Analytical chemistry

1-qualitative analysis. Is concerned with the identification of ions molecules elements and compounds present in 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 base up on the measurement of the volume of the standard reagent to find the quantity of substance
b- Is that type of quantitative analysis base up on the measurement of the weight of a precipitate t
o 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 .
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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

------- 1

$$\text{No.of mmols} = \frac{V(STP)}{22.4}$$

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

(n) is a howls number
1- Acid Base reaction
Examples
H_2SO_4
n = 2 [H^+] , M

$$\text{Eqwt} = \frac{\text{Mwt}}{2}$$

HCl

$$Eqwt = \frac{Mwt}{1}$$

H_3PO_4

$$Eqwt = \frac{Mwt}{3}$$

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

$BaSO_4$

$$Eqwt = \frac{Mwt}{4}$$

$$Eqwt = \frac{Mwt}{2}$$

$KAl(SO_4)_2$

n= cation K (1) x (+1) = 1

n= cation Al (1) + (+3) = 3

n= 4

$Fe^{+3} + SCN^{-} \rightarrow FeSCN^{+2}$ Complex formation reaction

n = 1 x (+ 3) = 3

3- Oxidation redaction reactions . n= numbers of electrons participate in oxidation redaction processes Redox)

As oxidizing agent $KMnO_4$

$KMnO_4 \rightarrow K^{+} + MnO_4^{-}$

a- in acid media

$MnO_4^{-} + 8H^{+} + 5e \leftrightarrow Mn^{+2} + 4H_2O$ n = 5 e

$Mn^{+7} \rightarrow Mn^{+2}$

$$Eqwt = \frac{Mwt}{5}$$

b- Dissolve in neutral media

$MnO_4^{-} + 4H^{+} + 3e \leftrightarrow MnO_2 + 2H_2O$ n = 3e

$Mn^{+7} \rightarrow Mn^{+4}$

$$\boxed{Eqwt = \frac{Mwt}{3}}$$

$$\boxed{Eqwt = \frac{Mwt}{3}}$$

c- Dissolve in alkaline media

$MnO_4^{-} + 1e \leftrightarrow MnO_4^{-2}$ n= 1e

$Mn^{+7} \rightarrow Mn^{+1}$

$$\boxed{Eqwt = \frac{Mwt}{1}}$$

Example for gas analysis

$$\underset{\text{(solid)}}{CaCO_3\downarrow} \xrightarrow[\text{heat}]{} \underset{\text{(solid)}}{CaO\downarrow} + \underset{\text{(gas)}}{CO_2\uparrow}$$

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

No.of meqt of $CaCO_3$ = no . of meqt CO_2

n = 2 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

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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

$NaCl \quad ===== \quad Na^+ + Cl^-$

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

$$CaC0_3 (s) + CO_2 (g) + H_2O (l) \leftrightarrow Ca^{+2} (aq) + 2HC0^-_3$$

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..

$$a A + bB \underset{k_2}{\overset{k_1}{\leftrightarrow}} c C + d D$$

$$\boxed{K_{eq} = \frac{[C]^c \; [D]^d}{[A]^a \; [B]^b}} \qquad \boxed{K_P = \frac{P_C{}^c \; P_D{}^d}{P_A{}^a \; P_B{}^b}} \qquad \text{---------(2)}$$

If the products and reactant in the gas form

$$N_2 (g) + 3 H_2 (g) \leftrightarrow 2NH_3 (g)$$

$$\boxed{K_P = \frac{P_{(NH3)}{}^2}{P_{(N2)} , P(H_2)^3}} \qquad \text{----------------(3)}$$

Explain the relation between K_{eq} (use molar concentration) and K_P (use partial pressure)

$PV = nRT$ it’s a general law of gas ----------(4)

P = partial pressure, V= volume of gas, R = gas constant, T= temperature , n= number of moles

$$P = \frac{n}{V} RT$$

--------------- $$C = \frac{n}{V}$$ C , molar concentration

$$C = \frac{P}{RT}$$

Then $P = C\,RT$ -------------- (6)

----------- (7)

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

$$K_P = \frac{(C_C\,RT)^c\,(C_D\,RT)^d}{(C_A\,RT)^a\,(C_B RT)^b} \qquad \text{-------------- (8)}$$

$$K_P = \frac{(C_C)^c\,(RT)^c\,(C_D)^d\,(RT)^d}{(C_A)^a\,(RT)^a\,(C_B)^b\,(RT)^b} \qquad \text{----------- (9)}$$

$$K_P = \frac{(C_C)^c\,(C_D)^d\,(RT)^{(c+d)}}{(C_A)^a\,(C_B)^b\,(RT)^{(a+b)}} \qquad \text{-------------- (10)}$$

$$K_P = \frac{(C_C)^c\,(C_D)^d}{(C_A)^a\,(C_B)^b}\,(RT)^{\{(c+d)-(a+b)\}}$$

$$K_p = K\,eq\,(RT)^{\{(c+d)-(a+b)\}}$$

Equilibrium involving precipitates and their ions

Solubility product - Solubility

The general equation :-

$M_mX_x \leftrightarrow mM^{+a} + xX^{-b}$ --------- (1)

Which describe the ionization of the slightly soluble ionic solid M_mX_x in the saturated solution (solid in contact with the solution) , is characterized by an equilibrium constant , i.e ,

--

$$K = \frac{[M^{+a}]^m [X^{-b}]^x}{MmXx}$$

O mXx is constant

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

The constant ,K_{sp} is could solubility product constant (solubility product)
If S the molar solubility (in mole per liter) of the substance MmXx , we have

$[M^{+a]} = mS$, and $[X^{-b}] = Xs$ substituting these value 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

$S = {}^{m+s}\sqrt{Ksp / m^m x^x}$ ----------------------- (6)

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

$[PO_4^{-3}] = 2S$. Hence , $K_{sp} = 3^3.2^2.S^{3+2} = 108S^5$

From which $S = {}^5\sqrt{Ksp / 108}$

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 MmXx , precipitation takes place only if

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

If I.P = Ksp , the solution is saturated , but no precipitate takes place . if I.P .< Ksp the solution is unsaturated , and there is a precipitate , it is dissolves , until I.P = Ksp

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 equilibrate with water, the dissociation process is adequately described by the equation

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

$Ksp = [Ba^{2+}] [IO3^-]^2$

EXAMPLE *3-9*

How rnany 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 $1.57 X 10^{-9}$

The equilibrium between the solid and its ions in solution is described by the . equation

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

and so

Ksp = $[Ba^{2+}]\,[IO3^-]^2 = 1.57 \times 10^{-9}$

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

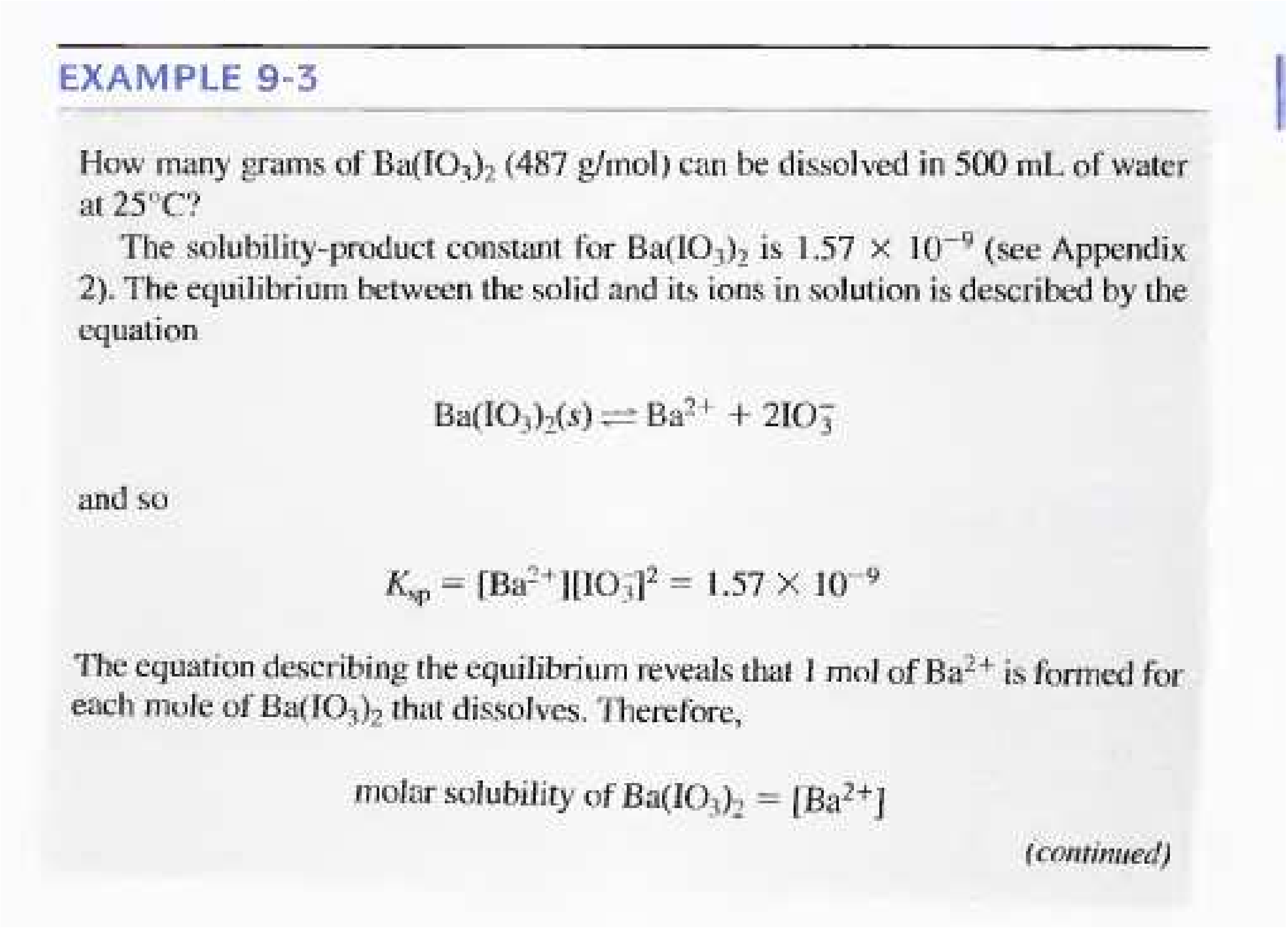
molar solubility of $[Ba(IO_3)_2] = [Ba^{2+}]$

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

$[IO3^-] = 2\,[Ba^{2+}]$

Substituting this last equation into the equilibrium-constant expression gives

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



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 1.57×10^{-9} (see Appendix 2). The equilibrium between the solid and its ions in solution is described by the equation

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

and so

$$K_{sp} = [Ba^{2+}][IO_3^-]^2 = 1.57 \times 10^{-9}$$

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,

$$\text{molar solubility of } Ba(IO_3)_2 = [Ba^{2+}]$$

(continued)

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

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

Substituting this last equation into the equilibrium-constant expression gives

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

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

Since 1 mol Ba^{2+} is produced for every mole of $Ba(IO_3)_2$,

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

To compute the number of millimoles of $Ba(IO_3)_2$ dissolved in 500 mL of solution, we write

$$\text{no. mmol } Ba(IO_3)_2 = 7.32 \times 10^{-4} \frac{\text{mmol } Ba(IO_3)_2}{\cancel{\text{mL}}} \times 500\ \cancel{\text{mL}}$$

The mass of $Ba(IO_3)_2$ in 500 mL is given by

$$\begin{aligned}\text{mass } Ba(IO_3)_2 = \\ &(7.32 \times 10^{-4} \times 500)\ \cancel{\text{mmol } Ba(IO_3)_2} \times 0.487 \frac{\text{g } Ba(IO_3)_2}{\cancel{\text{mmol } Ba(IO_3)_2}} \\ &= 0.178\ \text{g}\end{aligned}$$

There are two sources of barium ions: $Ba(NO_3)_2$ and $Ba(IO_3)_2$. The contribution from the former is 0.0200 M, and that from the latter is equal to the molar solubility, or $\frac{1}{2}[IO_3^-]$. Thus,

$$[Ba^{2+}] = 0.0200 + \frac{1}{2}[IO_3^-]$$

Substitution of these quantities into the solubility-product expression yields

$$\left(0.0200 + \frac{1}{2}[IO_3^-]\right)[IO_3^-]^2 = 1.57 \times 10^{-9}$$

Since the exact solution for $[IO_3^-]$ 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 $Ba(IO_3)_2$ is not large, and this is confirmed by the result obtained in Example 9-3. Moreover, barium ion from $Ba(NO_3)_2$ will further repress the limited solubility of $Ba(IO_3)_2$. Thus, it is reasonable to seek a provisional answer to the problem by assuming that 0.0200 is large with respect to $\frac{1}{2}[IO_3^-]$. That is, $\frac{1}{2}[IO_3^-] \ll 0.0200$, and

$$[Ba^{2+}] = 0.0200 + \frac{1}{2}[IO_3^-] \approx 0.0200\ M$$

The original equation then simplifies to

$$0.0200\,[IO_3^-]^2 = 1.57 \times 10^{-9}$$
$$[IO_3^-] = \sqrt{1.57 \times 10^{-9}/0.0200} = \sqrt{7.85 \times 10^{-8}} = 2.80 \times 10^{-4}\ M$$

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 Ba^{2+} arising from the dissociation of $Ba(IO_3)_2$, 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%.[1] Finally, then,

$$\text{solubility of } Ba(IO_3)_2 = \frac{1}{2}[IO_3^-] = \frac{1}{2} \times 2.80 \times 10^{-4} = 1.40 \times 10^{-4}\ M$$

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 $Ba(IO_3)_2$ by a factor of about 5.

EXAMPLE 9-5

Calculate the solubility of $Ba(IO_3)_2$ in a solution prepared by mixing 200 mL of 0.0100 M $Ba(NO_3)_2$ with 100 mL of 0.100 M $NaIO_3$.

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

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

$$\text{no. mmol } IO_3^- = 100 \cancel{\text{mL}} \times 0.100 \text{ mmol}/\cancel{\text{mL}} = 10.0$$

If the formation of $Ba(IO_3)_2$ is complete,

$$\text{no. mmol excess } NaIO_3 = 10.0 - 2 \times 2.00 = 6.00$$

Thus,

$$[IO_3^-] = \frac{6.00 \text{ mmol}}{200 \text{ mL} + 100 \text{ mL}} = \frac{6.00 \text{ mmol}}{300 \text{ mL}} = 0.0200 \text{ M}$$

As in Example 9-3,

$$\text{molar solubility of } Ba(IO_3)_2 = [Ba^{2+}]$$

Here, however,

$$[IO_3^-] = 0.0200 + 2[Ba^{2+}]$$

where $2[Ba^{2+}]$ represents the iodate contributed by the sparingly soluble $Ba(IO_3)_2$. We can obtain a provisional answer after making the assumption that $[IO_3^-] \approx 0.0200$; thus

$$\text{solubility of } Ba(IO_3)_2 = [Ba^{2+}] = \frac{K_{sp}}{[IO_3^-]^2} = \frac{1.57 \times 10^{-9}}{(0.0200)^2}$$

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

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:

$$\underset{\text{base}_1}{NH_3} + \underset{\text{acid}_2}{H_2O} \rightleftharpoons \underset{\substack{\text{conjugate}\\\text{acid}_1}}{NH_4^+} + \underset{\substack{\text{conjugate}\\\text{base}_2}}{OH^-} \tag{9-1}$$

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:

$$\underset{\text{base}_1}{H_2O} + \underset{\text{acid}_2}{HNO_2} \rightleftharpoons \underset{\substack{\text{conjugate}\\\text{acid}_1}}{H_3O^+} + \underset{\substack{\text{conjugate}\\\text{base}_2}}{NO_2^-} \tag{9-2}$$

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

$$\underset{\text{base}_1}{NH_3} + \underset{\text{acid}_2}{CH_3OH} \rightleftharpoons \underset{\substack{\text{conjugate}\\\text{acid}_1}}{NH_4^+} + \underset{\substack{\text{conjugate}\\\text{base}_2}}{CH_3O^-} \tag{9-3}$$

$$\underset{\text{base}_1}{CH_3OH} + \underset{\text{acid}_2}{HNO_2} \rightleftharpoons \underset{\substack{\text{conjugate}\\\text{acid}_1}}{CH_3OH_2^+} + \underset{\substack{\text{conjugate}\\\text{base}_2}}{NO_2^-} \tag{9-4}$$

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.

$$\begin{array}{llll}
\text{base}_1 & +\ \text{acid}_2 & \rightleftharpoons \text{acid}_1 & +\ \text{base}_2 \\
H_2O & +\ H_2O & \rightleftharpoons H_3O^+ & +\ OH^- \\
CH_3OH & +\ CH_3OH & \rightleftharpoons CH_3OH_2^+ & +\ CH_3O^- \\
HCOOH & +\ HCOOH & \rightleftharpoons HCOOH_2^+ & +\ HCOO^- \\
NH_3 & +\ NH_3 & \rightleftharpoons NH_4^+ & +\ NH_2^-
\end{array}$$

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

$$2H_2O \rightleftharpoons H_3O^+ + OH^- \qquad (9\text{-}9)$$

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

$$K = \frac{[H_3O^+][OH^-]}{[H_2O]^2} \qquad (9\text{-}10)$$

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

$$K[H_2O]^2 = K_w = [H_3O^+][OH^-] \tag{9-11}$$

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	0.114×10^{-14}
25	1.01×10^{-14}
50	5.47×10^{-14}
100	49×10^{-14}

EXAMPLE 9-1

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

Because OH^- and H_3O^+ are formed only from the dissociation of water, their concentrations must be equal:

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

Substitution into Equation 9-11 gives

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

$$[H_3O^+] = [OH^-] = \sqrt{K_w}$$

At 25°C,

$$[H_3O^+] = [OH^-] = \sqrt{1.00 \times 10^{-14}} = 1.00 \times 10^{-7}\ M$$

At 100°C, from Table 9-3,

$$[H_3O^+] = [OH^-] = \sqrt{49 \times 10^{-14}} = 7.0 \times 10^{-7}\ M$$

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

$$[OH^-] = 0.200 + [H_3O^+]$$

where $[H_3O^+]$ accounts for the hydroxide ions contributed by the solvent. The concentration of OH^- from the water is insignificant, however, when compared with 0.200, so we can write

$$[OH^-] \approx 0.200$$

$$pOH = -\log 0.200 = 0.699$$

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

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

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

Note that the approximation

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

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

$$HNO_2 + H_2O \rightleftharpoons H_3O^+ + NO_2^- \qquad K_a = \frac{[H_3O^+][NO_2^-]}{[HNO_2]}$$

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

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \qquad K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

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:

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \qquad K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+ \qquad K_a = \frac{[NH_3][H_3O^+]}{[NH_4^+]}$$

Multiplication of one equilibrium-constant expression by the other gives

$$K_aK_b = \frac{\cancel{[NH_3]}[H_3O^+]}{\cancel{[NH_4^+]}} \times \frac{\cancel{[NH_4^+]}[OH^-]}{\cancel{[NH_3]}} = [H_3O^+][OH^-]$$

but

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

and therefore

$$K_w = K_aK_b \qquad (9\text{-}14)$$

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

$$CN^- + H_2O \rightleftharpoons HCN + OH^-$$

Appendix 3 lists a K_a value of 6.2×10^{-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 are established that yield hydronium ions:

$$HA + H_2O \rightleftharpoons H_3O^+ + A^- \qquad K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

$$2H_2O \rightleftharpoons H_3O^+ + OH^- \qquad K_w = [H_3O^+][OH^-]$$

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

$$[A^-] \approx [H_3O^+] \qquad (9\text{-}15)$$

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 A^- ions. Thus,

$$c_{HA} = [A^-] + [HA] \qquad (9\text{-}16)$$

Substituting $[H_3O^+]$ for $[A^-]$ (see Equation 9-15) into Equation 9-16 yields

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

which rearranges to

$$[HA] = c_{HA} - [H_3O^+] \tag{9-17}$$

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

$$K_a = \frac{[H_3O^+]^2}{c_{HA} - [H_3O^+]} \tag{9-18}$$

which rearranges to

$$[H_3O^+]^2 + K_a [H_3O^+] - K_a c_{HA} = 0 \tag{9-19}$$

The positive solution to this quadratic equation is

$$[H_3O^+] = \frac{-K_a + \sqrt{K_a^2 + 4K_a c_{HA}}}{2} \tag{9-20}$$

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

$$K_a = \frac{[H_3O^+]^2}{c_{HA}} \tag{9-21}$$

and

$$[H_3O^+] = \sqrt{K_a c_{HA}} \tag{9-22}$$

EXAMPLE 9-7

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

$$HNO_2 + H_2O \rightleftharpoons H_3O^+ + NO_2^-$$

for which (see Appendix 2)

$$K_a = 7.1 \times 10^{-4} = \frac{[H_3O^+][NO_2^-]}{[HNO_2]}$$

Substitution into Equations 9-15 and 9-17 gives

$$[NO_2^-] = [H_3O^+]$$

$$[HNO_2] = 0.120 - [H_3O^+]$$

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

$$K_a = \frac{[H_3O^+]^2}{0.120 - [H_3O^+]} = 7.1 \times 10^{-4}$$

If we now assume that $[H_3O^+] \ll 0.120$, we find

$$\frac{[H_3O^+]^2}{0.120} = 7.1 \times 10^{-4}$$

$$[H_3O^+] = \sqrt{0.120 \times 7.1 \times 10^{-4}} = 9.2 \times 10^{-3} \text{M}$$

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 $[H_3O^+]$ is actually smaller than this figure, however, as we can see by calculating $\log (c_{HA}/K_a) = 2.2$, which, from Figure 9-3, suggests an error of about 4%. If a more accurate figure is needed, solution of the quadratic equation yields 8.9×10^{-3} M for the hydronium ion concentration.

EXAMPLE 9-8

Calculate the hydronium ion concentration in a solution that is 2.0×10^{-4} M in aniline hydrochloride, $C_6H_5NH_3Cl$.

In aqueous solution, dissociation of the salt to Cl^- and $C_6H_5NH_3^+$ is complete. The weak acid $C_6H_5NH_3^+$ dissociates as follows:

$$C_6H_5NH_3^+ + H_2O \rightleftharpoons C_6H_5NH_2 + H_3O^+ \qquad K_a = \frac{[H_3O^+][C_6H_5NH_2]}{[C_6H_5NH_3^+]}$$

If we look in Appendix 3, we find that the K_a for $C_6H_5NH_3^+$ is 2.51×10^{-5}. Proceeding as in Example 9-7, we have

$$[H_3O^+] = [C_6H_5NH_2]$$

$$[C_6H_5NH_3^+] = 2.0 \times 10^{-4} - [H_3O^+]$$

Comparison of 7.09×10^{-5} with 2.0×10^{-4} suggests that a significant error has been introduced by the assumption that $[H_3O^+] \ll c_{C_6H_5NH_3^+}$. (Figure 9-3 indicates that this error is about 20%.) Thus, unless only an approximate value for $[H_3O^+]$ is needed, it is necessary to use the more nearly exact expression (Equation 9-19)

$$\frac{[H_3O^+]^2}{2.0 \times 10^{-4} - [H_3O^+]} = 2.51 \times 10^{-5}$$

which rearranges to

$$[H_3O^+]^2 + 2.51 \times 10^{-5}[H_3O^+] - 5.02 \times 10^{-9} = 0$$

$$[H_3O^+] = \frac{-2.51 \times 10^{-5} + \sqrt{(2.54 \times 10^{-5})^2 + 4 \times 5.02 \times 10^{-9}}}{2}$$

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

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 NH_3 solution. The predominant equilibrium is

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

As shown on page 243.

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{1.00 \times 10^{-14}}{5.70 \times 10^{-10}} = 1.75 \times 10^{-5}$$

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

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

The predominant species in such solutions has been clearly demonstrated to be NH_3. Nevertheless, solutions of ammonia are still called ammonium hydroxide occasionally because at one time chemists thought that NH_4OH rather than NH_3 was the undissociated form of the base. Application of the mass law to the equilibrium as written yields

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

$$[NH_4^+] = [OH^-]$$

Both NH_4^+ and NH_3 come from the 0.0750 M solution. Thus,

$$[NH_4^+] + [NH_3] = c_{NH_3} = 0.0750\ M$$

If we substitute $[OH^-]$ for $[NH_4^+]$ in the second of these equations and rearrange, we find that

$$[NH_3] = 0.0750 - [OH^-]$$

(continued)

Substituting these quantities into the dissociation-constant expression yields

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

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

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

Comparing the calculated value for $[OH^-]$ with 7.50×10^{-2}, we see that the error in $[OH^-]$ is less than 2%. If needed, a better value for $[OH^-]$ 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 OCl^- and water is

$$OCl^- + H_2O \rightleftharpoons HOCl + OH^-$$

for which

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

Appendix 3 reveals that the acid dissociation constant for HOCl is 3.0×10^{-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

$$[\mathrm{OH^-}] = [\mathrm{HOCl}]$$

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

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

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

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

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

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 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	Ion-product constant, K_w	$2\,H_2O \rightleftharpoons H_3O^+ + OH^-$	$K_w = [H_3O^+][OH^-]$
Heterogeneous equilibrium between a slightly soluble substance and its ions in a saturated solution	Solubility product, K_{sp}	$BaSO_4(s) \rightleftharpoons Ba^{2+} + SO_4^{2-}$	$K_{sp} = [Ba^{2+}][SO_4^{2-}]$
Dissociation of a weak acid or base	Dissociation constant, K_a or K_b	$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$	$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$
		$CH_3COO^- + H_2O \rightleftharpoons OH^- + CH_3COOH$	$K_b = \frac{[OH^-][CH_3COOH]}{[CH_3COO^-]}$
Formation of a complex ion	Formation constant, β_n	$Ni^{2+} + 4CN^- \rightleftharpoons Ni(CN)_4^{2-}$	$\beta_4 = \frac{[Ni(CN)_4^{2-}]}{[Ni^{2+}][CN^-]^4}$
Oxidation/reduction equilibrium	K_{redox}	$MnO_4 + 5Fe^{2+} + 8H^+ \rightleftharpoons Mn^{2+} + 5Fe^{3+} + 4H_2O$	$K_{redox} = \frac{[Mn^{2+}][Fe^{3+}]^5}{[MnO_4^-][Fe^{2+}]^5[H^+]^8}$
Distribution equilibrium for a solute between immiscible solvents	K_d	$I_2(aq) \rightleftharpoons I_2(org)$	$K_d = \frac{[I_2]_{org}}{[I_2]_{aq}}$

FEATURE 9-1

Stepwise and Overall Formation Constants for Complex Ions

The formation of $Ni(CN)_4^{2-}$ (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.

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

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

$$Ni(CN)_2 + CN^- \rightleftharpoons Ni(CN)_3^- \qquad K_3 = \frac{[Ni(CN)_3^-]}{[Ni(CN)_2][CN^-]}$$

$$Ni(CN)_3^- + CN^- \rightleftharpoons Ni(CN)_4^{2} \qquad K_4 = \frac{[Ni(CN)_4^{2-}]}{[Ni(CN)_3^-][CN^-]}$$

Overall constants are designated by the symbol β_n. Thus,

$$Ni^{2+} + 2CN^- \rightleftharpoons Ni(CN)_2 \qquad \beta_2 = K_1K_2 = \frac{[Ni(CN)_2]}{[Ni^{2+}][CN^-]^2}$$

$$Ni^{2+} + 3CN \rightleftharpoons Ni(CN)_3^- \qquad \beta_3 = K_1K_2K_3 = \frac{[Ni(CN)_3^-]}{[Ni^{2+}][CN^-]^3}$$

$$Ni^{2+} + 4CN^- \rightleftharpoons Ni(CN)_4^{2-} \qquad \beta_4 = K_1K_2K_3K_4 = \frac{[Ni(CN)_4^{2-}]}{[Ni^{2+}][CN^-]^4}$$

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.

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.

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:

$$HA + H_2O \rightleftharpoons H_3O^+ + A^- \qquad K_a = \frac{[H_3O^+][A^-]}{[HA]} \tag{9-23}$$

$$A^- + H_2O \rightleftharpoons OH^- + HA \qquad K_b = \frac{[OH^-][HA]}{[A^-]} = \frac{K_w}{K_a} \tag{9-24}$$

◄ Buffered aspirin contains buffers to help prevent stomach irritation from the acidity of the carboxylic acid group in aspirin.

$$[HA] = c_{HA} - [H_3O^+] + [OH^-] \tag{9-25}$$

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.

$$[A^-] = c_{NaA} + [H_3O^+] - [OH^-] \tag{9-26}$$

$$[HA] \approx c_{HA} \tag{9-27}$$

$$[A^-] \approx c_{NaA} \tag{9-28}$$

$$[H_3O^+] = K_a \frac{c_{HA}}{c_{NaA}} \tag{9-29}$$

form of its negative logarithm and inverting the concentration ratio to keep all signs positive:

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

Therefore,

$$pH = pK_a + \log \frac{c_{NaA}}{c_{HA}} \tag{9-30}$$

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.

$$HCOOH + H_2O \rightleftharpoons H_3O^+ + HCOO^- \qquad K_a = 1.80 \times 10^{-4}$$

$$HCOO^- + H_2O \rightleftharpoons HCOOH + OH^- \qquad K_b = \frac{K_w}{K_a} = 5.56 \times 10^{-11}$$

K_a

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 H_3O^+ concentration. We can thus write

$$K_a = \frac{[H_3O^+][HCOO^-]}{[HCOOH]} = 1.80 \times 10^{-4}$$

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

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

Substitution into Equation 9-29 gives, with rearrangement,

$$[H_3O^+] = 1.80 \times 10^{-4} \times \frac{0.400}{1.00} = 7.20 \times 10^{-5}\ M$$

Note that the assumption that $[H_3O^+] \ll c_{HCOOH}$ and that $[H_3O^+] \ll c_{HCOO^-}$ is valid. Thus,

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

EXAMPLE 9-12

Calculate the pH of a solution that is 0.200 M in NH_3 and 0.300 M in NH_4Cl. In Appendix 3, we find that the acid dissociation constant K_a for NH_4^+ is 5.70×10^{-10}.

The equilibria we must consider are

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+ \qquad K_a = 5.70 \times 10^{-10}$$

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \qquad K_b = \frac{K_w}{K_a} = \frac{1.00 \times 10^{-14}}{5.70 \times 10^{-10}} = 1.75 \times 10^{-5}$$

(continued)

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

$$[NH_4^+] = c_{NH_4Cl} + [OH^-] - [H_3O^+] \approx c_{NH_4Cl} + [OH^-]$$
$$[NH_3] = c_{NH_3} + [H_3O^+] - [OH^-] \approx c_{NH_3} - [OH^-]$$

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_{NH_3} so that

$$[NH_4^+] \approx c_{NH_4Cl} = 0.300\text{ M}$$
$$[NH_3] \approx c_{NH_3} = 0.200\text{ M}$$

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

$$[H_3O^+] = \frac{K_a \times [NH_4^+]}{[NH_3]} = \frac{5.70 \times 10^{-10} \times c_{NH_4Cl}}{c_{NH_3}}$$
$$= \frac{5.70 \times 10^{-10} \times 0.300}{0.200} = 8.55 \times 10^{-10}\text{ M}$$

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_{NH_3}. Thus, we may write

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

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.

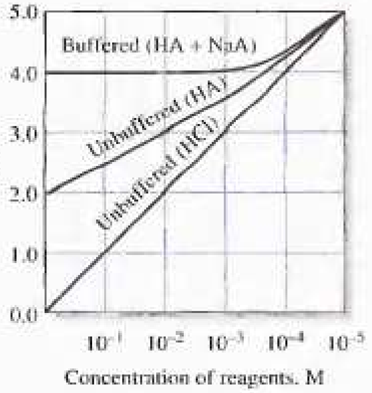


Figure 9-4 The effect of dilution of the pH of buffered and unbuffered solutions. The dissociation constant for HA is 1.00×10^{-4}. Initial solute concentrations are 1.00 M.

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 NH_4^+ in the buffer to NH_3:

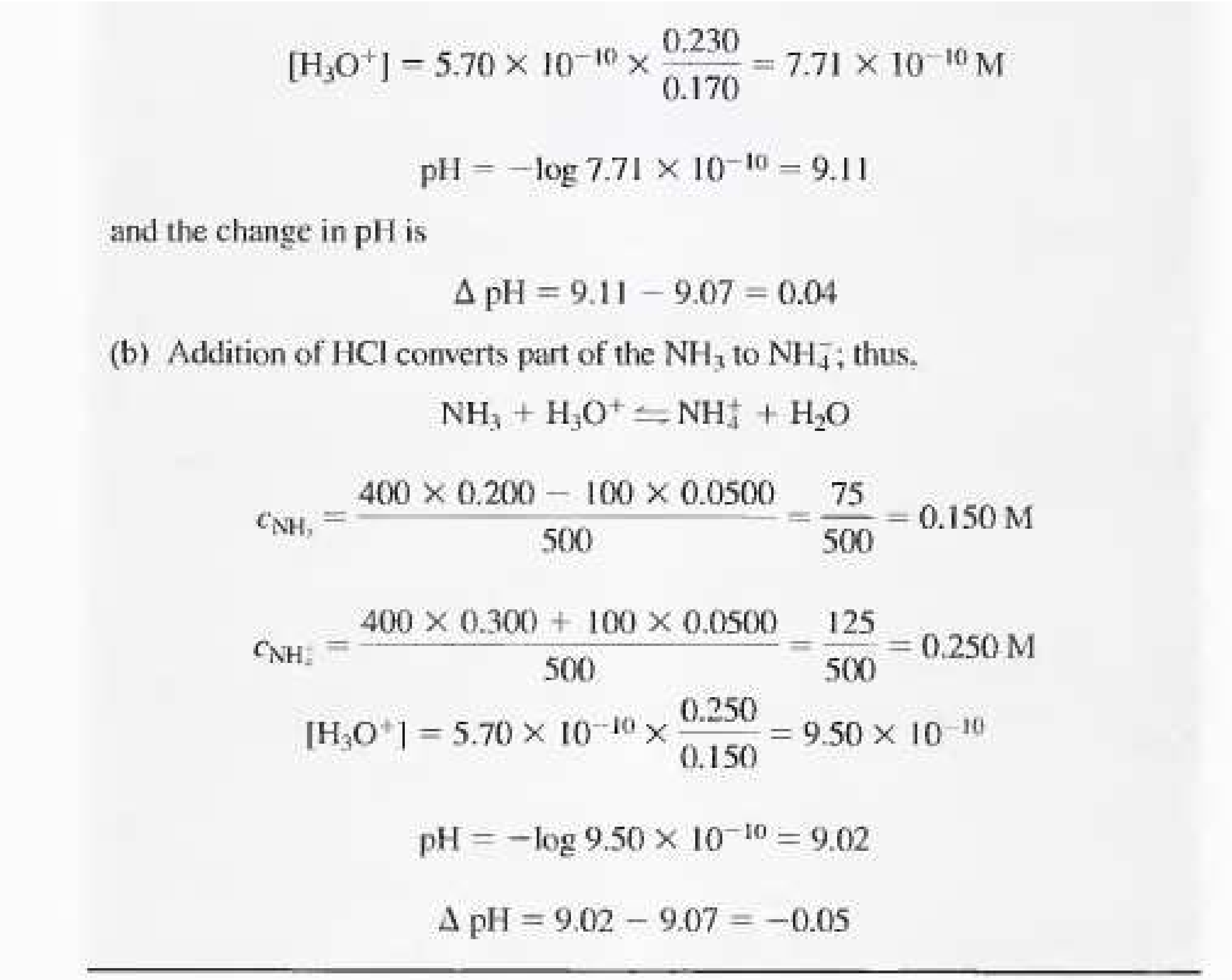
$$NH_4^+ + OH^- \rightleftharpoons NH_3 + H_2O$$

The analytical concentrations of NH_3 and NH_4Cl then become

$$c_{NH_3} = \frac{400 \times 0.200 + 100 \times 0.0500}{500} = \frac{85.0}{500} = 0.170 \text{ M}$$

$$c_{NH_4Cl} = \frac{400 \times 0.300 - 100 \times 0.0500}{500} = \frac{115}{500} = 0.230 \text{ M}$$

When substituted into the acid dissociation-constant expression for NH_4^+, these values yield



$$[H_3O^+] = 5.70 \times 10^{-10} \times \frac{0.230}{0.170} = 7.71 \times 10^{-10}\ M$$

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

and the change in pH is

$$\Delta\ pH = 9.11 - 9.07 = 0.04$$

(b) Addition of HCl converts part of the NH_3 to NH_4^-; thus.

$$NH_3 + H_3O^+ \rightleftharpoons NH_4^+ + H_2O$$

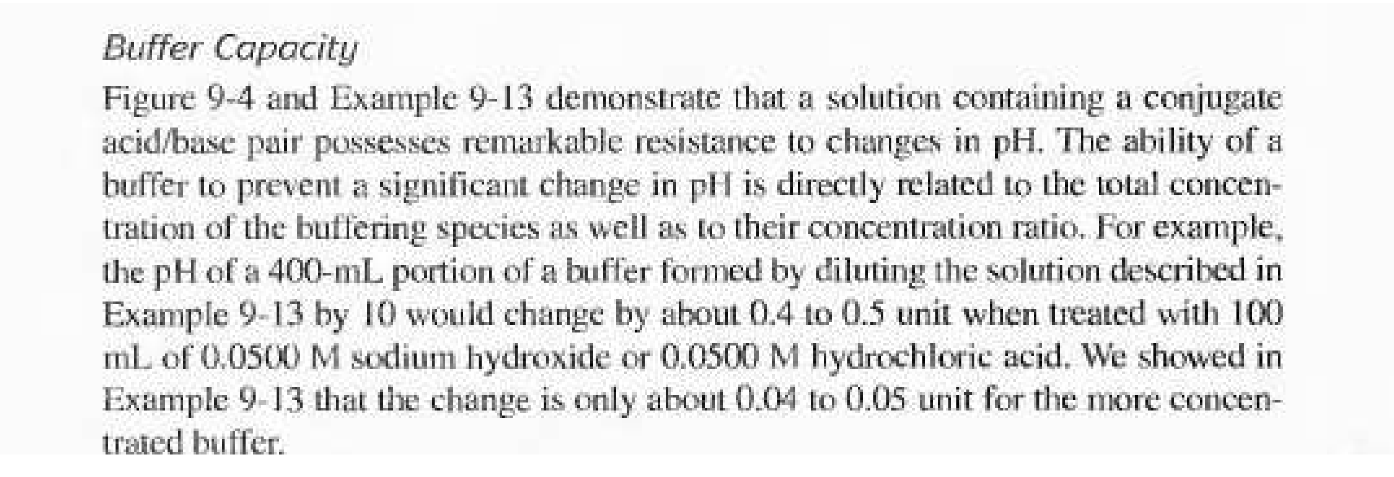
$$c_{NH_3} = \frac{400 \times 0.200 - 100 \times 0.0500}{500} = \frac{75}{500} = 0.150\ M$$

$$c_{NH_4^+} = \frac{400 \times 0.300 + 100 \times 0.0500}{500} = \frac{125}{500} = 0.250\ M$$

$$[H_3O^+] = 5.70 \times 10^{-10} \times \frac{0.250}{0.150} = 9.50 \times 10^{-10}$$

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

$$\Delta\ pH = 9.02 - 9.07 = -0.05$$



Buffer Capacity

Figure 9-4 and Example 9-13 demonstrate that a solution containing a conjugate acid/base pair possesses remarkable resistance to changes in pH. The ability of a buffer to prevent a significant change in pH is directly related to the total concentration of the buffering species as well as to their concentration ratio. For example, the pH of a 400-mL portion of a buffer formed by diluting the solution described in Example 9-13 by 10 would change by about 0.4 to 0.5 unit when treated with 100 mL of 0.0500 M sodium hydroxide or 0.0500 M hydrochloric acid. We showed in Example 9-13 that the change is only about 0.04 to 0.05 unit for the more concentrated buffer.

Ionic strength and activity

The ionic atmosphere surrounding each ion reduces it velocity ,causing the solution to behave as if its concentration is smaller than stoichiometric

a= Cf . where a= activity , C= molar concentration , f = activity coefficient

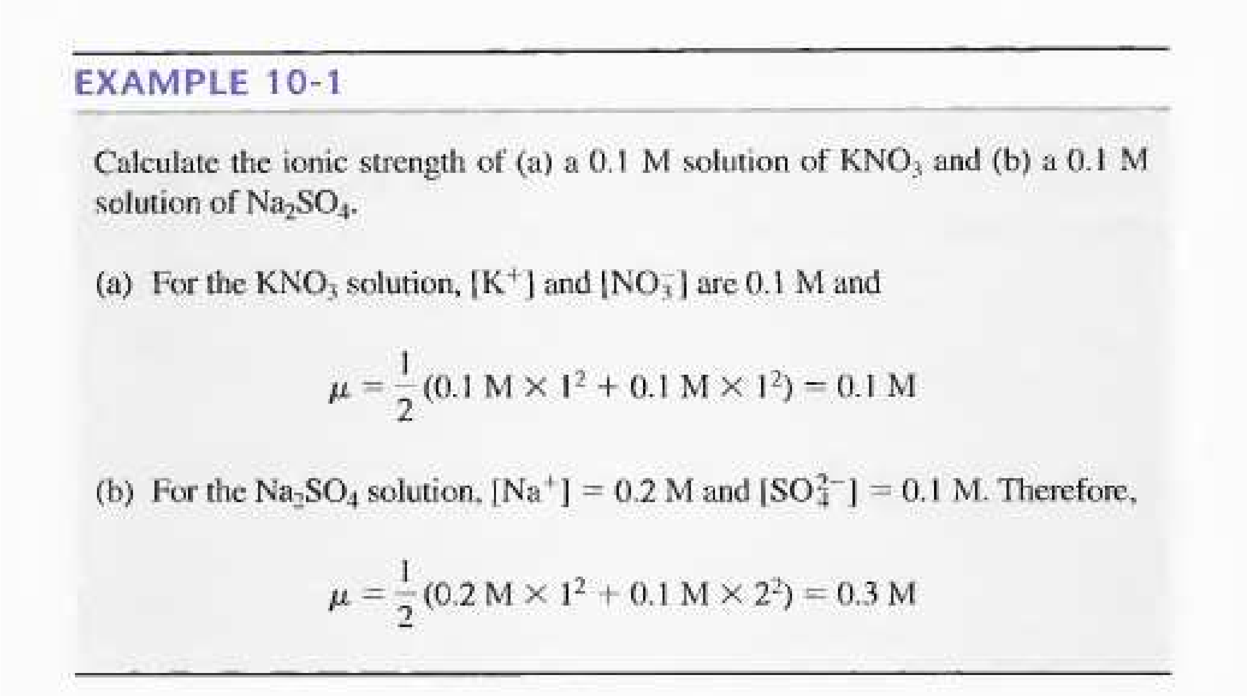
$u = 1/2\ (C_1z_1^2 + C_2z_2^2 + \text{-----} + C_nz_n^2) = 1/2 \sum C_iz_i^2$, u = ionic strength of the solution

The value of the f depends on the charge z of the ion on the ionic strength of the solution , according to the equation

$- \log f = Az^2 \sqrt{u}$,
A = constant , = 0.51 for the water at 25 °C

For better accuracy the following relation is used

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



EXAMPLE 10-1

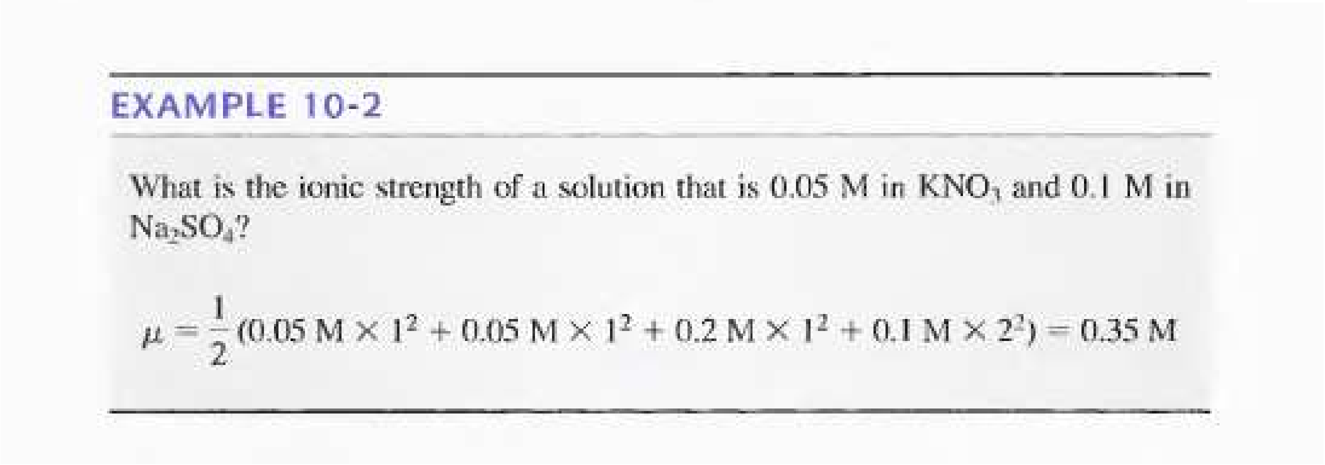
Calculate the ionic strength of (a) a 0.1 M solution of KNO_3 and (b) a 0.1 M solution of Na_2SO_4.

(a) For the KNO_3 solution, $[K^+]$ and $[NO_3^-]$ are 0.1 M and

$$\mu = \frac{1}{2}(0.1\ M \times 1^2 + 0.1\ M \times 1^2) = 0.1\ M$$

(b) For the Na_2SO_4 solution, $[Na^+] = 0.2\ M$ and $[SO_4^{2-}] = 0.1\ M$. Therefore,

$$\mu = \frac{1}{2}(0.2\ M \times 1^2 + 0.1\ M \times 2^2) = 0.3\ M$$



EXAMPLE 10-2

What is the ionic strength of a solution that is 0.05 M in KNO_3 and 0.1 M in Na_2SO_4?

$$\mu = \frac{1}{2}(0.05\ M \times 1^2 + 0.05\ M \times 1^2 + 0.2\ M \times 1^2 + 0.1\ M \times 2^2) = 0.35\ M$$

Example
Calculate the concentration and activity of each ion in a mixture obtained by mixing 25.0 mL of 0.120M $MnCl_2$ 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

Molarity of Mn^{2+} = , $M = \dfrac{25\ mL \times 0.120\ mmol/\ mL}{60\ mL} = 0.05\ mmol/\ mL$

Molarity of K^+ , $M = \dfrac{35\ mL \times 0.0.06\ mmol/\ mL}{60\ mL} = 0.035\ mmol/\ mL$

Molarity of Cl^- = 2 x mmole $MnCl_2$ + 1 x mmole KCl

Molarity of Cl^- , M $= \dfrac{\left(\dfrac{0.120\ mmmol}{mL}\right)\left(2\dfrac{mmolCl}{MnCl_2}\right) + (35.0\ mL)\left(\dfrac{0.060 mmolCl^-}{mL}\right)}{60\ mL} = 0.135\ mmol/\ mL$

The ionic strength of the solution is equal to

$u = 1/2(C_{Mn2+}\, z_{Mn2+}^{2} + C_{K+} z_{K+}^{2} + C_{Cl^-}\ z_{Cl}^{-2})$

$u = 1/2\{ (0.05) (2)^2 + (0.035) (1)^2 + (0.135) (-1)^2 \} = 0.185$

$-\log f_{Mn2+} = \dfrac{0.51 \times (2)^2 \sqrt{0.185}}{1 + \sqrt{0.185}}$ or $f_{Mn2+} = 0.243$

$-\log f_{K^+} = -\log f_{Cl-} = \dfrac{0.51 \times (1)^2 \sqrt{0.185}}{1 + \sqrt{0.185}}$ or $f_{K^+} = f_{Cl-} = 0.702$

$a_{K^+} = f_{K^+} \ .\ C_{K^+} = 0.702 \times 0.035 = 0.0246\ M$

$a_{Cl-} = f_{Cl-} \ .\ C_{Cl-} = 0.702 \times 0.135 = 0.095\ M$