5.
EXAMPLE 9-5

Calculate the solubility of Ba(IO₃)₂ in a solution prepared by mixing 200 mL of 0.0100 M Ba(NO₃)₂ with 100 mL of 0.100 M NaIO₃.

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

\[
\text{no. mmol } \text{Ba}^{2+} = 200 \text{ mL} \times 0.0100 \text{ mmol/mL} = 2.00 \\
\text{no. mmol IO}_3^- = 100 \text{ mL} \times 0.100 \text{ mmol/mL} = 10.0
\]

If the formation of Ba(IO₃)₂ is complete,

\[
\text{no. mmol excess NaIO}_3 = 10.0 - 2 \times 2.00 = 6.00
\]

Thus,

\[
[\text{IO}_3^-] = \frac{6.00 \text{ mmol}}{200 \text{ mL} + 100 \text{ mL}} = \frac{6.00 \text{ mmol}}{300 \text{ mL}} = 0.0200 \text{ M}
\]

As in Example 9-3,

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

Here, however,

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

where 2[Ba²⁺] represents the iodate contributed by the sparingly soluble Ba(IO₃)₂. We can obtain a provisional answer after making the assumption that [IO₃⁻] = 0.0200; thus

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

\[
= 3.93 \times 10^{-6} \text{ mol/L}
\]

Since the provisional answer is nearly four orders of magnitude less than 0.02 M, our approximation is justified, and the solution does not need further refinement.
9A-2 Acids and Bases

In 1923, two chemists, J. N. Brønsted in Denmark and J. M. Lowry in England, proposed independently a theory of acid/base behavior that is particularly useful in analytical chemistry. 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). Likewise, a molecule that can accept a proton behaves as a base if it encounters an acid.

\[ \text{acid}_1 \rightleftharpoons \text{base}_1 + \text{proton} \]

Here, acid$_1$ and base$_1$ are a conjugate acid/base pair.

Similarly, every base produces a conjugate acid as a result of accepting a proton. That is,

\[ \text{base}_2 + \text{proton} \rightleftharpoons \text{acid}_2 \]

When these two processes are combined, the result is an acid/base, or neutralization, reaction:

\[ \text{acid}_1 + \text{base}_2 \rightleftharpoons \text{base}_1 + \text{acid}_2 \]

The extent to which this reaction proceeds depends on the relative tendencies of the two bases to accept a proton (or the two acids to donate a proton).

Examples of conjugate acid/base relationships are shown in Equations 9-1 through 9-4.
Many solvents are proton donors or proton acceptors and can thus induce basic or acidic behavior in solutes dissolved in them. For example, in an aqueous solution of ammonia, water can donate a proton and thus acts as an acid with respect to the solute:

$$\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^- \quad (9-1)$$

In this reaction, ammonia (base$_1$) reacts with water, which is labeled acid$_2$, to give the conjugate acid ammonium ion (acid$_1$) and hydroxide ion, which is the conjugate base (base$_2$) of the acid water. In contrast, water acts as a proton acceptor, or base, in an aqueous solution of nitrous acid:

$$\text{H}_2\text{O} + \text{HNO}_2 \rightleftharpoons \text{H}_3\text{O}^+ + \text{NO}_2^- \quad (9-2)$$

Water is the classic example of an amphiprotic solvent—that is, a solvent that can act either as an acid (Equation 9-1) or as a base (Equation 9-2), depending on the solute. Other common amphiprotic solvents are methanol, ethanol, and anhydrous acetic acid. In methanol, for example, the equilibria analogous to those shown in Equations 9-1 and 9-2 are

$$\text{NH}_3 + \text{CH}_3\text{OH} \rightleftharpoons \text{NH}_4^+ + \text{CH}_3\text{O}^- \quad (9-3)$$

$$\text{CH}_3\text{OH} + \text{HNO}_2 \rightleftharpoons \text{CH}_3\text{OH}_2^+ + \text{NO}_2^- \quad (9-4)$$
9A-4 Autoprotolysis

Amphiprotic solvents undergo self-ionization, or autoprotolysis, to form a pair of ionic species. Autoprotolysis is yet another example of acid/base behavior, as illustrated by the following equations.

\[
\begin{align*}
\text{base}_1 + \text{acid}_2 & \rightleftharpoons \text{acid}_1 + \text{base}_2 \\
\text{H}_2\text{O} + \text{H}_2\text{O} & \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^- \\
\text{CH}_3\text{OH} + \text{CH}_3\text{OH} & \rightleftharpoons \text{CH}_3\text{OH}_2^- + \text{CH}_3\text{O}^- \\
\text{HCOOH} + \text{HCOOH} & \rightleftharpoons \text{HCOO}H_2^+ + \text{HCOO}^- \\
\text{NH}_3 + \text{NH}_3 & \rightleftharpoons \text{NH}_4^+ + \text{NH}_2^- 
\end{align*}
\]

The extent to which water undergoes autoprotolysis at room temperature is slight. Thus, the hydronium and hydroxide ion concentrations in pure water are only about \(10^{-7}\) M. Despite the small values of these concentrations, this dissociation reaction is of utmost importance in understanding the behavior of aqueous solutions.

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

Aqueous solutions contain small concentrations of hydronium and hydroxide ions as a consequence of the dissociation reaction

\[
2\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^- \tag{9-9}
\]

An equilibrium constant for this reaction can be formulated as shown in Equation 9-7:

\[
K = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]^2} \tag{9-10}
\]
The concentration of water in dilute aqueous solutions is enormous, however, when compared with the concentration of hydrogen and hydroxide ions. As a consequence, \([H_2O]^2\) in Equation 9-10 can be taken as constant, and we write

\[K[H_2O]^2 = K_w = [H_3O^+][OH^-]\]  \hspace{1cm} (9-11)

where the new constant \(K_w\) is given a special name, the ion-product constant for water.

| 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 | \(5.47 \times 10^{-14}\) |
| 100 | \(49 \times 10^{-14}\) |

**EXAMPLE 9-1**

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

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

\[\text{[H}_3\text{O}^+] = \text{[OH}^-\]\n
Substitution into Equation 9-11 gives
\[ [\text{H}_3\text{O}^+]^2 = [\text{OH}^-]^2 = K_w \]
\[ [\text{H}_3\text{O}^+] = [\text{OH}^-] = \sqrt{K_w} \]

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,
\[ [\text{H}_3\text{O}^+] = [\text{OH}^-] = \sqrt{49 \times 10^{-14}} = 7.0 \times 10^{-7} \text{ M} \]

**EXAMPLE 9-2**

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

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 dissociation of water. Therefore, we write

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

where \([\text{H}_3\text{O}^+]\) accounts for the hydroxide ions contributed by the solvent. The concentration of \(\text{OH}^-\) from the water is insignificant, however, when 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:

\[
[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.00 \times 10^{-14}}{0.200} = 5.00 \times 10^{-14} \text{ M}
\]

\[
pH = -\log 0.500 \times 10^{-14} = 13.301
\]

Note that the approximation

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

causes no significant error.

9B-6 Applying Acid-Base Dissociation Constants

When a weak acid or a weak base is dissolved in water, partial dissociation occurs. Thus, for nitrous acid, we can write

\[
\text{HNO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{NO}_2^-
\]

\[
K_a = \frac{[H_3O^+][NO_2^-]}{[\text{HNO}_2]}
\]

where \(K_a\) is the acid dissociation constant for nitrous acid. In an analogous way, the base dissociation constant for ammonia is

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

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

\[
\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^- \\
K_b = \frac{[\text{NH}_4^+] [\text{OH}^-]}{[\text{NH}_3]}
\]

\[
\text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3 + \text{H}_3\text{O}^+ \\
K_a = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]}
\]

Multiplication of one equilibrium-constant expression by the other gives

\[
K_a K_b = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]} \times \frac{[\text{NH}_4^+] [\text{OH}^-]}{[\text{NH}_3]} = [\text{H}_3\text{O}^+][\text{OH}^-]
\]

but

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

and therefore

\[
K_w = K_a K_b
\]  
(9-14)

This relationship is general for all conjugate acid/base pairs. Many compilations of equilibrium-constant data list only acid dissociation constants, since it is so easy to calculate basic dissociation constants by using Equation 9-14. For example, in Appendix 3, we find no data on the basic dissociation of ammonia (nor for any other bases). Instead, we find the acid dissociation constant for the conjugate acid, ammonium ion. That is,
EXAMPLE 9-6

What is $K_b$ for the equilibrium

$$\text{CN}^- + \text{H}_2\text{O} \rightleftharpoons \text{HCN} + \text{OH}^-$$

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

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

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

**Hydronium Ion Concentration of Solutions of Weak Acids**

When the weak acid HA is dissolved in water, two equilibria are established that yield hydronium ions:

$$\text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{A}^- \quad K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

$$2\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^- \quad K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$$

Ordinarily, 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 $\text{H}_3\text{O}^+$ ion is formed for each $\text{A}^-$ ion, and we write

$$[\text{A}^-] \approx [\text{H}_3\text{O}^+] \quad (9-15)$$

Furthermore, the sum of the molar concentrations of the weak acid and its conjugate base must equal the analytical concentration of the acid $c_{HA}$ because the solution contains no other source of $\text{A}^-$ ions. Thus,

$$c_{HA} = [\text{A}^-] + [\text{HA}] \quad (9-16)$$
Substituting \([H_3O^+]\) for \([A^-]\) (see Equation 9-15) into Equation 9-16 yields

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

which rearranges to

\[ [HA] = c_{HA} - [H_3O^+] \]  \hspace{1cm} (9-17)

When \([A^-]\) and \([HA]\) are replaced by their equivalent terms from Equations 9-15 and 9-17, the equilibrium-constant expression becomes

\[ K_a = \frac{[H_3O^+]^2}{c_{HA} - [H_3O^+]^2} \]  \hspace{1cm} (9-18)

which rearranges to

\[ [H_3O^+]^2 + K_a [H_3O^+] - K_a c_{HA} = 0 \]  \hspace{1cm} (9-19)

The positive solution to this quadratic equation is

\[ [H_3O^+] = \frac{-K_a + \sqrt{K_a^2 + 4K_a c_{HA}}}{2} \]  \hspace{1cm} (9-20)

As an alternative to using Equation 9-20, Equation 9-19 may be solved by successive approximations, as shown in Feature 9-4.

Equation 9-17 can frequently be simplified by making the additional assumption that dissociation does not appreciably decrease the molar concentration of HA. Thus, provided \([H_3O^+] \ll c_{HA}\), \(c_{HA} - [H_3O^+] \approx c_{HA}\), and Equation 9-18 reduces to

\[ K_a = \frac{[H_3O^+]^2}{c_{HA}} \]  \hspace{1cm} (9-21)

and

\[ [H_3O^+] = \sqrt{K_a c_{HA}} \]  \hspace{1cm} (9-22)
EXAMPLE 9-7

Calculate the hydronium ion concentration in 0.120 M nitrous acid. The principal equilibrium is

$$\text{HNO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{NO}_2^-$$

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

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

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, solution of the quadratic equation yields $8.9 \times 10^{-3}$ 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, $\text{C}_6\text{H}_5\text{NH}_3\text{Cl}$.

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:

$$\text{C}_6\text{H}_5\text{NH}_3^+ + \text{H}_2\text{O} \rightleftharpoons \text{C}_6\text{H}_5\text{NH}_2 + \text{H}_3\text{O}^+ \quad K_a = \frac{[\text{H}_3\text{O}^+][\text{C}_6\text{H}_5\text{NH}_2]}{[\text{C}_6\text{H}_5\text{NH}_3^+]}$$

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:

$$[\text{H}_3\text{O}^+] = [\text{C}_6\text{H}_5\text{NH}_2]$$

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

Comparison of $7.09 \times 10^{-3}$ with $2.0 \times 10^{-4}$ suggests 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 nearly exact expression (Equation 9-19)

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

which rearranges to

$$[\text{H}_3\text{O}^+]^2 + 2.51 \times 10^{-5} [\text{H}_3\text{O}^+] - 5.02 \times 10^{-9} = 0$$

$$[\text{H}_3\text{O}^+] = \frac{-2.51 \times 10^{-5} + \sqrt{(2.54 \times 10^{-3})^2 + 4 \times 5.02 \times 10^{-9}}}{2}$$

$$= 5.94 \times 10^{-5} \text{ M}$$

The quadratic equation can also be solved by the iterative method shown in Feature 9-4.
EXAMPLE 9-9

Calculate the hydroxide ion concentration of a 0.0750 M NH₃ solution. The predominant equilibrium is

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

As shown on page 243,

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

The chemical equation shows that

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

The techniques discussed in previous sections are readily adapted to the calculation of the hydroxide or hydronium ion concentration in solutions of weak bases. Aqueous ammonia is basic by virtue of the reaction

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

The predominant species in such solutions has been clearly demonstrated to be NH₃. Nevertheless, solutions of ammonia are still called ammonium hydroxide occasionally because at one time chemists thought that NH₄OH rather than NH₃ was the undissociated form of the base. Application of the mass law to the equilibrium as written yields

\[ K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} \]
\[ [\text{NH}_4^+] = [\text{OH}^-] \]
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
\[ [\text{NH}_3] = 0.0750 - [\text{OH}^-] \] (continued)

Substituting these quantities into the dissociation-constant expression yields
\[ \frac{[\text{OH}^-]^2}{7.50 \times 10^{-2} - [\text{OH}^-]} = 1.75 \times 10^{-5} \]
which is analogous to Equation 9-17 for weak acids. Provided that \( [\text{OH}^-] \ll 7.50 \times 10^{-2} \), this equation simplifies to
\[ [\text{OH}^-]^2 = 7.50 \times 10^{-2} \times 1.75 \times 10^{-5} \]
\[ [\text{OH}^-] = 1.15 \times 10^{-3} \text{ M} \]
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 needed, 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.

The equilibrium between \( \text{OCl}^- \) and water is
\[ \text{OCl}^- + \text{H}_2\text{O} \rightleftharpoons \text{HOCl} + \text{OH}^- \]
for which

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

Appendix 3 reveals that the acid dissociation constant for HOCl 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

\[ [\text{OH}^-] = [\text{HOCl}] \]

\[ [\text{OCl}^-] + [\text{HOCl}] = 0.0100 \]

\[ [\text{OCl}^-] = 0.0100 - [\text{OH}^-] \approx 0.0100 \]

Here we have assumed that \([\text{OH}^-] \ll 0.0100\). Substitution into the equilibrium-constant expression gives

\[ \frac{[\text{OH}^-]^2}{0.0100} = 3.33 \times 10^{-7} \]

\[ [\text{OH}^-] = 5.8 \times 10^{-5} \text{ M} \]

Note that the error resulting from the approximation is small.

**9B-3 Types of Equilibrium Constants Encountered in Analytical Chemistry**

Table 9-2 summarizes the types of chemical equilibria and equilibrium constants that are of importance in analytical chemistry. Simple applications of some of these constants are illustrated in the three sections that follow.
<table>
<thead>
<tr>
<th>Type of Equilibrium</th>
<th>Name and Symbol of Equilibrium Constant</th>
<th>Typical Example</th>
<th>Equilibrium-Constant Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dissociation of water</td>
<td>Ion-product constant, $K_w$</td>
<td>$2H_2O \rightleftharpoons H_3O^+ + OH^-$</td>
<td>$K_w = [H_3O^+][OH^-]$</td>
</tr>
<tr>
<td>Heterogeneous equilibrium</td>
<td>Solubility product, $K_{sp}$</td>
<td>$BaSO_4(s) \rightleftharpoons Ba^{2+} + SO_4^{2-}$</td>
<td>$K_{sp} = [Ba^{2+}][SO_4^{2-}]$</td>
</tr>
<tr>
<td>Dissociation of a weak acid or base</td>
<td>Dissociation constant, $K_a$ or $K_b$</td>
<td>$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$</td>
<td>$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$</td>
</tr>
<tr>
<td>Formation of a complex ion</td>
<td>Formation constant, $\beta_n$</td>
<td>$Ni^{2+} + 4CN^- \rightleftharpoons Ni(CN)_4^{2-}$</td>
<td>$\beta_n = \frac{[Ni(CN)_4^{2-}]}{[Ni^{2+}][CN^-]^4}$</td>
</tr>
<tr>
<td>Oxidation/reduction equilibrium</td>
<td>$K_{\text{redox}}$</td>
<td>$MnO_4^- + 5Fe^{3+} + 8H^+ \rightleftharpoons Mn^{2+} + 5Fe^{3+} + 4H_2O$</td>
<td>$K_{\text{redox}} = \frac{[Mn^{2+}][Fe^{3+}]^5}{[MnO_4^-][Fe^{2+}]^5[H^+]^8}$</td>
</tr>
<tr>
<td>Distribution equilibrium for a solute</td>
<td>$K_d$</td>
<td>$L_1(\text{aq}) \rightleftharpoons L_2(\text{org})$</td>
<td>$K_d = \frac{[L_1]<em>{\text{org}}}{[L_1]</em>{\text{aq}}}$</td>
</tr>
</tbody>
</table>

**FEATURE 9-1**

**Stepwise and Overall Formation Constants for Complex Ions**

The formation of $\text{Ni(CN)}_4^{2-}$ (Table 9-2) is typical in that it occurs in steps as shown. Note that *stepwise formation* constants are symbolized by $K_1$, $K_2$, and so forth.

\[
\text{Ni}^{2+} + \text{CN}^- \rightleftharpoons \text{Ni(CN)}^+ \quad K_1 = \frac{[\text{Ni(CN)}^+]}{[\text{Ni}^{2+}][\text{CN}^-]}
\]

\[
\text{Ni(CN)}^+ + \text{CN}^- \rightleftharpoons \text{Ni(CN)}_2^- \quad K_2 = \frac{[\text{Ni(CN)}_2^-]}{[\text{Ni(CN)}^+][\text{CN}^-]}
\]

\[
\text{Ni(CN)}_2^- + \text{CN}^- \rightleftharpoons \text{Ni(CN)}_3^{3-} \quad K_3 = \frac{[\text{Ni(CN)}_3^{3-}]}{[\text{Ni(CN)}_2^-][\text{CN}^-]}
\]

\[
\text{Ni(CN)}_3^{3-} + \text{CN}^- \rightleftharpoons \text{Ni(CN)}_4^{2-} \quad K_4 = \frac{[\text{Ni(CN)}_4^{2-}]}{[\text{Ni(CN)}_3^{3-}][\text{CN}^-]}
\]
Overall constants are designated by the symbol $\beta_n$. Thus,

$$\begin{align*}
Ni^{2+} + 2CN^- &\rightleftharpoons Ni(CN)_2^- & \beta_2 &= K_1K_2 = \frac{[Ni(CN)_2^-]}{[Ni^{2+}][CN^-]^2} \\
Ni^{2+} + 3CN^- &\rightleftharpoons Ni(CN)_3^- & \beta_3 &= K_1K_2K_3 = \frac{[Ni(CN)_3^-]}{[Ni^{2+}][CN^-]^3} \\
Ni^{2+} + 4CN^- &\rightleftharpoons Ni(CN)_4^- & \beta_4 &= K_1K_2K_3K_4 = \frac{[Ni(CN)_4^-]}{[Ni^{2+}][CN^-]^4}
\end{align*}$$

### 9C BUFFER SOLUTIONS

By definition, a buffer solution resists changes in pH with dilution or with addition of acids or bases. Generally, buffer solutions are prepared from a conjugate acid/base pair, such as acetic acid/sodium acetate or ammonium chloride/ammonia. Chemists use buffers to maintain the pH of solutions at a relatively constant and predetermined level. You will find many references to buffers throughout this text.

### 9C-1 Calculation of the pH of Buffer Solutions

A solution containing a weak acid, HA, and its conjugate base, $A^-$, may be acidic, neutral, or basic, depending on the position of two competitive equilibria:

$$\begin{align*}
HA + H_2O &\rightleftharpoons H_3O^+ + A^- & K_a &= \frac{[H_3O^+][A^-]}{[HA]} & (9-23) \\
A^- + H_2O &\rightleftharpoons OH^- + HA & K_b &= \frac{[OH^-][HA]}{[A^-]} = \frac{1}{K_a} & (9-24)
\end{align*}$$

Similarly, the first equilibrium will increase the concentration of $A^-$ by an amount equal to $[H_3O^+]$, and the second will decrease this concentration by the amount $[OH^-]$. Thus, the equilibrium concentration is given by a second equation similar to Equation 9-25.

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

A buffer is a mixture of a weak acid and its conjugate base or a weak base and its conjugate acid that resists changes in pH of a solution.

Buffers are used in all types of chemistry whenever it is desirable to maintain the pH of a solution at a constant and predetermined level.

Buffered aspirin contains buffers to help prevent stomach irritation from the acidity of the carboxylic acid group in aspirin.
\[ [\text{HA}] = c_{\text{HA}} \quad (9-27) \]
\[ [\text{A}^-] = c_{\text{NaA}} \quad (9-28) \]
\[ [\text{H}_3\text{O}^+] = \frac{c_{\text{HA}}}{K_a c_{\text{NaA}}} \quad (9-29) \]

To determine the pH of the solution, we will use the form of its negative logarithm and inverting the concentration ratio to keep all signs positive:

\[ -\log [\text{H}_3\text{O}^+] = -\log K_a + \log \frac{c_{\text{NaA}}}{c_{\text{HA}}} \]

Therefore,

\[ \text{pH} = pK_a + \log \frac{c_{\text{NaA}}}{c_{\text{HA}}} \quad (9-30) \]

If the assumptions leading to Equation 9-28 are not valid, the values for [HA] and [A\(^-\)] are given by Equations 9-24 and 9-25, respectively. If we take the negative logarithms of these expressions, we derive extended Henderson-Hasselbalch equations.

**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?

The pH of this solution will be affected by the \( K_w \) of formic acid and the \( K_b \) of formate ion.

\[ \text{HCOOH} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{HCOO}^- \quad K_a = 1.80 \times 10^{-4} \]
\[ \text{HCOO}^- + \text{H}_2\text{O} \rightleftharpoons \text{HCOOH} + \text{OH}^- \quad K_b = \frac{K_w}{K_a} = 5.56 \times 10^{-11} \]
Since the $K_a$ for formic acid is orders of magnitude larger than the $K_b$ for formate, the solution will be acidic and $K_a$ will determine the $\text{H}_3\text{O}^+$ concentration. We can thus write

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

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

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

Substitution into Equation 9-29 gives, with rearrangement.

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

Note that the assumption that $[\text{H}_3\text{O}^+] \ll c_{\text{HCOOH}}$ and that $[\text{H}_3\text{O}^+] \ll c_{\text{HCOO}^-}$ is valid. Thus,

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

---

**EXAMPLE 9-12**

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

$$\text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3 + \text{H}_3\text{O}^+ \quad K_a = 5.70 \times 10^{-10}$$

$$\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^- \quad K_b = \frac{K_w}{K_a} = \frac{1.00 \times 10^{-14}}{5.70 \times 10^{-10}} = 1.75 \times 10^{-5}$$

(continued)
Using the arguments that led to Equations 9-25 and 9-26, we obtain

\[
[NH_4^+] = c_{NH_4Cl} + [OH^-] - [H_3O^+] = c_{NH_4Cl} + [OH^-]
\]

\[
[\text{NH}_3] = c_{\text{NH}_4} + [H_3O^+] - [OH^-] = c_{NH_4} - [OH^-]
\]

Because \( K_b \) is several orders of magnitude larger than \( K_a \), we have assumed that the solution is basic and that \([OH^-]\) is much larger than \([H_3O^+]\). Thus, we have neglected the concentration of \( H_3O^+ \) in these approximations.

Also assume that \([OH^-]\) is much smaller than \( c_{NH_4Cl} \) and \( c_{\text{NH}_4} \) so that

\[
[NH_4^+] = c_{NH_4Cl} = 0.300 \text{ M}
\]

\[
[\text{NH}_3] = c_{\text{NH}_4} = 0.200 \text{ M}
\]

Substituting into the acid dissociation constant for \( NH_4^+ \), we obtain a relationship similar to Equation 9-29. That is,

\[
[H_3O^+] = \frac{K_a \times [NH_4^+]}{[\text{NH}_3]} = \frac{5.70 \times 10^{-10} \times c_{NH_4Cl}}{c_{\text{NH}_4}} = \frac{5.70 \times 10^{-10} \times 0.300}{0.200} = 8.55 \times 10^{-10} \text{ M}
\]

To check the validity of our approximations, we calculate \([OH^-]\). Thus,

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

which is certainly much smaller than \( c_{NH_4Cl} \) or \( c_{\text{NH}_4} \). Thus, we may write

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

### 9C-2 Properties of Buffer Solutions

In this section, we illustrate the resistance of buffers to changes of pH brought about by dilution or addition of strong acids or bases.
The Effect of Dilution
The pH of a buffer solution remains essentially independent of dilution until the concentrations of the species it contains are decreased to the point where the approximations used to develop Equations 9-27 and 9-28 become invalid. Figure 9-4 contrasts the behavior of buffered and unbuffered solutions with dilution. For each, the initial solute concentration is 1.00 M. The resistance of the buffered solution to changes in pH during dilution is clear.

The Effect of Added Acids and Bases
Example 9-13 illustrates a second property of buffer solutions, their resistance to pH change after addition of small amounts of strong acids or bases.

---

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.

(a) Addition of NaOH converts part of the NH₄⁺ in the buffer to NH₃:

\[ \text{NH}_4^+ + \text{OH}^- \rightarrow \text{NH}_3 + \text{H}_2\text{O} \]

The analytical concentrations of NH₃ and NH₄Cl 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 NH₄⁺, these values yield

---

Figure 9-4: The effect of dilution of the pH of buffered and unbuffered solutions. The dissociation constant for HA is \(1.00 \times 10^{-4}\). Initial solute concentrations are 1.00 M.
Ionic strength and activity
The ionic atmosphere surrounding each ion reduces its velocity, causing the solution to behave as if its concentration is smaller than stoichiometric.

\[ a = C f \]

where \( a \) = activity, \( C \) = molar concentration, \( f \) = activity coefficient

\[ u = \frac{1}{2} \left( C_1 z_1^2 + C_2 z_2^2 + \ldots + C_n z_n^2 \right) = \frac{1}{2} \sum C_i z_i^2 \]

\( u \) = ionic strength of the solution
The value of the f depends on the charge z of the ion on the ionic strength of the solution, according to
the equation

- \( \log f = A z^2 \sqrt{u} \),

A = constant, = 0.51 for the water at 25 °C

For better accuracy the following relation is used

- \( \log f = A z^2 \sqrt{u} / (1 + \sqrt{u}) \),

**Example 10-1**

Calculate the ionic strength of (a) a 0.1 M solution of KNO₃ and (b) a 0.1 M solution of Na₂SO₄.

(a) For the KNO₃ solution, [K⁺] and [NO₃⁻] are 0.1 M and

\[ \mu = \frac{1}{2} \left( 0.1 \text{ M} \times 1^2 + 0.1 \text{ M} \times 1^2 \right) = 0.1 \text{ M} \]

(b) For the Na₂SO₄ solution, [Na⁺] = 0.2 M and [SO₄²⁻] = 0.1 M. Therefore,

\[ \mu = \frac{1}{2} \left( 0.2 \text{ M} \times 1^2 + 0.1 \text{ M} \times 2^2 \right) = 0.3 \text{ M} \]

**Example 10-2**

What is the ionic strength of a solution that is 0.05 M in KNO₃ and 0.1 M in Na₂SO₄?

\[ \mu = \frac{1}{2} \left( 0.05 \text{ M} \times 1^2 + 0.05 \text{ M} \times 1^2 + 0.2 \text{ M} \times 1^2 + 0.1 \text{ M} \times 2^2 \right) = 0.35 \text{ M} \]

Example

Calculate the concentration and activity of each ion in a mixture obtained by mixing 25.0 mL of 0.120M MnCl₂ solution and 35.0 mL of 0.06 M KCl solution?
The volume of the mixture is 60 mL. Assuming that the dissociation of the salts is complete:

\[
\text{Molarity of Cl}^- = 2 \times \text{mmol MnCl}_2 + 1 \times \text{mmole KCl}
\]

<table>
<thead>
<tr>
<th>Volume</th>
<th>Molarity of Ion</th>
<th>Molarity Calculation</th>
</tr>
</thead>
<tbody>
<tr>
<td>25 mL</td>
<td>Mn(^{2+})</td>
<td>(\frac{25 \text{ mL} \times 0.120 \text{ mmol/mL}}{60 \text{ mL}} = 0.05 \text{ mmol/mL})</td>
</tr>
<tr>
<td>35 mL</td>
<td>K(^+)</td>
<td>(\frac{35 \text{ mL} \times 0.06 \text{ mmol/mL}}{60 \text{ mL}} = 0.035 \text{ mmol/mL})</td>
</tr>
</tbody>
</table>

The ionic strength of the solution is equal to:

\[
u = \frac{1}{2} \left( C_{\text{Mn}^{2+}} z_{\text{Mn}^{2+}}^2 + C_{\text{K}^+} z_{\text{K}^+}^2 + C_{\text{Cl}^-} z_{\text{Cl}^-}^2 \right)
\]

\[
u = \frac{1}{2} \{ (0.05) (2)^2 + (0.035) (1)^2 + (0.135) (-1)^2 \} = 0.185
\]

\[
-\log f_{\text{Mn}^{2+}} = -\log f_{\text{Cl}^-} = \frac{0.51 \times (2)^2 \sqrt{0.185}}{1 + \sqrt{0.185}} \quad \text{or} \quad f_{\text{Mn}^{2+}} = 0.243
\]

\[
-\log f_{\text{K}^+} = -\log f_{\text{Cl}^-} = \frac{0.51 \times (1)^2 \sqrt{0.185}}{1 + \sqrt{0.185}} \quad \text{or} \quad f_{\text{K}^+} = f_{\text{Cl}^-} = 0.702
\]

\[a_{\text{K}^+} = f_{\text{K}^+} \quad C_{\text{K}^+} = 0.702 \times 0.035 = 0.0246 \text{ M}\]

\[a_{\text{Cl}^-} = f_{\text{Cl}^-} \quad C_{\text{Cl}^-} = 0.702 \times 0.135 = 0.095 \text{ M}\]