Al-Mustansiriyah University

College of Science/Department of Chemistry

Analytical Chemistry

م.م. سهير عبد الهادي مهدي

Introduction

Chemistry: The science deals with the study of matter, including its composition, structure, physical properties, and reactivity. It is divided into five fields:

A. Organic chemistry.

B. Inorganic chemistry.

C. Physical chemistry.

D. Biochemical chemistry.

E. Analytical chemistry.

Analytical chemistry

Is a measurement science consisting of a set of powerful ideas and methods that are useful in all fields of science, engineering, and medicine.

- **Analytical chemistry concerned with determines the composition of substances. It comprises of two branches:**

1. **Qualitative analysis reveals the identity of the elements and compounds in a sample.**

2. **Quantitative analysis indicates the amount of each substance in a sample.**

Chemical Analytical Methods

- **Gravimetric methods:** Determine the mass of the analyte or some compound chemically related to it.
- **Volumetric methods:** Measure the volume of a solution containing sufficient reagent to react completely with the analyte.
- **Electroanalytical methods:** Measure electrical properties such as potential, current, resistance, and quantity of electrical charge.

- **Spectroscopic methods:** Explore the interaction between electromagnetic radiation and analyte atoms or molecules or the emission of radiation by analytes.

What is role of analytical chemistry?

Analytical Chemistry

Clinical analytical chemistry
e.g. analysis of blood or urine.

Environmental analytical chemistry e.g. heavy metals in soil or water.

Industrial sector
Analysis of steel during its production

Agricultural sector
e.g.analysis of fertilization needs from quantitative analysis of plants and soil.

Quality control
e.g. analysis of vitamin content in food samples.

Quantity control
e.g. analysis of automobile exhaust gases and mercaptan content of household gas.

Fundamental Concepts

1- Atomic weight of element:

The mass of a single atom in grams is much too small a number for convenience, and chemists therefore use a unit called an ***atomic mass unit (amu)*** also known as a ***dalton (Da)***. One ***amu*** is defined as exactly 1/12 the mass of carbon isotope ^{12}C and equal to 1 .66054 x 10^{-24} g.

Example: prove that carbon weighing 1.0 x10^{-3} g contains 5.01x 10^{19} carbon atom?

Solution:

$$1\times 10^{-3}\,g\times \frac{1\,amu}{1.66054\times 10^{-24}g}\times \frac{1\,C\,atom}{12.011\,amu}=5.01\times 10^{19}\,C\,atom$$

2- Molecular weight.

The sum of the atomic weights of all the atoms in a molecule.

Molecular weight = Summation of atomic weight

Example: Calculate the molecular weight of water.

Solution:

A water molecule, H_2O, has,

2 Hydrogen	2×1.0080 amu
1 Oxygen	1×15.9994 amu
Total molecular weight	$= 18.0154$ amu ≈ 18.02

Example: Calculate the molecular weight of methyl alcohol.

Solution:

The molecular formula is CH_3OH or CH_4O. Then:

1 carbon	1×12.011 amu = 12.011	amu
4 hydrogen	4×1.008 amu = 4.032	amu
1 oxygen	1×15.999 amu = 15.999	amu
Total molecular weight	= 32.04	amu

Home work.

Calculate the molecular weight of C_8H_{18}, $C_7H_{14}O_2$, $C_2H_5N_2SO_4$.

amu =14.0067 for N2
= 32.065 for S

3- Chemical equation.

- **Representation of chemical reaction in terms of symbols and formula of reactants and products .**

- **Reactants written in left hand side.**

- **Products written in right hand side.**

- **numbers of atoms of different elements are the same on both sides of arrow is called balanced chemical equation.**

$$A + B \xrightarrow{Direction\ of\ reaction} C + D$$

Classification of chemical reactions.

1) Combination reaction:

$$2Mg(S) + O_2(g) \rightarrow 2MgO(s)$$

2) Decomposition reaction:

$$2Pb(NO_3)_2\,(s) \rightarrow 2PbO(s) + 4NO_2(g) + O_2(g)$$

3) Displacement reactions:

$$Zn(S) + CuSO_4(aq) \rightarrow ZnSO_4(aq) + Cu(s)$$

$$Cu\,(s) + 2AgNO_3(aq) \rightarrow Cu(NO_3)_2(aq) + 2Ag\,(s)$$

4) Double Displacement reactions:

- **Precipitation reaction**:

$$AgNO_3(aq) + NaCl(aq) \rightarrow AgCl(s) + NaNO_3$$

- **Neutralization reaction:**

$$NaOH\ (aq) + HCl\ (aq) \rightarrow NaCl(aq) + H_2O$$

5) Redox reaction:

$$ZnO + C \rightarrow Zn + CO$$

ZnO reduce to Zn ------- Reduction

O oxidize to CO -------- Oxidation

6) Exothermic reaction and Endothermic reaction:

- **Endothermic reaction**

$$CaCO_3 + Energy \rightarrow CaO + CO_2$$

- **Exothermic reaction:**

$$C + O_2 \rightarrow CO_2(g) + Energy$$

4- **Mole (mol).**

- **Is the number of Avogadro's number of atom, molecule, electron and proton (6.022 x 10^{23}).**

- **The numbers of moles of substance is calculated from.**

$$\boxed{no.\,of\ moles = \frac{mass\ of\ substance\ (g)}{molecular\ weight\ (\frac{g}{mol})}}$$

$$Millimole\ (mmol) = 10^{-3}\ mol\ \ and\ 10^{3} mmol = 1\ mol$$

5- Molar mass $\mathcal{M}$ of a substance.

- **Is the mass in grams of 1 mole of that substance.**

1 mole of C = 12 gram of carbon (molar mass) = 6.022 x 10^{23} atoms of C

1 mole of H = 1 gram of hydrogen (molar mass) = 6.022 x 10^{23} atoms of H

1 mole of O = 16 grams of oxygen (molar mass) = 6.022 x 10^{23} atoms of O

Example: Calculate the molar mass of formaldehyde CH_2O.

Solution:

$$\begin{aligned}\mathcal{M}_{CH_2O} &= \frac{1\ \cancel{\text{mol C}}}{\text{mol CH}_2\text{O}} \times \frac{12.0\ \text{g}}{\cancel{\text{mol C}}} + \frac{2\ \cancel{\text{mol H}}}{\text{mol CH}_2\text{O}} \times \frac{1.0\ \text{g}}{\cancel{\text{mol H}}} \\ &\quad + \frac{1\ \cancel{\text{mol O}}}{\text{mol CH}_2\text{O}} \times \frac{16.0\ \text{g}}{\cancel{\text{mol O}}} \\ &= 30.0\ \text{g/mol CH}_2\text{O}\end{aligned}$$

Example: Find the number of moles and millimoles of benzoic acid ($\mathcal{M}$ = 122.1 g/mol) that are contained in 2.00 g of the pure acid.

Solution:

If we use HB_z to represent benzoic acid, we can write that 1 mole of HB_z has a mass of 122.1 g. Therefore,

$$\text{amount HBz} = 2.00\ \cancel{\text{g HBz}} \times \frac{1\ \text{mol HBz}}{122.1\ \cancel{\text{g HBz}}} = 0.0164\ \text{mol HBz}$$

To obtain the number of millimoles, we divide by the millimolar mass (0.1221 g/mmol), that is,

$$\text{amount HBz} = 2.00\ \cancel{\text{g HBz}} \times \frac{1\ \text{mmol HBz}}{0.1221\ \cancel{\text{g HBz}}} = 16.4\ \text{mmol HBz}$$

$$\text{Or,}\ \ \text{no. of moles} = \frac{\text{mass of substance (g)}}{\text{molar mass }(\frac{\text{g}}{\text{mol}})}$$

$$\text{no. of moles} = \frac{2\ \text{g}}{122.1(\frac{\text{g}}{\text{mol}})} = 0.0164\ \text{mol}$$

$$= 0.0164\ \text{mol} \times \frac{10^3\ \text{mmol}}{1\ \text{mol}} = 16.4\ \text{mmol HBz}$$

6- Equivalent weight.

- **Is the molecular weight divided by the number of reacting units (no.of equivalent = valency).**

$$\boxed{\boldsymbol{Equivalent\ Weight = \frac{molecular\ weight}{no.of\ equivalent}}}$$

- **For acid:** the number of reacting units is the no. of hydrogen ions that will furnish.

For example:

$HCl \leftrightarrow H^+ + Cl^-$ $\quad eq.wt.HCl = \frac{M.wt.}{1}$

$H_2SO_4 \leftrightarrow 2H^+ + SO_4^{-2}$ $\quad eq.wt.H_2SO_4 = \frac{M.wt.}{2}$

$CH_3COOH \leftrightarrow H^+ + CH_3COO^-$ $\quad eq.wt.CH_3COOH = \frac{M.wt.}{1}$

For Phosphoric Acid (H_3PO_4) the equivalent weight depends on the reaction as shown below.

$H_3PO_4 \overset{M.O}{\Longleftrightarrow} H^+ + H_2PO_4^-$ $\quad eq.wt. = \frac{M.wt.}{1}$

$H_3PO_4 \overset{Ph.ph}{\Longleftrightarrow} 2H^+ + HPO_4^{2-}$ $\quad eq.wt. = \frac{M.wt.}{2}$

$H_3PO_4 \overset{CaCl_2}{\Longleftrightarrow} 3H^+ + PO_4^{3-}$ $\quad eq.wt. = \frac{M.wt.}{3}$

- **For bases:** the number of reacting units is the no. of hydrogen ions that will react with it.

For example:

$KOH + H^+ \rightarrow K^+ + H_2O$ $\qquad eq.wt. = M.wt.$

$Ba(OH)_2 + 2H^+ \rightarrow Ba^{2+} + 2H_2O$ $\qquad eq.wt. = \frac{M.wt.}{2}$

$Fe_3O_3 + 6H^+ \rightarrow 2Fe^{3+} + 3H_3O$ $\qquad eq.wt. = \frac{M.wt.}{6}$

- **For salts:**

$$eq.wt. = \frac{M.wt.of\ salt}{no.of\ positive\ ion\ or\ no.of\ negative\ ion}$$

For example:

$$Ag^{+}NO_3^{-} + H^{+}Cl^{-} \rightarrow Ag^{+}Cl^{-} + H^{+}NO_3^{-}$$

$$eq.wt.of\ Ag^{+}NO_3^{-} = \frac{M.wt.of\ Ag^{+}NO_3^{-}}{1}$$

$$eq.wt.of\ Ag_2{}^{+}NO_3^{-2} = \frac{M.wt.}{2}$$

$$eq.wt.of\ Al^{+3}PO_4^{-3} = \frac{M.wt.}{3}$$

$$eq.wt.of\ Ca_3^{+2}(PO_4)_2^{-3} = \frac{M.wt.}{6}$$

- **For oxidation / reduction reactions:**

$$eq.wt.of\ reducing\ agent = \frac{M.wt.}{no.of\ electrons\ loosed\ for\ one\ molcule}$$

$$eq.wt.of\ oxidizing\ agent = \frac{M.wt.}{no.of\ electrons\ accepted\ for\ one\ molcule}$$

For example:

$Mn^{+7}O_4{}^{-} + H^{+} + 5e \rightarrow Mn^{+2} + H_2O$ …………. *In acidic medium*

$$eq.wt.of\ Mn^{+7}O_4^{-} = \frac{M.wt.}{5}$$

$Mn^{+7}O_4{}^{-} + H_2O \rightarrow Mn^{+4}O_2{}^{-} + OH^{-}$ …………… *In basic medium*

$$eq.wt.of\ Mn^{+7}O_4^{-} = \frac{M.wt.}{3}$$

- **For reaction involving formation of a precipitate or soluble complex ion:**

$$\boxed{eq.wt.of\ complex\ ion\ = \frac{M.wt.}{no.of\ charges}}$$

For example:

$AgNO_3 \rightarrow Ag^{+} + NO_3^{-}$ $\qquad eq.wt. = \frac{M.wt.of\ AgNo_3}{1}$

$HgCl_2 \leftrightarrow Hg^{2+} + 2Cl^{-}$ $\qquad eq.wt. = \frac{M.wt.of\ HgCl_2}{2}$

$Ag + 2NH_3 \rightarrow Ag^{+}(NH_3)_2^{-}$ $\qquad eq.wt.of\ Ag^{+}(NH_3)_2^{-} = \frac{M.wt.}{1}$

$Cu^{+2} + 4NH_3 \rightarrow Cu\ (NH_3)_4^{-2}$ $\qquad eq.wt.of\ Cu(NH_3)_4^{-2} = \frac{M.wt.}{2}$

Home work:

Calculate the equivalent weights of the following substances as acids or bases: (a) HCl, (b) $Ba(OH)_2$, (c) $KH(IO_3)_2$, (d) H_2SO_3, (e) CH_3COOH.

Solutions and Their Concentrations

Solution: is a homogeneous mixture of two or more substances.

A minor species in a solution is called **solute** and the major species is the **solvent**.

Solute (minor species) + Solvent (major species) → Solution

$$NaCl_{(s)} + H_2O_{(l)} \longrightarrow \text{Salt Solution}$$

There are four fundamental ways of expressing solution concentration:

a) Molar concentration.

It is defined as the number of moles of that species that is contained in 1 liter of the solution (not 1 L of the solvent).

$$\text{molar concentration} = \frac{no.moles\ solute}{volume\ in\ liters}$$

Symbolized by M, which has the dimensions of mol/L, or $\boldsymbol{mol\ L^{-1}}$.

$$1M = 1\,mol\,L^{-1} = 1\,\frac{mol}{L} = 1\,mmol\,L^{-1} = 1\,\frac{mmol}{L}$$

Example: Calculate the molar concentration of ethanol in an aqueous solution that contains 2.30 g of C_2H_5OH (46.07 g/mol) in 3.50 L of solution.

Solution:

To calculate molar concentration, we must find both the amount of ethanol and the volume of the solution. The volume is given as 3.50 L, so all we need to do is convert the mass of ethanol to the corresponding amount of ethanol in moles.

$$n = 2.30\ g \times \frac{1\ mol\ of\ ethanol}{46.07\ g\ ethanol} = 0.04992\ mol\ ethanol$$

To obtain the molar concentration, we divide the amount by the volume. Thus,

$$M = \frac{0.04992\ mol}{3.50\ L}$$

$$= 0.0143\ \text{mol}\ /\text{L}$$

There are two ways of expressing molar concentration:

a) **Molar analytical concentration (Analytical concentration).**

A solution gives the total number of moles of a solute in 1 liter of the solution (or the total number of millimoles in 1 mL).

Note

In the above example, the molar concentration that we calculated is also the molar analytical concentration ($c\mathrm{C_2H_5OH} = 0.0143$ M) because the solute ethanol molecules are intact following the solution process.

b) **Molar equilibrium concentration (Equilibrium concentration).**

Refers to the molar concentration of a particular species in a solution at equilibrium.

To specify the molar equilibrium concentration of a species, it is necessary to know how the solute behaves when it is dissolved in a solvent.

Equilibrium molar concentrations are usually symbolized by placing square brackets around the chemical formula for the species.

For example:

Solution of H_2SO_4 with an analytical concentration of ($cH_2SO_4 = 1.0$ M), we write

$$[H_2SO_4] = 0.00\ \text{M} \qquad [H^+] = 1.01\ \text{M}$$

$$[HSO_4^-] = 0.99\ \text{M} \qquad [SO_4^{2-}] = 0.01\ \text{M}$$

Example: Calculate the analytical and equilibrium molar concentrations of the solute species in an aqueous solution that contains 285 mg of trichloroacetic acid, Cl_3CCOOH (163.4 g/mol), in 10.0 mL (the acid is 73% ionized in water).

Solution:

Cl_3CCOOH= HA.

$$amount\ of\ HA = n_{HA} = 285\,\cancel{mg\ HA} \times \frac{1\cancel{g\ HA}}{1000\ \cancel{mg}\ HA} \times \frac{1\ mol\ HA}{163.4\ \cancel{g\ HA}} = 1.744 \times 10^{-3}\ mol\ HA$$

The molar analytical concentration, C_{HA}, is then

$$C_{HA} = \frac{1.744 \times 10^{-3} mol\ HA}{10\ mL} \times \frac{1000\ mL}{1L} = 0.174\,\frac{mol\ HA}{L} = 0.174\ M$$

In this solution, 73% of the HA dissociates, giving H^+ and A^-:

$$HA \leftrightarrow H^+ + A^-$$

The equilibrium concentration of HA is then 27% of $C_{HA,}$ Thus,

$$[HA] = C_{HA} \times \frac{100-73}{100} = 0.174 \times 0.27 = 0.047\,\frac{mol}{L} = 0.047\ M$$

The equilibrium concentration of A^- is equal to 73% of the analytical concentration of HA, that is,

$$[A^-] = \frac{73\ mol\ A^-}{100\ mol\ HA} \times 0.174\ \frac{mol\ HA}{L} = 0.127\ M$$

Because 1 mole of H^+ is formed for each mole of A^-, we can also write

$$[H^+] = [A^-] = 0.127\ M$$

and

$$C_{HA} = [HA] + [A^-] = 0.047 + 0.127 = 0.174\ M$$

Example: Describe the preparation of 2.00 L of 0.108 M $BaCl_2$ from $BaCl_2.2H_2O$ (244.3 g/mol).

Solution:

To determine the number of grams of solute to be dissolved and diluted to 2.00 L, we note that 1 mole of the dihydrate yields 1 mole of $BaCl_2$. Therefore, to produce this solution we will need

$$2.00\,\cancel{L} \times \frac{0.108\ mol\ BaCl_2.2H_2O}{\cancel{L}} = 0.216\ mol\ BaCl_2.2H_2O$$

The mass of $BaCl_2.2H_2O$ is then

$$0.216\ \cancel{mol\ BaCl_2.2H_2O} \times \frac{244.3\ g\ BaCl_2.2H_2O}{\cancel{mol\ BaCl_2.2H_2O}} = 52.8\ g\ BaCl_2.2H_2O$$

Dissolve 52.8 $g\ BaCl_2.2H_2O$ in water and dilute to 2 L.

Example: Describe the preparation of 500 mL of 0.0740 M Cl^- solution from solid $BaCl_2.2H_2O$ (244.3 g/mol).

Solution:

$$mass\ BaCl_2.2H_2 = \frac{0.0740\ \cancel{mol\ Cl}}{\cancel{L}} \times 0.500\cancel{L} \times \frac{1\ mol\ \cancel{BaCl_2.2H_2O}}{2\ \cancel{mol\ Cl}} \times \frac{244.3\ g\ BaCl_2.2H_2O}{\cancel{mol\ BaCl_2.2H_2O}} =$$

$$4.52\ g\ BaCl_2.2H_2O$$

Dissolve 4.52 $g\ BaCl_2.2H_2O$ in water and dilute to 0.500L or 500 mL.

b) Percent concentration.

Three common methods are used to express a percent concentration.

$$\text{weight percent}(w/w) = \frac{\text{weight solute}}{\text{weight solution}} \times 100\%$$

$$\text{volume percent}(v/v) = \frac{\text{volume solute}}{\text{volume solution}} \times 100\%$$

$$\text{weight/volume percent}(w/v) = \frac{\text{weight solute, g}}{\text{volume solution, mL}} \times 100\%$$

Parts per Million and Parts per Billion.

For very dilute solutions, parts per million (ppm) and Parts per Billion (ppb) are convenient ways to express concentration:

$$C_{ppm} = \frac{mass\ of\ solute\ (g)}{mass\ of\ solution\ (g)} \times 10^6\ ppm$$

$$C_{ppm} = \frac{mass\ solute\ (mg)}{volume\ solution\ (L)}\ ppm$$

$$C_{ppb} = \frac{mass\ solute\ (g)}{mass\ solution\ (g)} \times 10^9\ ppb$$

$$C_{ppb} = \frac{mass\ solute\ (\mu g)}{volume\ solution\ (L)}\ ppb$$

Example: What is the molar concentration of K$^+$ in a solution that contains 63.3 ppm of $K_3Fe(CN)_6$ (329.3 g/mol)?

Solution

Because the solution is so dilute, it is reasonable to assume that its density is1.00 g/mL.

63.3 ppm $K_3Fe(CN)_6$ = 63.3 mg $K_3Fe(CN)_6$/L

$$\frac{no.mol\ K_3Fe(CN)_6}{L} = \frac{63.3\ \cancel{mg\ K_3Fe(CN)_6}}{L} \times \frac{1\ \cancel{g\ K_3Fe(CN)_6}}{1000\ \cancel{mg\ K_3Fe(CN)_6}} \times \frac{1\ mol\ K_3Fe(CN)_6}{329.3\ \cancel{g\ K_3Fe(CN)_6}} = 1.922 \times 10^{-4}\ M$$

$$[K^+] = \frac{1.922\times10^{-4}\ \cancel{mol\ K_3Fe(CN)_6}}{L} \times \frac{3\ mol\ K^+}{1\ \cancel{mol\ K_3Fe(CN)_6}} = 5.77 \times 10^{-4}\,\frac{mol\ K^+}{L} = 5.77 \times 10^{-4}\ M$$

c) Solution-Diluent Volume Ratios.

The composition of a dilute solution is sometimes specified in terms of the volume of a more concentrated solution and the volume of solvent used in diluting it. The volume of the former is separated from that of the latter by a colon.

For example:

1:4 HCl (i.e. solution contains four volumes of water for each volume of concentrated hydrochloric acid.)

1:1HCl (i.e. solution contains one volume of water for each volume of concentrated hydrochloric acid.)

3:2 H_3Po_4 (i.e. solution contains two volumes of water for three volume of concentrated H_3Po_4)

d) p-Functions.

The concentration of a species frequently express in terms of p-function, p-value. The p-value is the negative logarithm (to the base 10) of the molar concentration of that species. Thus, for the species X,

$$pX = -\log[X]$$

Example: Calculate the p-value for each ion in a solution that is 2.00×10^{-3} M in NaCl and 5.4×10^{-4} M in HCl.

$$pH = -\log[H^+] = -\log[5.4 \times 10^{-4}] = 3.27$$

To obtain pNa , we write

$$pNa = -\log[Na^+] = -log[2.00 \times 10^{-3}] = 2.699$$

The total Cl^-concentration is given by sum of the concentration of the two solutes:

$$[Cl^-] = 2.00 \times 10^{-3}\,\mathrm{M} + 5.4 \times 10^{-4}\,\mathrm{M}$$

$$= 2.00 \times 10^{-3} M + 0.54 \times 10^{-3}\ M = 2.54 \times 10^{-3} M$$

$$pCl = -\log[Cl^-] = -\log 2.54 \times 10^{-3} = 2.595$$

Example: Calculate the molar concentration of Ag^+ in a solution that has a *pAg* of 6.372.

Solution:

$$\mathrm{pAg} = -\log\,[\mathrm{Ag}^+] = 6.372$$

$$log[Ag^+] = -6.372$$

$$[Ag^+] = 10^{-6.372} = 4.4246 \times 10^{-7} \approx 4.25 \times 10^{-7} M$$

Density and Specific Gravity of Solutions

Density of a substance is its mass per unit volume, unit (kg/L or g/mL).

$$Density = \frac{mass, (kg, g)}{Volume, (L, mL)}$$

Specific gravity Specific gravity is the ratio of the mass of a substance to the mass of an equal volume of water. (Specific gravity is dimensionless).

Example: Calculate the molar concentration of HNO_3 (63.0 g/mol) in a solution that has a specific gravity of 1.42 and is 70.5% HNO_3 (w/w).

Solution:

Let us first calculate the mass of acid per liter of concentrated solution.

$$\frac{g\ HNO_3}{L\ reagent} = \frac{1.42\ \cancel{kg\ reagent}}{L\ reagent} \times \frac{10^3\ \cancel{g\ reagent}}{\cancel{kg\ reagent}} \times \frac{70.5\ g\,HNO_3}{100\ \cancel{g\ reagent}} = \frac{1001\ g\ HNO_3}{L\ reagent}$$

Then,

$$C_{HNO_3} = \frac{1001\ \cancel{g\ HNO_3}}{L\ reagent} \times \frac{1\ mol\ HNO_3}{63.0\ \cancel{g\ HNO_3}} = \frac{15.9\ mol\ HNO_3}{L\ reagent} \approx 16\ M$$

Example: Describe the preparation of 100 mL of 6.0 M HCl from a concentrated solution that has a specific gravity of 1.18 and is 37% (w/w) HCl (36.5 g/mol).

Solution

$$C_{HCl} = \frac{1.18\times 10^{3}\ \cancel{g\ reagent}}{L\ reagent}\times\frac{37\ \cancel{g\ HCl}}{100\ \cancel{g\ reagent}}\times\frac{1\ mol\ HCl}{\cancel{36.5\ g\ HCl}} = 12\ M$$

The number of moles HCl required is given by

$$\boldsymbol{no.}\,mol\ HCl = 100\ \cancel{ml}\times\frac{\cancel{1\ L}}{\cancel{1000\ mL}}\times\frac{6\ mol\ HCl}{\cancel{L}} = 0.600\ mol\ HCl$$

Finally, to obtain the volume of concentrated reagent we write

$$\boldsymbol{V_{concd}\times C_{concd} = V_{dil}\times C_{dil}} \longrightarrow$$

$$\boldsymbol{V_{concd}\times C_{concd} = V_{dil}\times C_{dil}}$$

$$\boldsymbol{L_{concd}\times\frac{mol_{concd}}{L_{concd}} = L_{dil}\times\frac{mol_{dil}}{L_{dil}}}$$

$$\boldsymbol{mL_{concd}\times\frac{mmol_{concd}}{mL_{concd}} = mL_{dil}\times\frac{mmol_{dil}}{mL_{dil}}}$$

$$V_{concd}\times\frac{12\ mol}{L} = 0.600\ mol\ HCl$$

$$V_{concd\ \ reagent} = 0.600\ mol\ HCl\times\frac{1\ L_{reagen\ \ t}}{12\ mol\ HCl} = 0.0500L\ or\ 50.0\ mL$$

Therefore, dilute 50 mL of the concentrated reagent to 600 mL.

Solutions and Their Concentrations:

Formality, F: **is the number of moles of solute contained in each liter of solution. A synonym of molar analytical concentration.**

Molality, m: **is concentration expressed as moles of substance per kilogram of solvent .**

$$\boldsymbol{molality = m = \frac{mole\ of\ solute}{kg\ of\ solvent}}$$

Example: Find the molarity and molality of 37.0 wt. % HCl. If the density of solution is 1.19 g/mL, molecular mass of HCl is 36.46 g/mol

Solution:

For molarity (molar concentration), we need to find the moles of HCl per liter of solution.

$$Mass\ of\ HCl\ per\ liter = \frac{1.19\ g\ \cancel{solution}}{\cancel{mL}} \times \frac{1000\ \cancel{mL}}{1L} \times \frac{37\ g\ HCl}{100\ g\ \cancel{solution}} = 4.40\ \times 10^2\ \frac{g\ HCl}{L}$$

$$Molrity = \frac{mol\ HCl}{L\ solution} = \frac{4.40\ \times 10^2\ \cancel{g\ HCl}}{L} \times \frac{1\ mol}{36.46\cancel{g\ HCl}} = 12.1\ \frac{mol}{L} = 12.1\ M$$

For molality, we need to find the moles o HCl per kilogram of solvent (which is H_2O).

The solution is 37 wt. % HCl, so we know that 100 g of solution contains 37 g of HCl and

100-37=63 g of H_2O = $\frac{1\ kg}{1000\ g} = 0.063\ kg\ H_2O$

$$m = \frac{mol\ HCl}{kg\ of\ solvent}$$

$$Molality = m = \frac{(37\ g\ HCL \times 1\ mol/36.46\ g\ HCl}{0.063\ kg\ H_2O} = 16.1\ m$$

Example: What is the molality of a solution containing 5.0g NaCl dissolved in 25.0g water?

Solution:

$$Molality\ (m) = \frac{moles\ of\ solute}{kg\ of\ solvent}$$

$$no.\ of\ moles = \frac{mass\ of\ substance\ (g)\ of\ NaCl}{molecular\ weight\ \left(\frac{g}{mol}\right) of NaCl} = \frac{5\ g}{58.44\ g/mol} = 0.086\ mol$$

❖ $$\boldsymbol{m} = \frac{0.086\ mol}{25\ \cancel{g}\ water} \times \frac{1000\ \cancel{g}\ water}{kg\ water} = \frac{3.44\ mol}{kg\ water} = \mathbf{3.44\ m}$$

Example: A solution of H_2SO_4 with a molal concentration of 8.010 m has a density of 1.354 g/mL. What is the molar concentration of this solution?

$$Molality\ (m) = \frac{8.010\ mol}{1kg\ of\ solvent}$$

Molecular weight of H_2SO_4=98.0768 g/mol

$$mass\ of\ solute = 8.010\ mol \times \frac{98.0768\ g}{mol} = 785.6\ g$$

$$total\ mass\ in\ 8.010\ m\ solution\ = mass\ of\ solute\ + mass\ of\ solvent = 785.6\ g + 1000\ g = 1785.6\ g$$

$$Density = \frac{mass\ of\ solution}{volume\ of\ solution}$$

$$Volume\ of\ solution = \frac{mass\ of\ solution}{Density} = \frac{1785.6\ g}{1.354\frac{g}{mL}} = 1318.76\ mL = 1.31876\ L$$

$$M = \frac{8.010\ mol}{1.31876\ L} = 6.0739\ M$$

Normality, N: is number of equivalents of solute contained in 1 L of solution or the number of milliequivalents in 1 mL.

The equivalent and milliequivalent, like the mole and millimole, are units for describing the amount of a chemical species.

The **normality N or normal concentration $C_{N\,(A)}$** for a solution of the species A is given by the equations:

$$N = C_{N(A)} = \frac{no.eq\ A}{no.L\ solution}$$

$$N = C_{N(A)} = \frac{no.meq\ A}{no.mL\ solution}$$

Some useful Algebraic Relationships:

$$amount\ A = no.meq\ A = \frac{mass\ A\ (g)}{meqw\ A\ (\frac{g}{meq})}$$

$$amount\ A = no.eq\ A = \frac{mass\ A\ (g)}{eqw\ A\ (\frac{g}{eq})}$$

$$amount\ A = no.meq\ A = V(L) \times N_{(A)}(\frac{eq}{L})$$

$$amount\ A = no.meq\ A = V(mL) \times N_{(A)}(\frac{meq}{mL})$$

The normality, N, of a redox reagent is *n times the molarity*, where n is the number of electrons donated or accepted by that species in a chemical reaction.

$$N = n\ M$$

Example: Describe the preparation of 5.000 L of 0.1000 N Na_2CO_3 (105.99 g/mol) from the primary-standard solid, assuming the solution is to be used for titrations in which the reaction is

$$CO_3^{2-} + 2H^+ \rightarrow H_2O + CO_2$$

Solution

$$amount\ A = no.meq\ A = V(L) \times N_{(A)}(\frac{eq}{L})$$

$$amount\ Na_2CO_3 = V_{soln}(L) \times N_{Na_2CO_3}(\frac{eq}{L})$$

$$= 5.000\ L \times 0.1000 \frac{eq}{L} = 0.5000\ eqNa_2CO_3$$

Rearranging the equation $\boxed{amount\ A = no.eq\ A = \frac{mass\ A\ (g)}{eqw\ A\ (\frac{g}{eq})}}$

$$mass\ Na_2CO_3 = no.eq\ Na_2CO_3 \times eqw\ Na_2CO_3$$

$$= 0.5000\ \cancel{eq}Na_2CO_3 \times \frac{105.99\ g\ Na_2CO_3}{2\ \cancel{eq}\ Na_2CO_3} = 26.50\ g$$

Thus, dissolve 26.50 g in water and dilute to 5.000L

Example: A solution containing 25.0 mL of oxalic acid required 13.78 mL of 0.041 62 N $KMnO_4$ for titration, according to Reaction below. Find the normality and molarity of the oxalic acid.

$$5H_2C_2O_4 + 2MnO_4^- + 6H^+ \rightleftharpoons 2Mn^{2+} + 10CO_2 + 8H_2O$$

Solution:

$$N_1V_1 = N_2V_2$$

$$N_1(25.0mL) = (0.04162\,N)(13.78\,mL)$$

$$N_1 = 0.02294\,equiv/L$$

Because there are two equivalents per mole of oxalic acid in reaction above

$$M = \frac{N}{n} = \frac{0.02294}{2} = 0.01147\,M$$

Example: Exactly 50.00 mL of an HCl solution required 29.71 mL of 0.03926 N $Ba(OH)_2$ to give an end point with bromocresol green indicator. Calculate the normality of the HCl.

Note that the molar concentration of Ba $(OH)_2$ is one half its normality, that is,

$$M = N \times \frac{1}{2} = 0.03926 \frac{meq}{mL} \times \frac{1\ mmol}{2\ meq} = 0.01963\ M$$

Solution:

Because we are basing our calculations on the milliequivalent, we write

$$no.meq\ HCl = no.meq\ Ba(OH)_2$$

The number of milliequivalents of standard is obtained by substituting into equation below.

$$amount\ A = no.meq\ A = V(mL) \times N(\frac{meq}{mL})$$

$$amount\ Ba(OH)_2 = 29.71\ \cancel{mL\ Ba(OH)_2} \times 0.03926 \frac{meq\ Ba(OH)_2}{\cancel{mL\ Ba(OH)_2}}$$

To obtain the number of milliequivalents of HCl, we write

$$amount\ HCl = (29.71 \times 0.03926)\cancel{meqBa(OH)_2} \times \frac{1\ meq\ HCl}{\cancel{1\ meq\ Ba(OH)_2}}$$

❖ $$\text{amount of HCl} = 50.00\ \text{mL} \times N_{HCl} = (29.71 \times 0.03926 \times 1)\text{meq HCl}$$

$$N_{HCl} = \frac{(29.71 \times 0.03926 \times 1)meq\ HCl}{50.00\ mL\ HCl} = 0.02333\ N$$

Type of solutions

On the basis of amount of solute, solutions can be classified as

- ✓ **Concentrated Solutions**
- ✓ **Dilute solutions.**

Concentrated solutions contains large amount of solute whereas dilute solutions contains less amount of solute.

Classification of solutions according to amount of solute:

On the basis of dissolution of solute in solvent, solutions can be classified in three types; saturated, unsaturated and supersaturated solutions.

Saturated solutions: **is the solution in which solvent is not capable of dissolving any more solute at given temperature.**

Unsaturated solutions: **can be defined as the solution in which solvent is capable of dissolving any more solute at given temperature. In other words, solvent does not contain enough amount of solute in it and can dissolve more solute.**

Super saturated solutions: **solution contains large amount of solute at that temperature and as temperature will become reduce, the extra solute will crystallize quickly.**

Classification of solution based on solute particle size:

True solution: is a homogeneous solution in which the solute particles have diameters less than 10^{-7}cm. i.e., the solute particles are of molecular dimensions. The particles are invisible even under powerful microscopes.

For example, sodium chloride in water is a true solution. Most ionic compounds form true solutions in water. Organic compounds like sugar and urea also form true solutions in water.

Suspensions solution: is a heterogeneous mixture in which one or more components have a particle size greater than 10^{-5}cm. Very often these particles are visible to the naked eye.

For example, sand in water, sodium chloride in benzene, turmeric in water.

Colloids solution: is a solution in which the particle size ranges between 10^{-7} and

10^{-5} cm.

For example, milk, blood, honey, ink, gum, starch solution.

Chemical Equilibrium

Many reactions used in analytical chemistry never result in complete conversion of reactants to products. Instead, they proceed to a state of chemical equilibrium in which the ratio of concentrations of reactants and products is constant.

Equilibrium-Constant Expressions:

Consider a generalized equation for a chemical equilibrium

$$wW + xX \leftrightarrow yY + zZ$$

- **Capital letters represent the formulas of participating chemical reactants and products.**
- **Small letters whole numbers required to balance the equation.**
- **the equation says that 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 for this reaction is

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

Where the square-bracketed terms are:

1. Molar concentrations if they represent dissolved solutes.

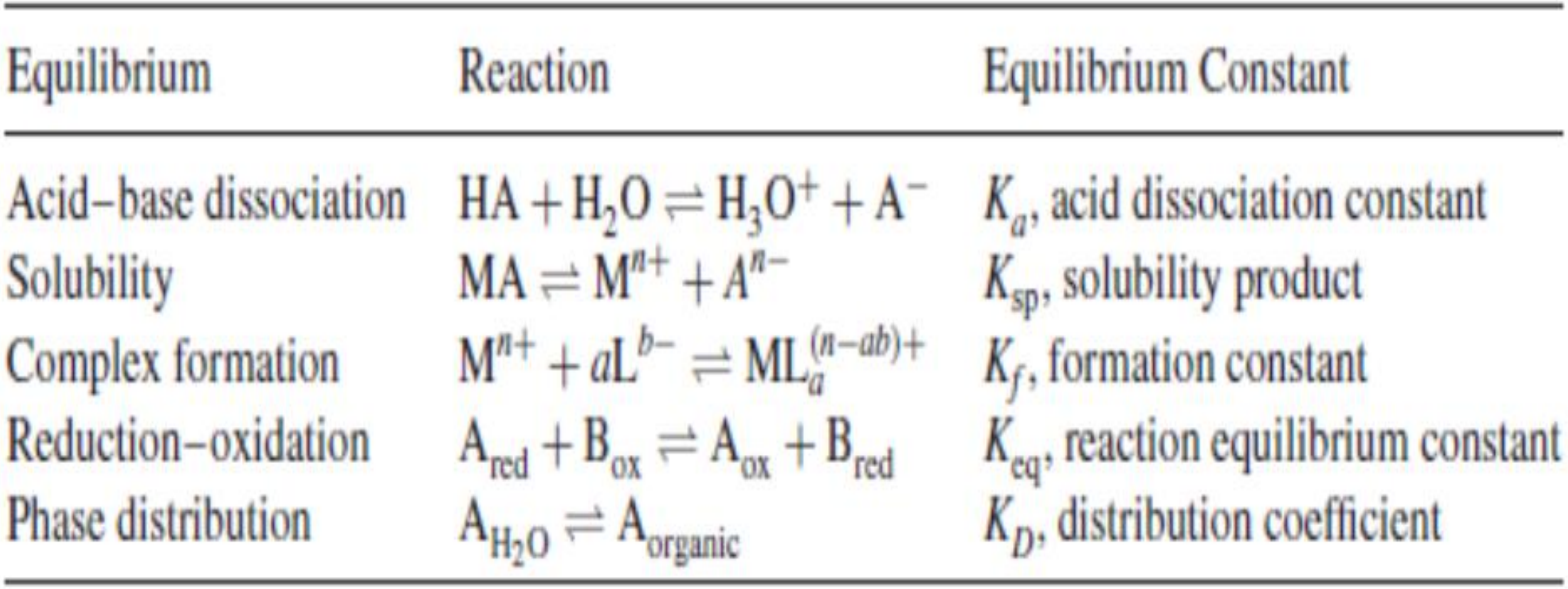
2. Partial pressures in atmospheres if they are gas-phase reactants or products. In such an instance, we will often replace the square bracketed term (say [Z] in Equation) with the symbol p_z, which stands for the partial pressure of the gas Z in atmospheres.

3. 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. The equilibrium-constant expression simplifies to

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

Types of Equilibrium Constants in Analytical Chemistry:

Table below summarizes the types of chemical equilibrium constants that are of importance in analytical chemistry.



Equilibrium	Reaction	Equilibrium Constant
Acid–base dissociation	$HA + H_2O \rightleftharpoons H_3O^+ + A^-$	K_a, acid dissociation constant
Solubility	$MA \rightleftharpoons M^{n+} + A^{n-}$	K_{sp}, solubility product
Complex formation	$M^{n+} + aL^{b-} \rightleftharpoons ML_a^{(n-ab)+}$	K_f, formation constant
Reduction–oxidation	$A_{red} + B_{ox} \rightleftharpoons A_{ox} + B_{red}$	K_{eq}, reaction equilibrium constant
Phase distribution	$A_{H_2O} \rightleftharpoons A_{organic}$	K_D, distribution coefficient

Example: The chemicals A and B react as follows to produce C and D:

$$A + B \leftrightarrow C + D \qquad\qquad K = \frac{[C][D]}{[A][B]}$$

The equilibrium constant K has a value of 0.30. Assume 0.20 mol of A and 0.50 mol of $B$are dissolved in 1.00 L and the reaction proceeds. Calculate the concentrations of reactants and products at equilibrium.

Solution:

Initial concentration of A is 0.20 M and B is 0.50 M, while C and D are initially 0 M.

After the reaction has reached equilibrium, the concentrations of A and B will be decreased and those of C and D will be increased. Let x represent the equilibrium concentration of C or the moles/liter of A and B reacting. Since we get one mole of D with each mole of C, the concentration of D will also be x. We may represent the initial concentration of A and B as the analytical concentrations, C_A and C_B. The equilibrium concentrations are [A] and [B]. The concentrations of A and B will each be diminished by x, that is, $[A] = C_A - x$ and $[B] = C_B - x$. So the equilibrium concentrations are

	[A]	[B]	[C]	[D]
Initial	*0.2*	*0.5*	*0*	*0*
Change (X=mmol/mL reacting)	*-x*	*-x*	*+x*	*+x*
Equilibrium	*0.20-x*	*0.50-x*	*x*	*x*

We can substitute these values in the equilibrium constant expression and solve for *x*:

$$K = \frac{[C][D]}{[A][B]} = 0.30 = \frac{(x)(x)}{(0.2 - x)(0.50 - x)}$$

$$x^2 = (0.1 - 0.2x - 0.50x + x^2)\ 0.30$$

$$x^2 = (0.1 - 0.7x + x^2)0.30$$

$$x^2 = 0.03 - 0.21\,x + 0.30x^2$$

$$0.7x^2 - 0.21x - 0.030 = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$= \frac{-0.21 \pm \sqrt{(0.21)^2 - 4(0.70)(-0.030)}}{2(0.7)}$$

$$= \frac{-0.21 \pm \sqrt{0.044 + 0.084}}{1.40} = 0.11M$$

$$[A] = 0.20 - x = 0.09M$$

$$[B] = 0.50 - x = 0.39$$

$$[C] = [D] = x = 0.11\ M$$

Example:

A and B react as follows:

$$A + 2B \rightleftharpoons 2C \qquad K = \frac{[C]^2}{[A][B]^2}$$

Assume 0.10 mol of A is reacted with 0.20 mol of B in a volume of 1000 mL; $K = 1.0 \times 10^{10}$. What are the equilibrium concentrations of A, B, and C?

Solution

We have stoichiometrically equal amounts of A and B, so both are virtually all reacted, with trace amounts remaining. Let x represent the equilibrium concentration of A. At equilibrium, we have

$$\begin{array}{ccccc} A & + & 2B & \rightleftharpoons & 2C \\ x & & 2x & & 0.20 - 2x \approx 0.20 \end{array}$$

For each mole of A that either reacts (or is produced), we produce (or remove) two moles of C, and consume (or produce) two moles of B. Substituting into the equilibrium constant expression,

$$\frac{(0.20)^2}{(x)(2x)^2} = 1.0 \times 10^{10}$$

$$\frac{0.040}{4x^3} = 1.0 \times 10^{10}$$

$$x = [A] = \sqrt[3]{\frac{4.0 \times 10^{-2}}{4.0 \times 10^{10}}} = \sqrt[3]{1.0 \times 10^{-12}} = 1.0 \times 10^{-4} M$$

$$B = 2x = 2.0 \times 10^{-4} M$$

Applying the Ion-Product Constant for Water

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

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

An equilibrium constant for this reaction:

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

The concentration of water in dilute aqueous solutions is enormous, when compared with the concentration of hydronium and hydroxide ions. $[H_2O]^2$in equation above can be taken as constant.

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

K_w, is the ion-product constant for water.

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

Solution:

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

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

We substitute this equality into Equation

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

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

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

At 25 °C and 100 °C K_w equal to 1.01×10^{-14} and 49×10^{-14} respectively

At 25 °C,

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

At 100°C,

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

Solubility (S)

Is the maximum amount of solute that will dissolve in a given amount of solvent at a specific temperature and pressure.

Solubility is often expressed as

- **Mass of solute per volume of solvent (g/L)**
- **mass of solute per mass of solvent (g/g)**
- **moles of solute per volume (mol/L) ,(molar solubility).**

Solubility of a substance depends on:

- **Temperature**
- **nature of solute or solvent**
- **pH**

Using 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.

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

The equilibrium constant can be written as:

$$K = \frac{[Ba^{2+}][IO_3^-]^2}{[Ba(IO_3)_2(s)]}$$

The concentration of a compound in its solid state is, however, constant. Therefore, the previous equation can be rewritten in the form

$$K[Ba(IO_3)_2(s)] = K_{sp} = [Ba^{2+}][IO_3^-]^2$$

K_{sp}, is the solubility-product constant or the solubility product.

Note:

When we say that a sparingly soluble salt is completely dissociated, we do not imply that all of the salt dissolves.

What we mean is that the very small amount that does go into solution dissociates completely.

The Solubility of a Precipitate in Pure Water

With the solubility-product expression, we can calculate the solubility of a sparingly soluble substance that ionizes completely in water.

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

Solution

The solubility-product constant for $Ba(IO_3)_2$ is 1.57×10^{-9}. The equilibrium between the solid and its ions in solution is described by the equation

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

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,

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

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 $Ba(IO_3)_2$,

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

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

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

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

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

Acids and Bases

Acid–Base Theories

Several acid–base theories have been proposed to explain or classify acidic and basic properties of substances.

1. Arrhenius theory.

According to the Arrhenius, an *acid* is any substance that ionizes (partially or completely) in water to give hydrogen ions (which associate with the solvent to give hydronium ions, H_3O^+):

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

A *base* ionizes in water to give hydroxide ions.

***Weak (partially ionized) bases* generally ionize as follows:**

$$B + H_2O \rightleftharpoons BH^+ + OH^-$$

While *strong bases* such as metal hydroxides (e.g., NaOH) dissociate as

$$M(OH)_n \rightarrow M^{n+} + nOH^-$$

This theory is obviously restricted to water as the solvent.

2. Theory of solvent system.

This theory recognizes the ionization of a solvent to give a cation and an anion; for example

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

or

$$2NH_3 \rightleftharpoons NH_4^+ + NH_2^-$$

An *acid* is defined as a solute that yields the characteristic cation of the solvent, while a *base* is a solute that yields the characteristic anion of the solvent.

3. Brønsted-Lowry theory.

This theory states that an ***acid*** is any substance that can donate a proton, and a ***base*** is any substance that can accept a proton. Thus, we can write a “half-reaction” a

$$acid = H^{+} + base$$

The acid and base of a half-reaction are called conjugate pairs.

Free protons do not exist in solution, and there must be a proton acceptor (base) before a proton donor (acid) will release its proton. That is, there must be a combination of two half-reactions.

However, it cannot exhibit its acidic behavior unless there is a base present to accept the proton.

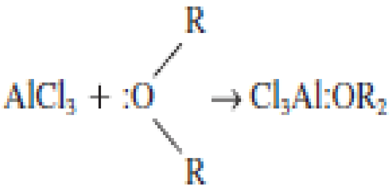
4. Lewis theory.

Lewis introduced the electronic theory of acids and bases.

In the Lewis theory, an *acid* is a substance that can accept an electron pair and a *base* is a substance that can donate an electron pair. Nonhydrogen-containing substances are included as acids.

Examples of acid–base reactions in the Lewis theory are as follows:

$$H^+ \text{ (solvated)} + :NH_3 \rightarrow H:NH_3^+$$

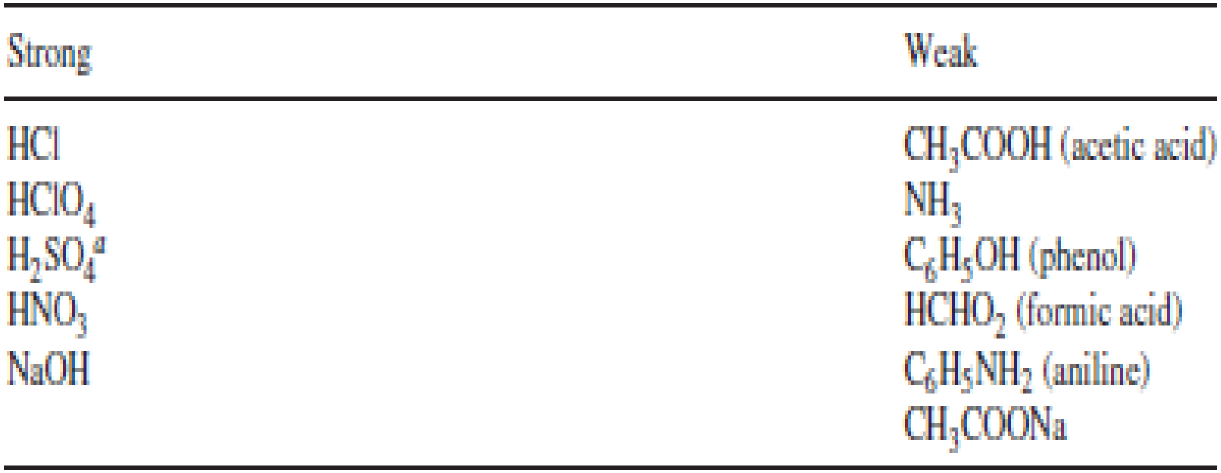


$$AlCl_3 + :OR_2 \rightarrow Cl_3Al:OR_2$$

In the second example, aluminum chloride is an acid and ether is a base.

Acid-Base Equilibria in Water

- **When an acid or base is dissolved in water, it will dissociate, or ionize, the amount of ionization being dependent on the strength of the acid or the base.**
- **A “strong” electrolyte is completely dissociated, while a “weak” electrolyte is partially dissociated.**
- **Table below lists some common electrolytes, some strong and some weak.**



Strong	Weak
HCl	CH_3COOH (acetic acid)
$HClO_4$	NH_3
H_2SO_4[a]	C_6H_5OH (phenol)
HNO_3	$HCHO_2$ (formic acid)
NaOH	$C_6H_5NH_2$ (aniline)
	CH_3COONa

- **When a weak acid or a weak base is dissolved in water, partial dissociation occurs. Thus, for below reactions, we can write after simplified**

$$HCl + H_2O \rightarrow H_3O^+ + Cl^-$$

$$HOAc + H_2O \rightleftharpoons H_3O^+ + OAc^-$$

$$HCl \rightarrow H^+ + Cl^-$$

$$HOAc \rightleftharpoons H^+ + OAc^-$$

$$K_a = \frac{[H^+][OAC^-]}{[HOAC]}$$

$$H_2O \rightleftharpoons H^+ + OH^-$$

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

K_a ***and*** K_w **are the molar equilibrium constants.**

K_w **is exactly 1.00 × 10^{-14} at 24°C and even at 25°C.**

$$[H^+][OH^-] = 1.0 \times 10^{-14}$$

In pure water, then, the concentrations of these two species are equal since there are no other sources of H^+or OH^-except H_2O dissociation:

$$[\mathrm{H^+}] = [\mathrm{OH^-}]$$

Therefore,

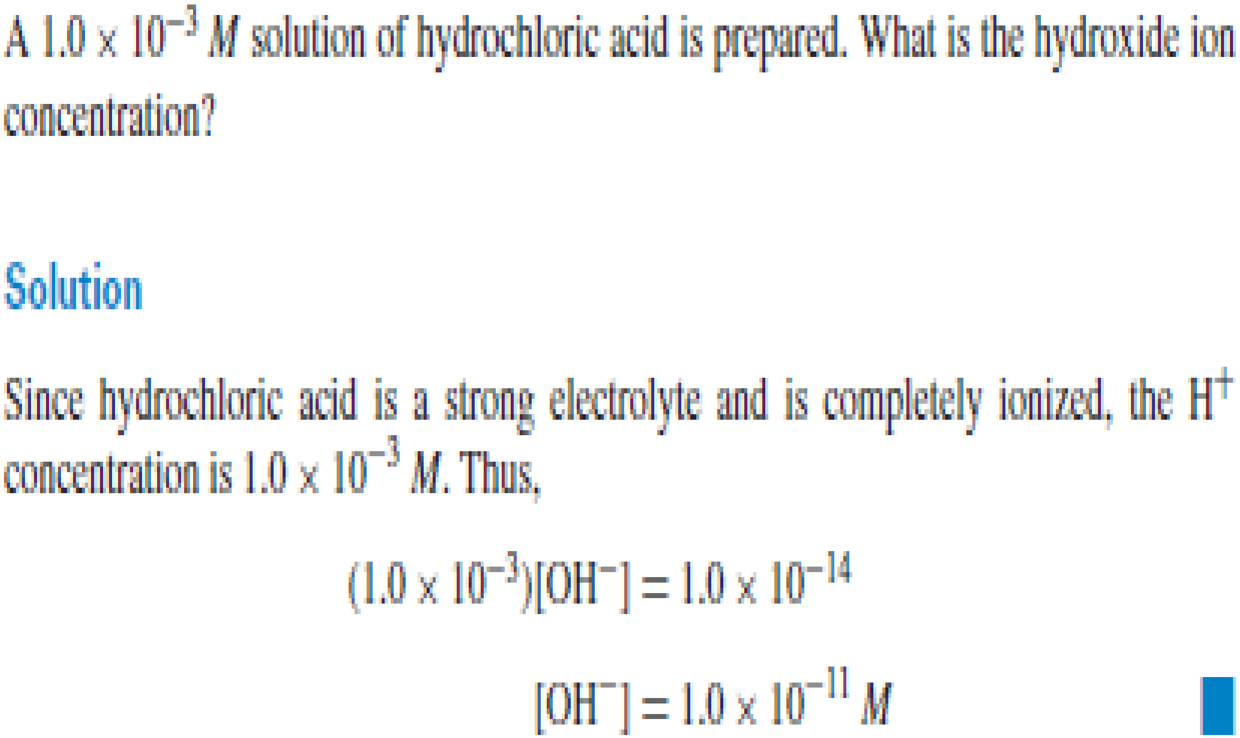
$$[\mathrm{H^+}][\mathrm{H^+}] = 1.0 \times 10^{-14}$$

$$[\mathrm{H^+}] = 1.0 \times 10^{-7}\ M \equiv [\mathrm{OH^-}]$$

If an acid is added to water, we can calculate the hydroxide ion concentration if we know the hydrogen ion concentration from the acid.

But when the hydrogen ion concentration from the acid is very small, 10^{-6}M or less, the contribution to $[H^+]$ from the ionization of water cannot be neglected.

Example:



A 1.0×10^{-3} M solution of hydrochloric acid is prepared. What is the hydroxide ion concentration?

Solution

Since hydrochloric acid is a strong electrolyte and is completely ionized, the H^+ concentration is 1.0×10^{-3} M. Thus,

$$(1.0 \times 10^{-3})[OH^-] = 1.0 \times 10^{-14}$$

$$[OH^-] = 1.0 \times 10^{-11}\ M$$ ■

The pH Scale:

The concentration of H^+ or OH^- in aqueous solution can vary over extremely wide ranges, from *1 M* or greater to *10^{-14} M* or less. To construct a plot of H^+ concentration against some variable would be very difficult if the concentration changed from, say, *10^{-1} M* to *10^{-13} M*.

It is more convenient to compress the acidity scale by placing it on a logarithm basis. The *pH* of a solution was defined by Sørenson as

$$pH = -\log[H^+]$$

The minus sign is used because most of the concentrations encountered are less than *1 M*, and so this designation gives a positive number.

A similar definition is made for the hydroxide ion concentration:

$$pOH = -\log[OH^-]$$

$$-\log K_w = -\log[H^+][OH^-] = -\log[H^+] - \log[OH^-]$$

$$\boxed{pK_w = pH + pOH}$$

At 25°C,

$$\boxed{14.00 = pH + pOH}$$

Example:

Calculate the pH of a 2.0×10^{-3} *M* solution of HCl.

Solution

HCl is completely ionized, so

$$[H^+] = 2.0 \times 10^{-3}\ M$$

$$pH = -\log(2.0 \times 10^{-3}) = 3 - \log\ 2.0 = 3 - 0.30 = 2.70$$

Example:

Calculate the pOH and the pH of a 5.0×10^{-2} *M* solution of NaOH at 25°C.

Solution

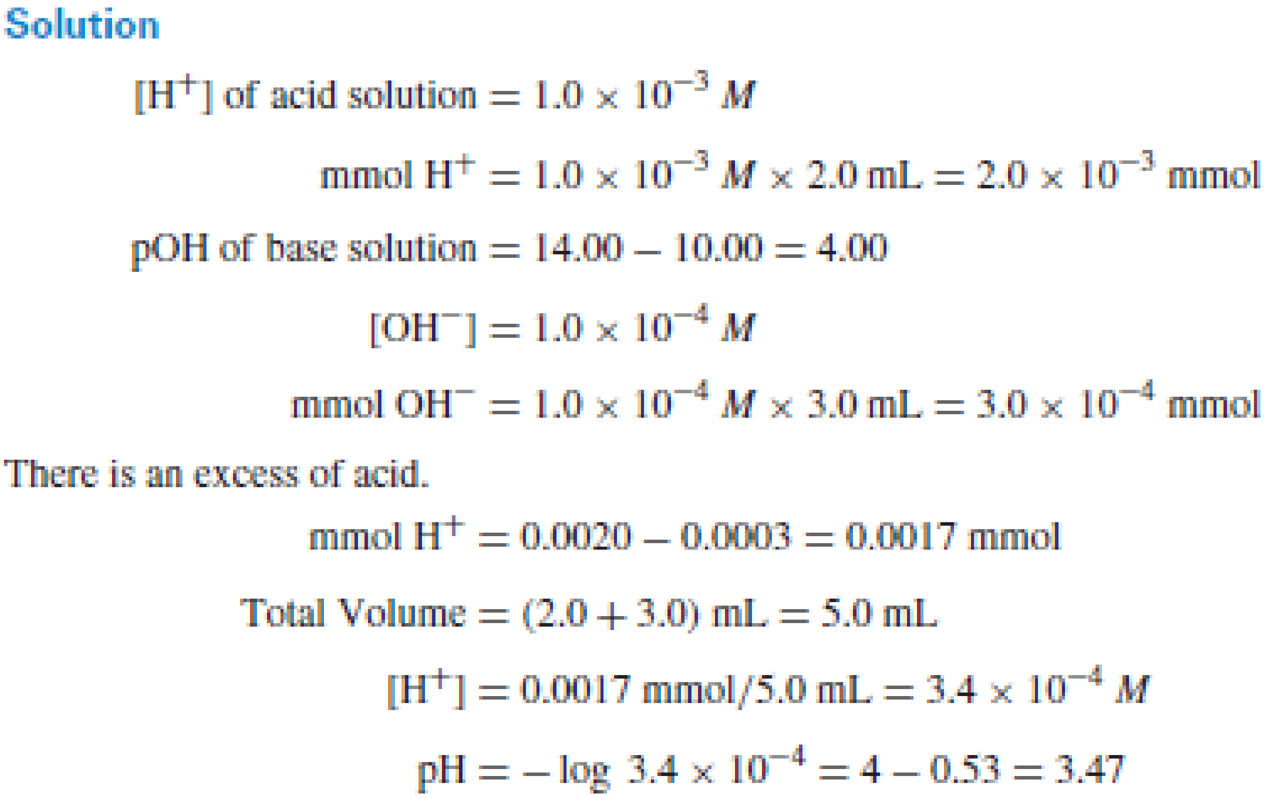
$$[OH^-] = 5.0 \times 10^{-2}\ M$$

$$pOH = -\log(5.0 \times 10^{-2}) = 2 - \log\ 5.0 = 2 - 0.70 = 1.30$$

$$pH + 1.30 = 14.00$$

$$pH = 12.70$$

Example : Calculate the pH of a solution prepared by mixing 2.0mL of a strong acid solution of pH 3.00 and 3.0mL of a strong base of pH 10.00.



Solution

$$[\mathrm{H^+}] \text{ of acid solution} = 1.0 \times 10^{-3}\ M$$

$$\text{mmol } \mathrm{H^+} = 1.0 \times 10^{-3}\ M \times 2.0\ \text{mL} = 2.0 \times 10^{-3}\ \text{mmol}$$

$$\text{pOH of base solution} = 14.00 - 10.00 = 4.00$$

$$[\mathrm{OH^-}] = 1.0 \times 10^{-4}\ M$$

$$\text{mmol } \mathrm{OH^-} = 1.0 \times 10^{-4}\ M \times 3.0\ \text{mL} = 3.0 \times 10^{-4}\ \text{mmol}$$

There is an excess of acid.

$$\text{mmol } \mathrm{H^+} = 0.0020 - 0.0003 = 0.0017\ \text{mmol}$$

$$\text{Total Volume} = (2.0 + 3.0)\ \text{mL} = 5.0\ \text{mL}$$

$$[\mathrm{H^+}] = 0.0017\ \text{mmol}/5.0\ \text{mL} = 3.4 \times 10^{-4}\ M$$

$$\text{pH} = -\log\ 3.4 \times 10^{-4} = 4 - 0.53 = 3.47$$

Weak Acids and Bases.

Strong acids and bases in which ionization is assumed to be complete. Since the concentration of H^+ or OH^- is determined readily from the concentration of the acid or base.

Weak acids (or bases) are only partially ionized.

Mineral (inorganic) acids and bases such as HCl, $HClO_4$,HNO_3, and NaOH are strong electrolytes that are totally ionized in water; most organic acids and bases, as found in clinical applications, are weak.

The ionization constant can be used to calculate the amount ionized and, from this, the pH. The acidity constant for acetic acid at 25°C is 1.75×10^{-5}:

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

When acetic acid ionizes, it dissociates to equal portions of H^+ and OAc^- by such an amount that the computation on the left side of Equation will always be equal to 1.75×10^{-5}:

$$HOAc \rightleftharpoons H^+ + OAc^-$$

If the original concentration of acetic acid is *C* and the concentration of ionized acetic acid species (H^+ and OAc^-) is *x*, then the final concentration for each species at equilibrium is given by

$$\begin{array}{cccc} HOAc & \rightleftharpoons H^+ & + & OAc^- \\ (C-x) & x & & x \end{array}$$

Example:

Calculate the pH and pOH of a 1.00×10^{-3} *M* solution of acetic acid.

Solution

$$\text{HOAc} \rightleftharpoons \text{H}^+ + \text{OAc}^-$$

The concentrations of the various species in the form of an ICE table are as follows:

	[HOAc]	[H$^+$]	[OAc$^-$]
Initial	1.00×10^{-3}	0	0
Change (x = mmol/mL HOAc ionized)	$-x$	$+x$	$+x$
Equilibrium	$1.00 \times 10^{-3} - x$	x	x

$$\frac{(x)(x)}{1.00 \times 10^{-3} - x} = 1.75 \times 10^{-5}$$

If $C_{HA} > 100K_a$, x can be neglected compared to C_{HA}.

$$\frac{x^2}{1.00 \times 10^{-3}} = 1.75 \times 10^{-5}$$

$$x = 1.32 \times 10^{-4}\ M \equiv [\text{H}^+]$$

Therefore,

$$\text{pH} = -\log(1.32 \times 10^{-4}) = 4 - \log 1.32 = 4 - 0.12 = 3.88$$

$$\text{pOH} = 14.00 - 3.88 = 10.12$$

Using 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

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

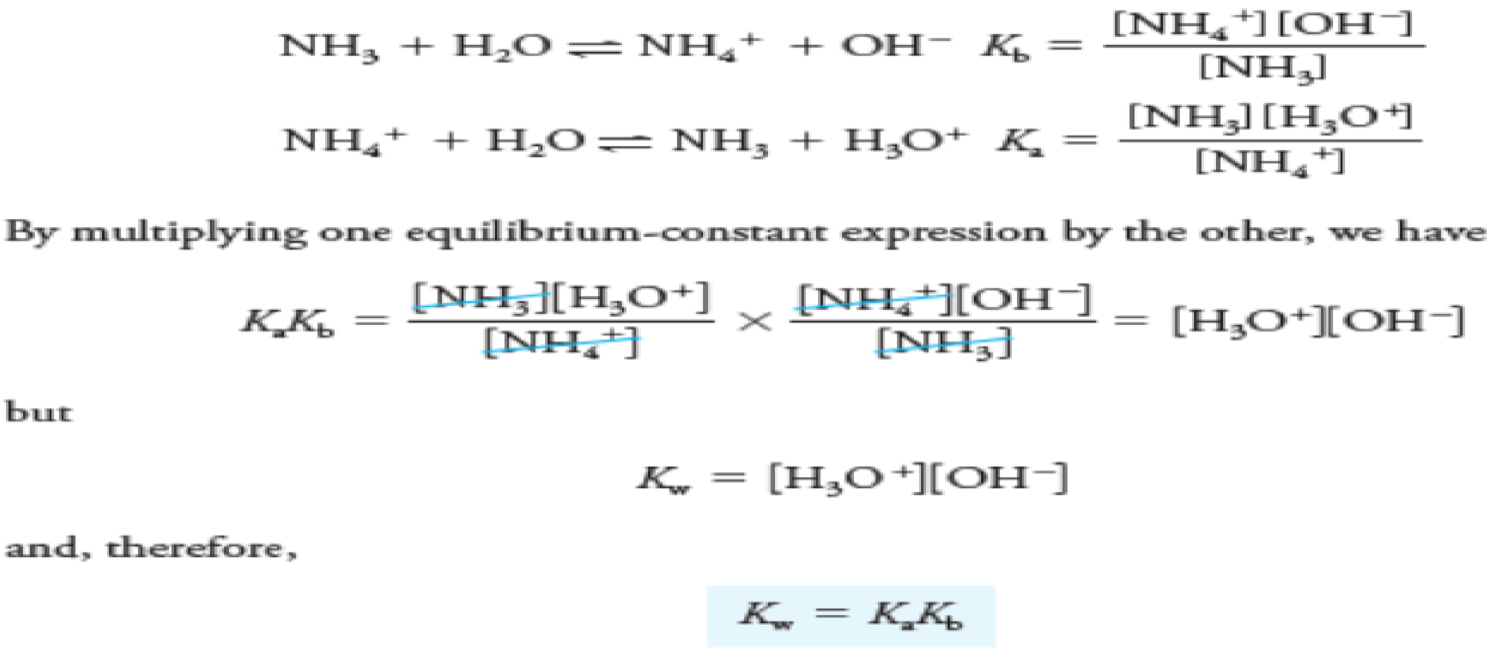
Where K_a is the acid *dissociation constant for nitrous acid*. In an analogous way, the base *dissociation constant for ammonia* is

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

Notice that $[H_2O]$ does not appear in the denominator of either equation because the concentration of water is so large relative to the concentration of the weak acid or base.

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:



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

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

By multiplying one equilibrium-constant expression by the other, we have

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

but

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

and, therefore,

$$\boxed{K_w = K_aK_b}$$

This relationship is general for all conjugate acid/base pairs. Many compilations of equilibrium-constant data list only acid dissociation constants because it is so easy to calculate dissociation constants for bases by using above equation.

For example,

The acid dissociation constant for the conjugate acid, ammonium ion equal 5.70 × 10^{-10}. That is,

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

and we can write

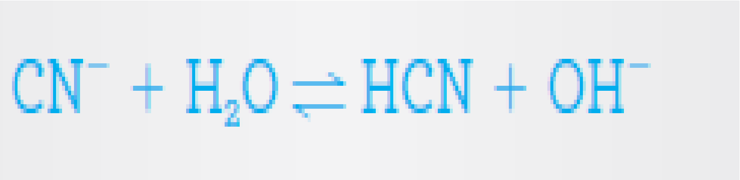
$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{K_w}{K_a} = \frac{1.00 \times 10^{-14}}{5.00 \times 10^{-10}} = 1.75 \times 10^{-5}$$

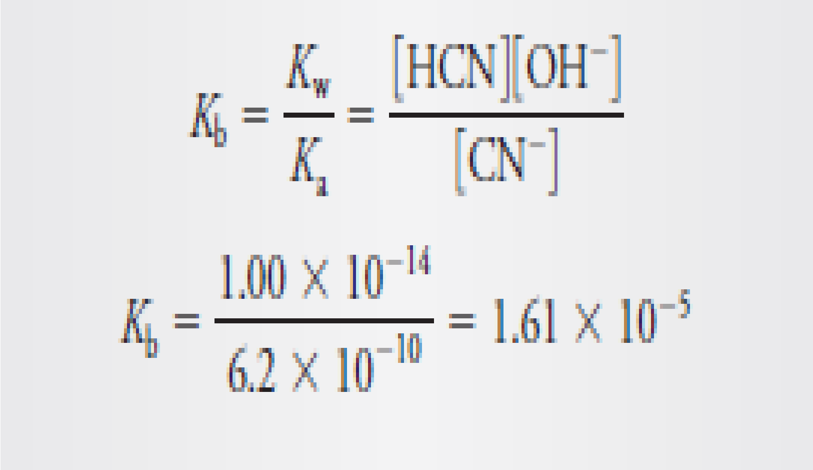
Example:

What is K_b for the equilibrium, if K_a value of 6.2×10^{-10} for HCN.

Solution:



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



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

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

Hydronium Ion Concentration of Solutions of Weak Acids

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

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

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

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

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

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. Therefore,

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

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

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

which rearranges to

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

When $[A^-]$ and $[HA]$ are replaced by their equivalent terms

The equilibrium-constant expression becomes

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

which rearranges to

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

The positive solution to this quadratic equation is

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

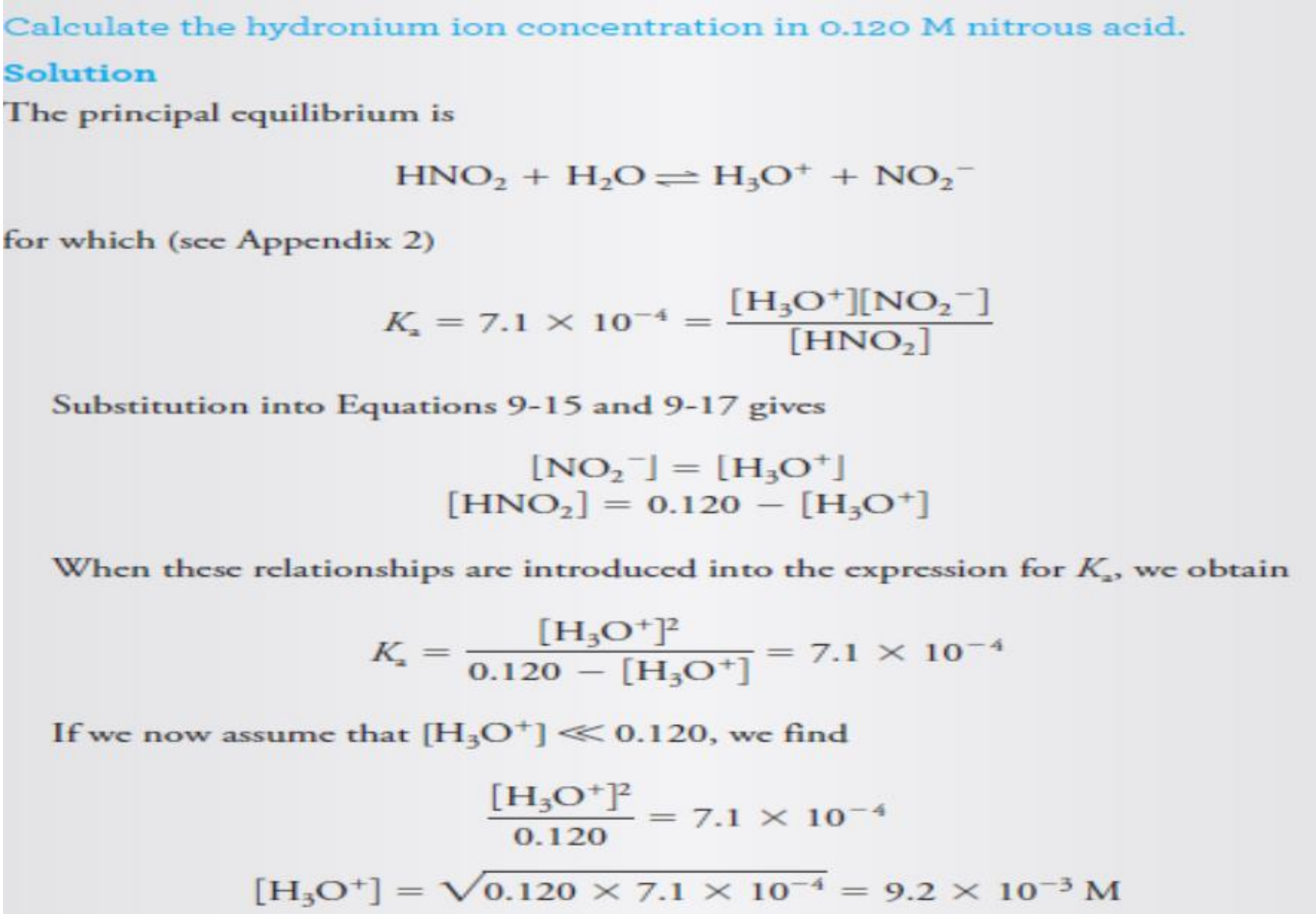
$$\text{if } [H_3O^+] \ll c_{HA},\ c_{HA} - [H_3O^+] \approx c_{HA},$$

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

and

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

Example:



Calculate the hydronium ion concentration in 0.120 M nitrous acid.

Solution

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

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

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

Hydronium Ion Concentration of Solutions of Weak Bases

We can adapt the techniques of the previous sections to calculate the hydroxide or hydronium ion concentration in solutions of weak bases.

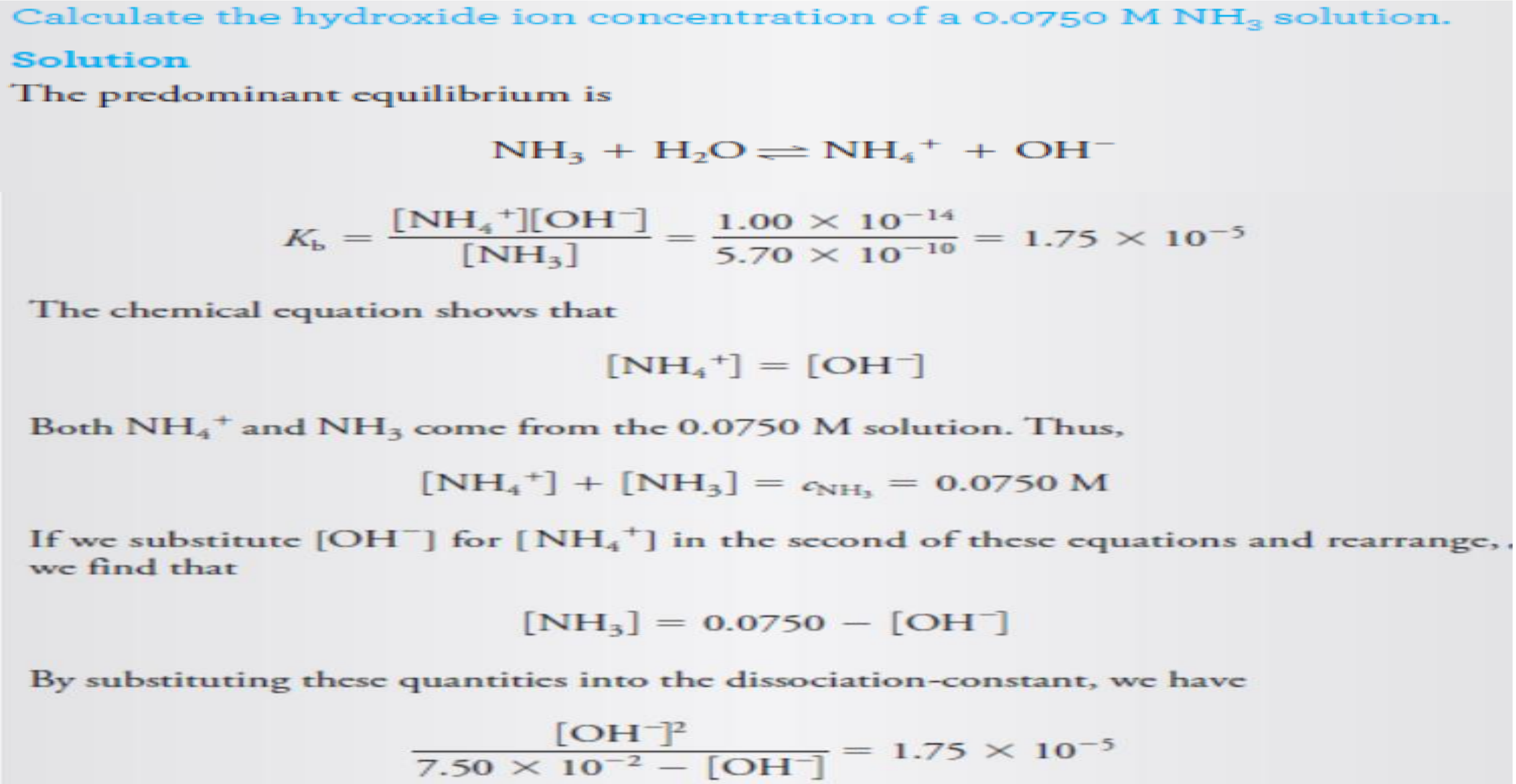
Aqueous ammonia is basic as a result of the reaction

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

We write the equilibrium constant for the reaction as

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

Example:



Calculate the hydroxide ion concentration of a 0.0750 M NH_3 solution.

Solution

The predominant equilibrium is

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

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

The chemical equation shows that

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

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

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

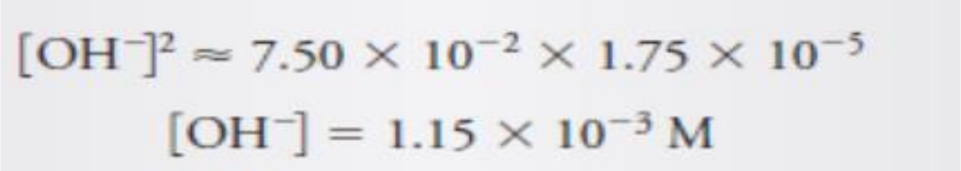
If we substitute $[OH^-]$ for $[NH_4^+]$ in the second of these equations and rearrange, we find that

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

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

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

This is analogous to weak acids. If we assume that $[OH^-] << 7.50 \times 10^{-2}$, this equation simplifies to



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

$$[OH^-] = 1.15 \times 10^{-3} \text{ M}$$

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, such as acetic acid/sodium acetate or ammonium chloride/ammonia.

- Scientists and technologists in most areas of science and in many industries use buffers to maintain the pH of solutions at a relatively constant and predetermined level.

Calculating 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 positions of two competitive equilibria:**

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

$$A^- + H_2O \rightleftharpoons OH^- + HA \quad K_b = \frac{[OH^-][HA]}{[A^-]} = \frac{K_w}{K_a}$$

- **If the first equilibrium lies farther to the right than the second, the solution is *acidic*. If the second equilibrium is more favorable, the solution is *basic*.**

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

- To find the pH of a solution containing both an acid, HA, and its conjugate base, NaA, we need to express the equilibrium concentrations of HA and NaA in terms of their analytical concentrations, c_{HA} and c_{NaA}.

- If we look closely at the two equilibria, we find that,
  - The first reaction decreases the concentration of HA by an amount equal to $[H_3O^+]$,
  - The second increases the HA concentration by an amount equal to $[OH^-]$.

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

$$A^- + H_2O \rightleftharpoons OH^- + HA \quad K_b = \frac{[OH^-][HA]}{[A^-]} = \frac{K_w}{K_a}$$

Thus, the species concentration of HA is related to its analytical concentration by the equation.

$$[HA] = c_{HA} - [H_3O^+] + [OH^-] \qquad \text{............(*)}$$

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 $[OH^-]$. Therefore, the equilibrium concentration is given by a second equation

$$[A^-] = c_{NaA} + [H_3O^+] - [OH^-] \qquad \text{..............(**)}$$

Assumption

1. **Because of the inverse relationship between $[H_3O^+]$ and $[OH^-]$, it is always possible to eliminate one or the other from above Equations.**
2. **The difference in concentration between $[H_3O^+]$ and $[OH^-]$ is usually so small relative to the molar concentrations of acid and conjugate base.**

That above Equations simplify to:

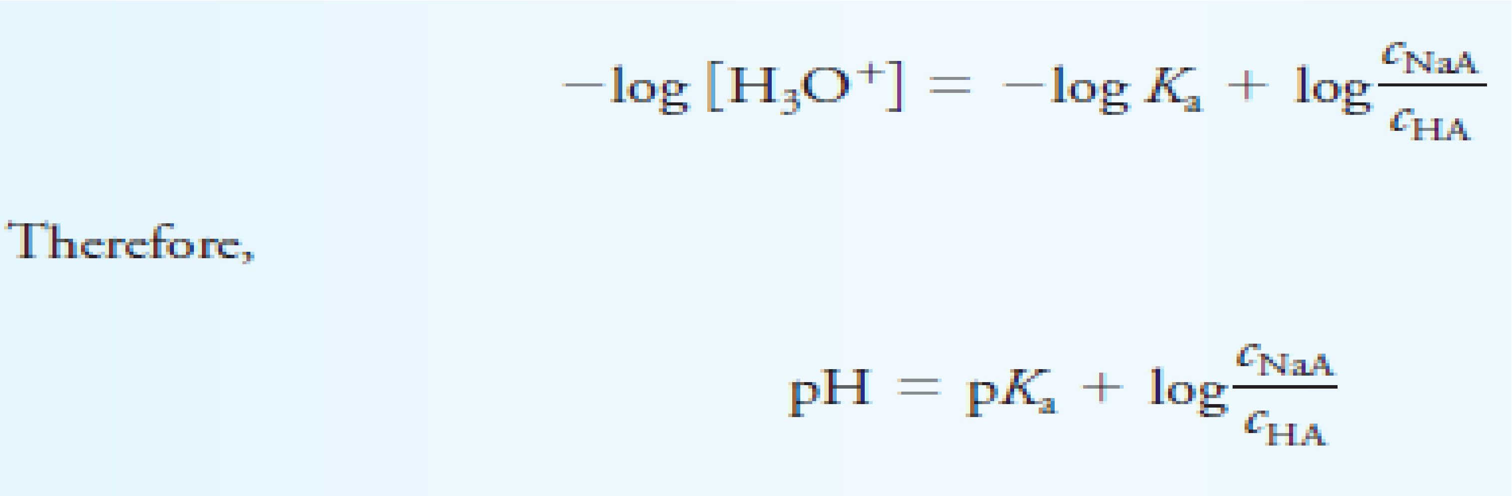
$$[HA] \approx c_{HA}$$
$$[A^-] \approx c_{NaA} \qquad \text{...............(***)}$$

If we then substitute Equations into the dissociation-constant expression and rearrange the result, we have

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

The Henderson-Hasselbalch Equation.

The Henderson-Hasselbalch equation, which is used to calculate the pH of buffer solutions, is frequently encountered in the biological literature and biochemical texts. It is obtained by expressing each term in the form of its negative logarithm and inverting the concentration ratio to keep all signs positive:



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

Therefore,

$$\mathrm{pH} = \mathrm{p}K_a + \log \frac{c_{\mathrm{NaA}}}{c_{\mathrm{HA}}}$$

Example: 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_w of formic acid and the K_b of formate ion.

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

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

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 H_3O^+ concentration. We can thus write

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

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

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

By substituting these expressions into K_a Equation and rearranging, we have

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

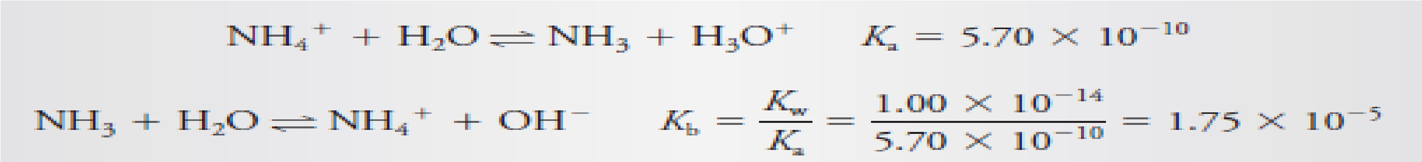
Notice that our assumptions that $[H_3O^+] << c_{HCOOH}$ and that $[H_3O^+] << c_{HCOO-}$ are valid. Therefore,

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

Example: Calculate the pH of a solution that is 0.200 M in NH_3 and0.300 M in NH_4Cl.

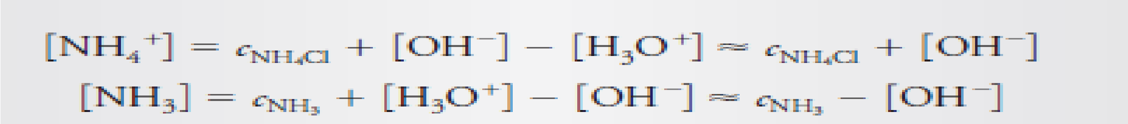
Solution:

K_a for NH_4^+ is 5.70 × 10^{-10}. The equilibria we must consider are



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

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

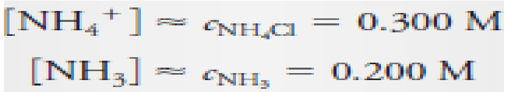


$$[NH_4^+] = c_{NH_4Cl} + [OH^-] - [H_3O^+] \approx c_{NH_4Cl} + [OH^-]$$

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

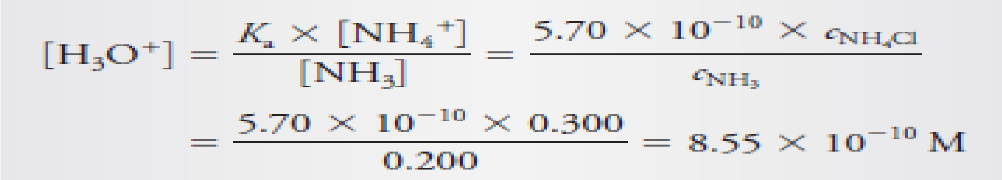
Because K_b is several orders of magnitude larger than K_a, we have assumed that the solution is basic and that $[OH^-]$ is much larger than $[H_3O^+]$. Thus, we have neglected the concentration of H_3O^+ in these approximations.

We also assume that $[OH^-]$ is much smaller than c_{NH4Cl} and c_{NH3} so that



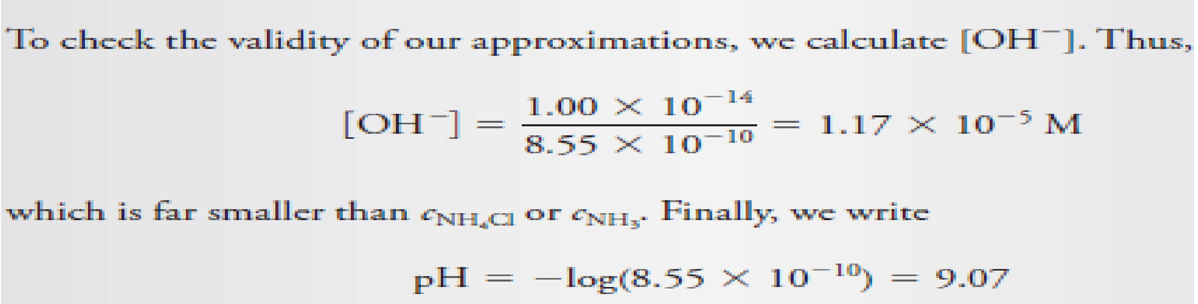
$$[NH_4^+] \approx c_{NH_4Cl} = 0.300\ M$$

$$[NH_3] \approx c_{NH_3} = 0.200\ M$$



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

$$= \frac{5.70 \times 10^{-10} \times 0.300}{0.200} = 8.55 \times 10^{-10}\ M$$



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

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

which is far smaller than c_{NH_4Cl} or c_{NH_3}. Finally, we write

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

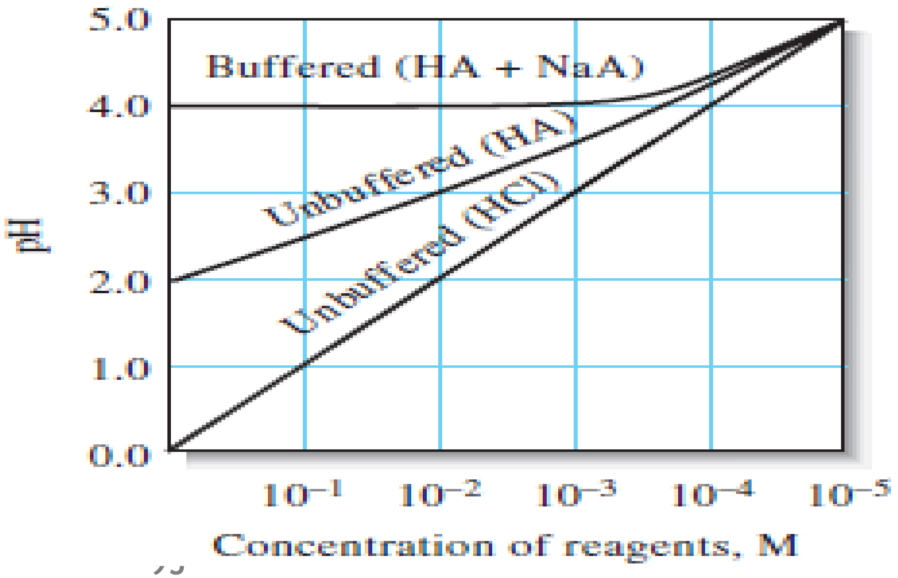
Properties of Buffer Solutions

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 (***)become invalid. Figure below 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 clearly shown.

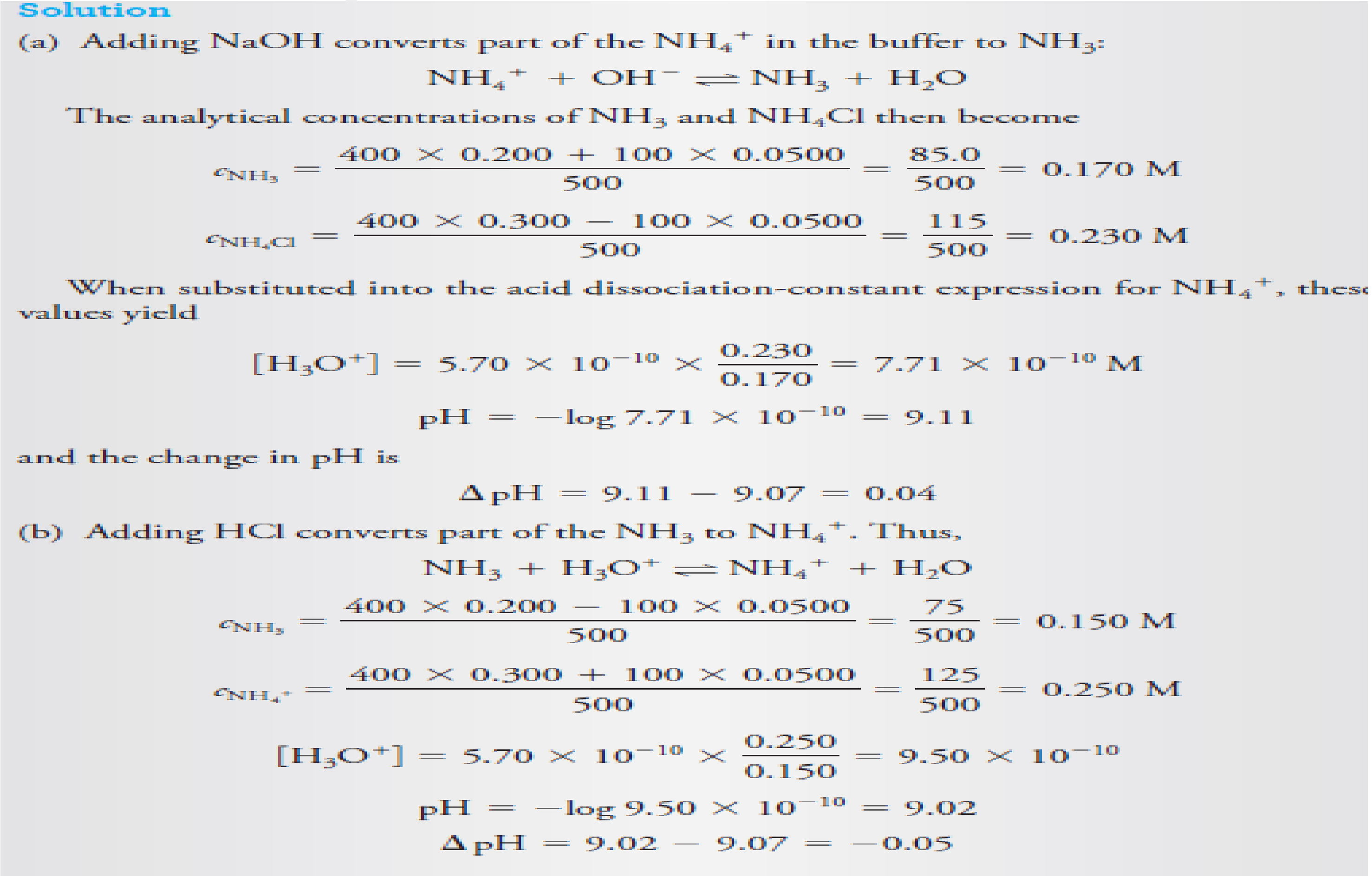
Figure Show the effect of dilution of the pH of buffered and unbuffered solutions. The dissociation constant for HA is 1.00×10^{-4}. Initial solute concentrations are 1.00 M.



The Effect of Added Acids and Bases

Example below illustrates a second property of buffer solutions, their resistance to pH change after addition of small amounts of strong acids or bases.

Example: 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 above Example



Solution

(a) Adding 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

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

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

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) Adding HCl converts part of the NH_3 to NH_4^+. Thus,

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

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

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

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

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

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

Note

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.

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*. For example, if we let c_T be the sum of the analytical concentrations of acetic acid and sodium acetate in a typical buffer solution, we may write

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

α_0, the fraction of the total concentration of acid that is un dissociated, define as

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

and α_1, the fraction dissociated, as

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

Alpha values are unit less ratios whose sum must equal unity. That is,

$$\alpha_0 + \alpha_1 = 1$$

Alpha values depend only on $[H_3O^+]$ and K_a and are independent of c_T . To derive expressions for α_0, we rearrange the dissociation-constant expression to

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

The total concentration of acetic acid, c_T, is in the form of either HOAc or OAc^-. Thus,

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

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

When rearranged, this equation becomes

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

But according to Equation below,

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

So,

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

.... (****)

To derive a similar expression for α_1, we rearrange the dissociation-constant expression to

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

substitute into Equation (****)

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

Rearranging this expression gives α_1.

$$\boxed{\alpha_1 = \frac{[\mathrm{OAc^-}]}{c_T} = \frac{K_a}{[\mathrm{H_3O^+}] + K_a}} \qquad \text{.............}(*****)$$

Figure below illustrates how α_0 and α_1 vary as a function of pH. The data for these plots were calculated from Equations (****) and (*****).

Figure below illustrates how α_0 and α_1 vary as a function of pH. The data for these plots were calculated from Equations (****) and (*****).

You can see that the two curves cross at the point where pH = pK_{HOAc} = 4.74. At this point, the concentrations of acetic acid and acetate ion are equal, and the fractions of the total analytical concentration of acid both equal one half.

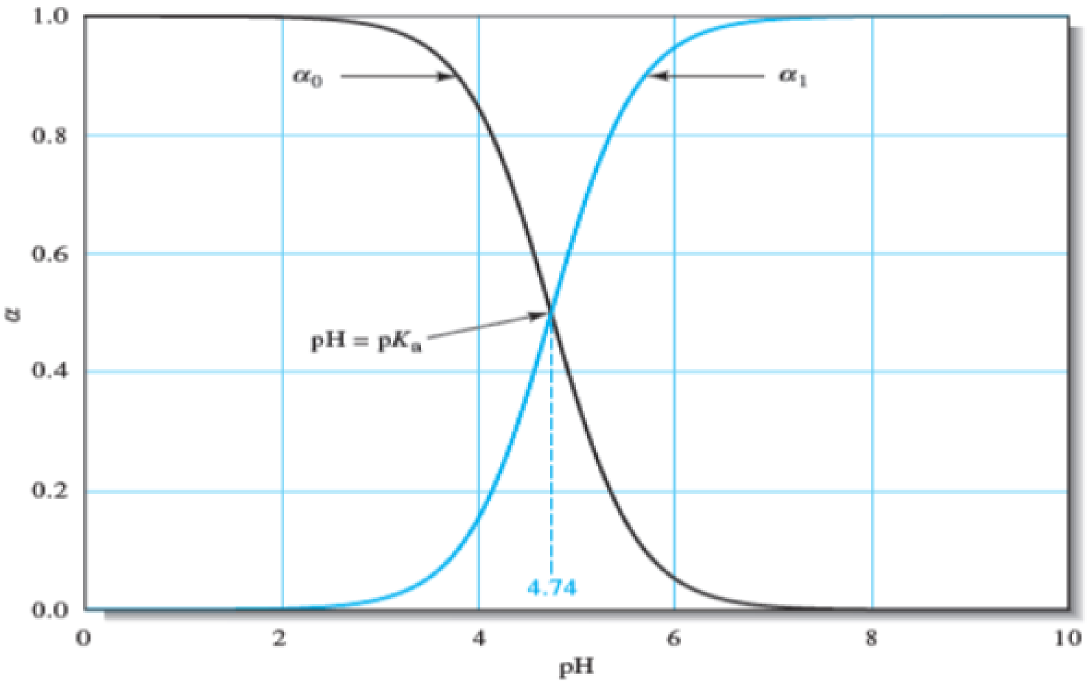


Figure shows the Variation in α with pH. Note that most of the transition between α_0 and α_1 occurs within ±1 pH unit of the crossover point of the two curves. The crossover point where $\alpha_0 = \alpha_1 = 0.5$ occurs when pH = pK_{HOAc} = 4.74.

Buffer Capacity

The *buffer capacity, β,* 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, buffer capacity is given by

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

Where:

dc_b is the number of moles per liter of strong base added to the buffer.

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.***
- **Buffer capacity depends not only on the total concentration of the two buffer components but also on their concentration ratio. As Figure below shows buffer capacity decreases fairly rapidly as the concentration ratio of acid to conjugate base becomes larger or smaller than 1 (the logarithm of the ratio increases above or decreases below zero). For this reason, the pK_a of the acid chosen for a given application should lie within ±1 unit of the desired pH for the buffer to have a reasonable capacity.**

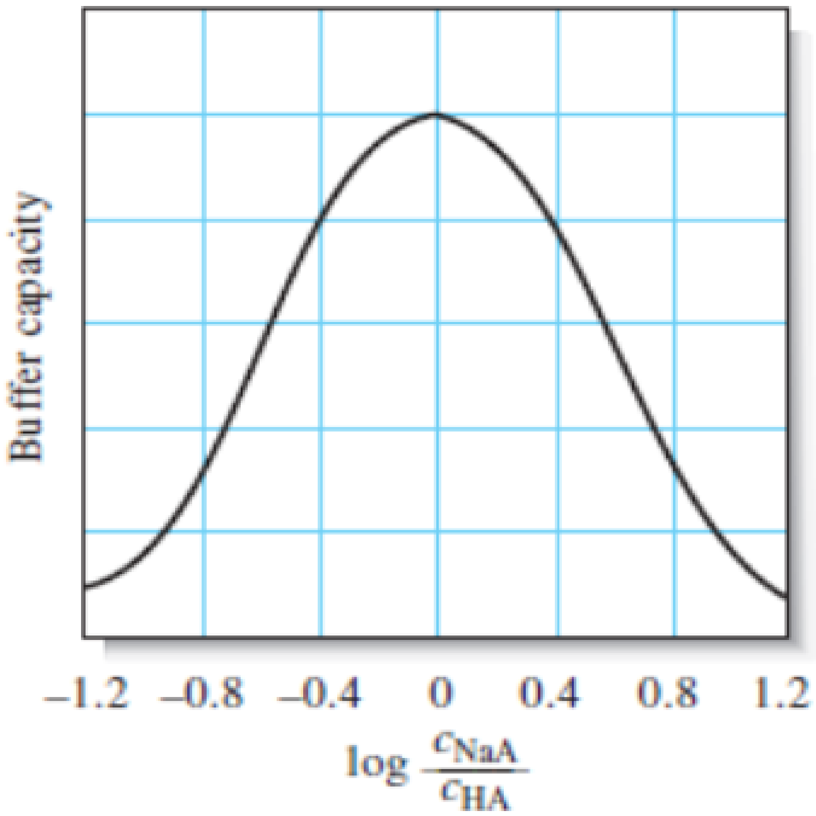


Figure shows buffer capacity as a function of the logarithm of the ratio c_{NaA}/c_{HA}. The maximum buffer capacity occurs when the concentration of acid and conjugate base are equal, that is, when $\alpha_0 = \alpha_1 = 0.5$.

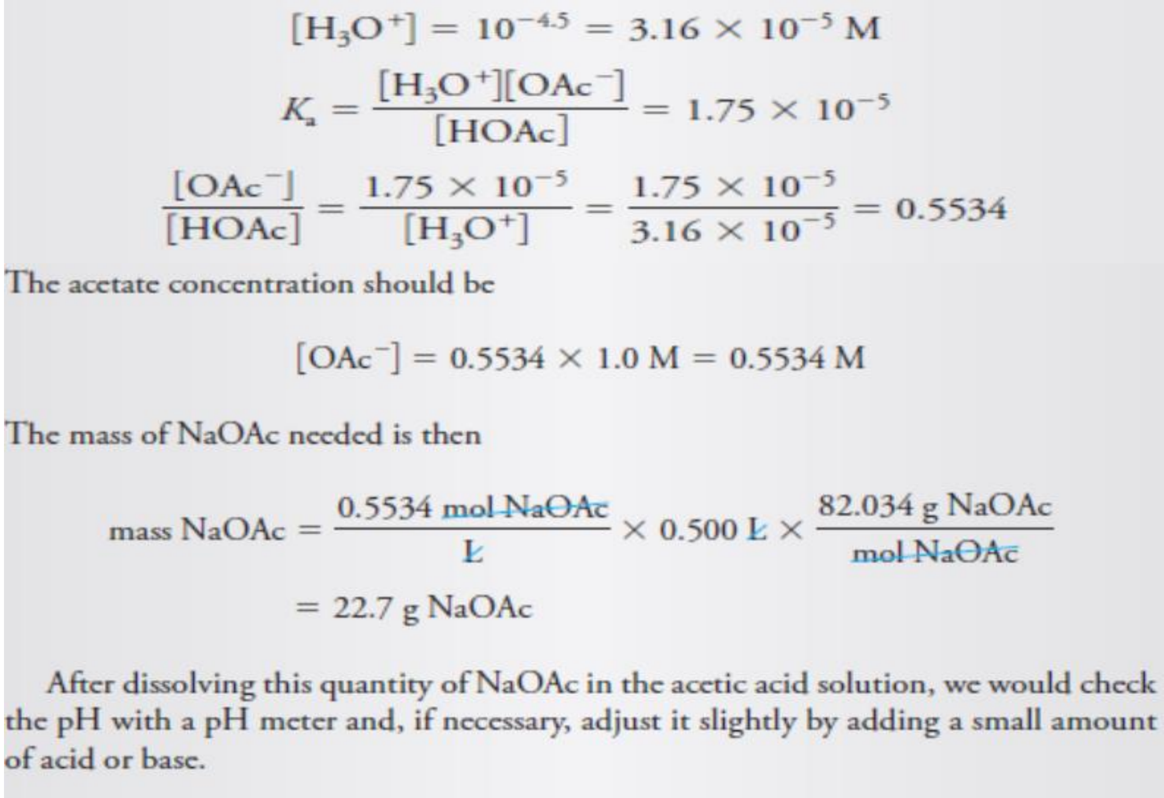
Preparation of Buffers.

A buffer solution of any desired pH can be prepared by combining calculated quantities of a suitable conjugate acid/base pair.

Example: 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 H_3O^+ concentration should be



$$[H_3O^+] = 10^{-4.5} = 3.16 \times 10^{-5}\ M$$

$$K_a = \frac{[H_3O^+][OAc^-]}{[HOAc]} = 1.75 \times 10^{-5}$$

$$\frac{[OAc^-]}{[HOAc]} = \frac{1.75 \times 10^{-5}}{[H_3O^+]} = \frac{1.75 \times 10^{-5}}{3.16 \times 10^{-5}} = 0.5534$$

The acetate concentration should be

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

The mass of NaOAc needed is then

$$\text{mass NaOAc} = \frac{0.5534\ \cancel{\text{mol NaOAc}}}{\cancel{L}} \times 0.500\ \cancel{L} \times \frac{82.034\ \text{g NaOAc}}{\cancel{\text{mol NaOAc}}}$$

$$= 22.7\ \text{g NaOAc}$$

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.

Gravimetric Methods of Analysis

Gravimetric methods: are quantitative methods that are based on determining the mass of a pure compound to which the analyte is chemically related.

❖ **Yields highly accurate and precise data.**

1- Precipitation gravimetry, the analyte is separated from a solution of the sample as a precipitate and is converted to a compound of known composition that can be weighed.

2- Volatilization gravimetry, the analyte is separated from other constituents of a sample by converting it to a gas of known chemical composition. The mass of the gas then serves as a measure of the analyte concentration.

3- Electrogravimetry, the analyte is separated by deposition on an electrode by an electrical current. The mass of this product then provides a measure of the analyte concentration.

4- gravimetric titrimetry, the mass of a reagent of known concentration required to react completely with the analyte provides the information needed to determine the analyte concentration.

1- Precipitation gravimetry.

a) Preparation of the analyte (sample solution) .

b) Converted to sparingly soluble precipitate (Precipitation process).

c) Filtration

d) Washing (to be free from an impurities) .

e) Drying and/or Igniting (converting to a product of known composition).

f) Weighing.

g) Calculation.

Example:

Precipitation method for determining calcium in water.

In this technique.

1. **An excess of oxalic acid, $H_2C_2O_4$, is added to an aqueous solution of the sample.**
2. **Ammonia is then added, which neutralizes the acid and causes essentially all of the calcium in the sample to precipitate as calcium oxalate.**

The reactions are

$$2NH_3 + H_2C_2O_4 \rightarrow 2NH_4^+ + C_2O_4^{2-}$$

$$Ca^{2+}(aq) + C_2O_4^{2-}(aq) \rightarrow CaC_2O_4(s)$$

3. The CaC_2O_4 precipitate is filtered using a weighed filtering crucible, then dried and ignited. This process converts the precipitate entirely to calcium oxide.

The reaction is

$$CaC_2O_4(s) \xrightarrow{\Delta} CaO(s) + CO(g) + CO_2(g)$$

4. After cooling, the crucible and precipitate are weighed, and the mass of calcium oxide is determined by subtracting the known mass of the crucible.

Properties of Precipitates and Precipitating Reagents

- ***Specifically* (rare):** **react only with a single chemical species.**

An example : Dimethylglyoxime, which, is a specific reagent that precipitates only Ni^{2+} from alkaline solutions.

$$\text{Dimethylglyoxime} \longrightarrow Ni^{2+}$$

- ***Selectively* (common):** **react with a limited number of species.**

An example of a selective reagent is $AgNO_3$. The only common ions that it precipitates from acidic solution are $Cl^-, Br^-, I^- \& SCN^-$.

$$AgNO_3 \longrightarrow Cl^-, Br^-, I^- \& SCN^-$$

Ideal precipitating reagent would react with the analyte to give a product that is:

1. **easily filtered and washed free of contaminants;**
2. **of sufficiently low solubility that no significant loss of the analyte occurs during filtration and washing;**
3. **unreactive with constituents of the atmosphere;**
4. **known chemical composition after it is dried or, if necessary, ignited.**

Particle Size and Filterability of Precipitates

Factors That Determine the Particle Size of Precipitates

The particle size of solids formed by precipitation varies enormously.

- ❖ **At one extreme are colloidal suspensions,**
- ✓ **tiny particles are invisible to the naked eye ($10^{-7}$to 10^{-4} cm in diameter).**
- ✓ **no tendency to settle from solution and are difficult to filter.**
- ✓ **At the other extreme are particles with dimensions on the order of tenths of a millimeter or greater.**
- ✓ **The temporary dispersion of such particles in the liquid phase is called a crystalline suspension.**
- ✓ **The particles of a crystalline suspension tend to settle spontaneously and are easily filtered.**

❖ **However, the particle size of a precipitate is influenced by**

- **Precipitate solubility.**
- **Temperature.**
- **Reactant concentrations.**
- **Rate at which reactants are mixed.**

The net effect of these variables can be accounted for, at least qualitatively, by assuming that the particle size is related to a single property of the system called relative supersaturation or Von Weimarn ratio, where

$$\text{Relative supersaturation (RS)} = \frac{Q-S}{S}$$

Q = concentration of the solute at any instant.
S= Equilibrium solubility.

$$\text{Particle size} \propto \frac{1}{RS}$$

When RS is large, the precipitate tends to be colloidal.

When RS is small, the precipitate tends to be crystalline solid.

Mechanism of Precipitate Formation

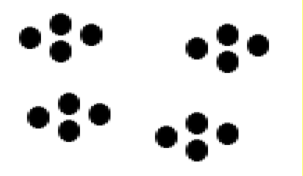
- When a solution of precipitating agent is added to a test solution to form a precipitate, such as in the addition of $AgNO_3$ to a chloride solution to precipitate $AgCl$.

The actual precipitation occurs in a series of steps:

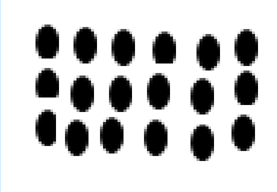
1.supersaturated solution → 2. Nucleation → 3. Particle Growth

Is an unstable solution that contains a higher solute concentration than a saturated solution. As excess solute precipitates with time, supersaturation decreases to zero.

Is a process in which a minimum number of atoms, ions, or molecules join together to give a stable solid.



Nuclei join together to form a crystal of a certain geometric shape.



Experimental Control of Particle Size

1. dilute sample solutions and dilute reagents (minimize Q↓)
2. slow addition of precipitating agent with good stirring (minimize Q↓)
3. in hot solution (S↑)
4. pH control, acidity solution (S↑)

Example : precipitation of calcium oxalate

a. in mildly acidic, calcium oxalate → large, easily filtered crystals (moderately soluble)

b. adding aqueous ammonia → pH↑ → completed precipitate.

- Precipitates with very low solubilities, such as many sulfides and hydrous oxides, generally form a colloids.

Colloidal Precipitates

- ✓ **Individual colloidal particles are so small that they are not retained by ordinary filters.**

- ✓ **Coagulation (or agglomeration) of colloids: converting a colloid suspension into a filterable solid , by heating, by stirring, and by adding an electrolyte to the medium.**

- ✓ **Colloidal suspensions are stable because all of the particles of the colloid are either positively or negatively charged and thus repel one another.**

- ✓ **The charge results from cations or anions that are bound to the surface of the particles.**

- ✓ **colloidal particles are charged by placing them between charged plates where some of the particles migrate toward one electrode while others move toward the electrode of the opposite charge.**

- ✓ **The process by which ions are retained on the surface of a solid is known as adsorption.**

Adsorption : **is a process in which a substance (gas, liquid, or solid) is held on the surface of a solid. In contrast, absorption is retention of a substance within the pores of a solid.**

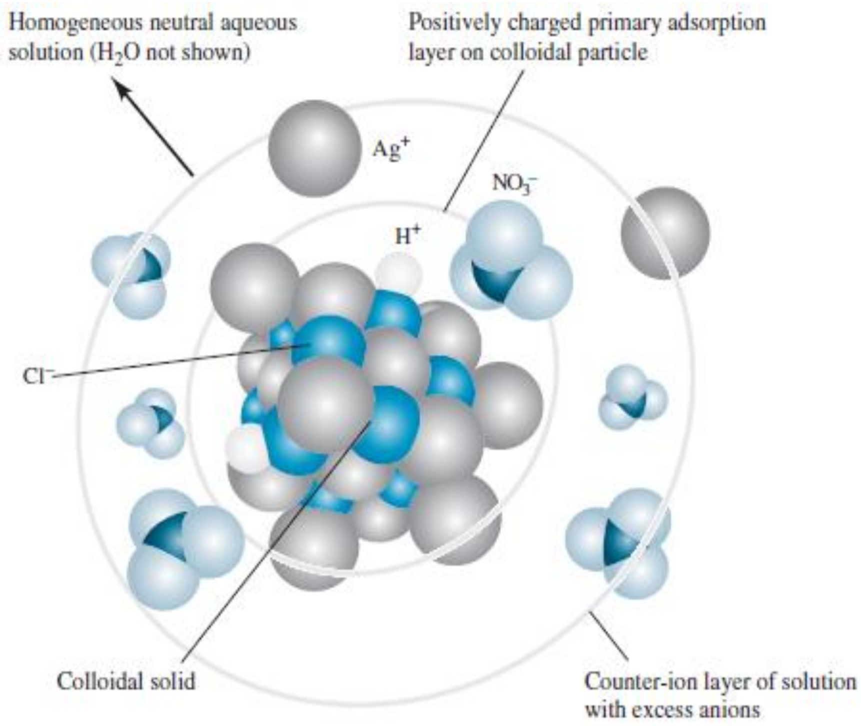


Figure: A colloidal silver chloride particle suspended in a solution of silver nitrate.

- **Figure** shows a colloidal silver chloride particle in a solution that contains an excess of silver nitrate.
- Attached directly to the solid surface is the **primary adsorption layer**, which consists mainly of adsorbed silver ions.
- Surrounding the charged particle is a layer of solution, called the **counter-ion layer**, which contains sufficient excess of negative ions (principally nitrate) to just balance the charge on the surface of the particle.
- The primarily adsorbed silver ions and the negative counter-ion layer constitute an **electric double layer** that imparts stability to the colloidal suspension.
- As colloidal particles approach one another, this double layer exerts an electrostatic repulsive force that prevents particles from colliding and adhering.

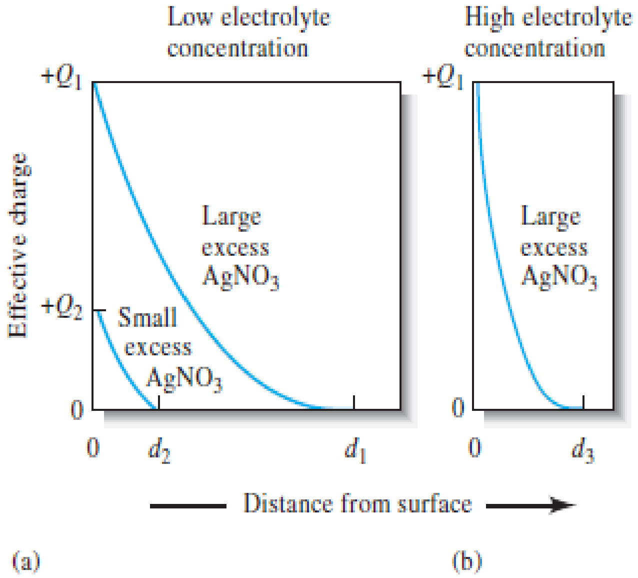


Figure: Effect of $AgNO_3$ and electrolyte concentration on the thickness of the double layer surrounding a colloidal AgCl particle in a solution containing excess $AgNO_3$.

- **Figure a** shows the effective charge on two silver chloride particles.
- upper curve represents a particle in a solution that contains a reasonably large excess o f silver nitrate
- lower curve depicts a particle in a solution that has a much lower silver nitrate content.
- The effective charge can be thought of as a measure of the repulsive force that the particle exerts on like particles in the solution.
- The effective charge falls off rapidly as the distance from the surface increases, and it approaches zero at the points d_1 or d_2.
- These decreases in effective charge (in both cases positive) are caused by the negative charge of the excess counter-ions in the double layer surrounding each particle.
- At points d_1 and d_2, the number of counter-ions in the layer is approximately equal to the number of primarily adsorbed ions on the surfaces of the particles; therefore, the effective charge of the particles approaches zero at this point.

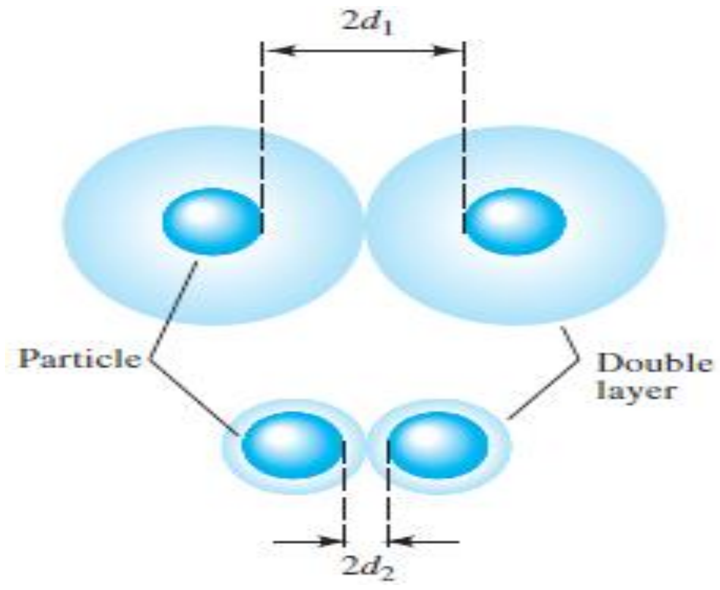


Figure: The electrical double layer of a colloid consists of a layer of charge adsorbed on the surface of the particle (the primary adsorption layer) and a layer of opposite charge (the counter-ion layer) in the solution surrounding the particle. Increasing the electrolyte concentration has the effect of decreasing the volume of the counter-ion layer, thereby increasing the chances for coagulation.

- The upper portion of Figure depicts two silver chloride particles and their counter-ion layers as they approach each other in the concentrated silver nitrate just considered.
- The effective charge on the particles prevents them from approaching one another more closely than about $2d_1$ a distance that is too great for coagulation to occur.
- As shown in the lower part of Figure , in the more dilute silver nitrate solution, the two particles can approach within $2d_2$ of one another.
- The concentration of silver nitrate is further decreased, the distance between particles becomes small enough for the forces of agglomeration to take effect and a coagulated precipitate to appear.

- **Coagulation of a colloidal suspension can often be brought about by**
- **A short period of (1) heating, particularly if accompanied by (2) stirring.**
  - ✓ **Heating decreases the number of adsorbed ions and thus the thickness, di, of the double layer.**
  - ✓ **The particles may also gain enough kinetic energy to overcome the barrier to close approach imposed by the double layer.**
- **(3) Adding an electrolyte: If we add a suitable ionic compound to a colloidal suspension, the concentration of counter-ions increases in the vicinity of each particle.**
  - ✓ **As a result, the volume of solution that contains sufficient counter-ions to balance the charge of the primary adsorption layer decreases.**
  - ✓ **The net effect of adding an electrolyte is thus a shrinkage of the counter-ion layer.**
  - ✓ **The particles can then approach one another more closely and agglomerate.**

❖ Peptization of Colloids:

- ✓ Peptization is a process by which a coagulated colloid returns to its dispersed state.
- ✓ When a coagulated colloid is washed, some of the electrolyte responsible for its coagulation is leached from the internal liquid in contact with the solid particles.
- ✓ Removal of this electrolyte has the effect of increasing the volume of the counter-ion layer.
- ✓ The repulsive forces responsible for the original colloidal state are then reestablished, and particles detach themselves from the coagulated mass.
- ✓ The washings become cloudy as the freshly dispersed particles pass through the filter.

Practical Treatment of Colloidal Precipitates.

Digestion: is a process in which a precipitate is heated in the solution from which it was formed (the mother liquor) and allowed to stand in contact with the solution.

Mother liquor: is the solution from which a precipitate was formed.

1- Crystalline Precipitates: Crystalline precipitates are generally more easily filtered and purified than are coagulated colloids. In addition, the size of individual crystalline particles, and thus their filterability, can be controlled to some extent.

(The particle size of crystalline solids can often be improved significantly by minimizing Q or maximizing S, or both. The value of Q is can often be minimized by using dilute solutions and adding the precipitating reagent slowly, with good mixing. Often, S is increased by precipitating from hot solution or by adjusting the pH of the precipitation medium.)

2- Coprecipitation: **a process in which normally soluble compounds are carrier out of solution by a precipitate.**

There are four types of coprecipitation.

1) **Surface adsorption.**
2) **Mixed-crystal formation.**
3) **Occlusion.**
4) **Mechanical entrapment.**

1), 2) → **Equilibrium processes**

3), 4) → **Arise from the kinetics of crystal growth**

1. Surface adsorption

specific surface areas(SA)↑→ adsorption↑

SA = (cm^2)/mass(g)

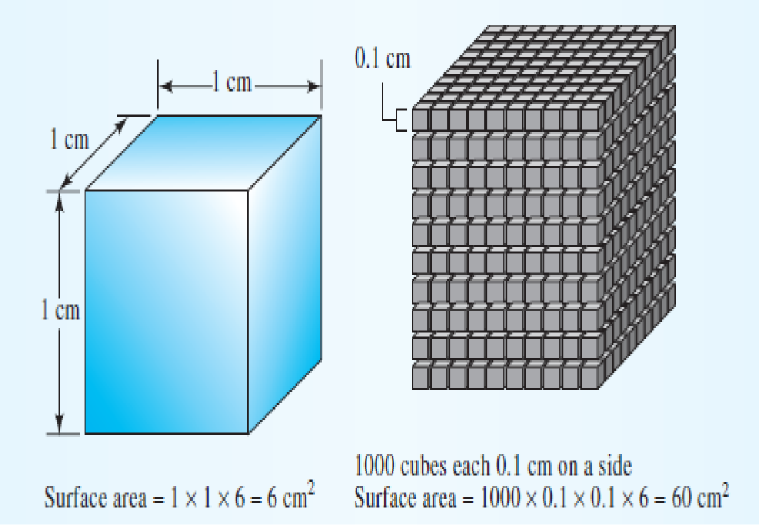


Figure: Increase in surface area per unit mass with decrease in particle size.

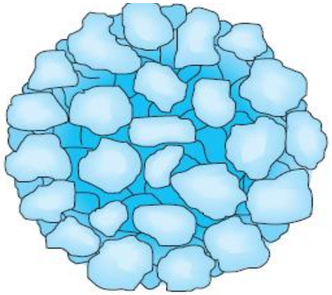


Figure: A coagulated colloid. This figure suggests that a coagulated colloid continues to expose a large surface area to the solution from which it was formed.

- ✓ Adsorption is often the major source of contamination in coagulated colloids but of no significance in crystalline precipitates.
- ✓ In adsorption, a normally soluble compound is carried out of solution on the surface of a coagulated colloid. This compound consists of the primarily adsorbed ion and an ion of opposite charge from the counter-ion layer.

Methods for Minimizing Adsorbed Impurities on Colloids

a. Digestion:

particle size↑→ specific surface area↓→ adsorption↓

b. Washing with volatile electrolyte solution:

Example: in Ag^+analysis, primary adsorbed ion : Cl washing with an acidic solution → counter-ion layer : H^+→ HCl volatilized when precipitate is dried

c. Reprecipitation, double precipitation:

2. Mixed-Crystal Formation: In mixed-crystal formation, one of the ions in the crystal lattice of a solid is replaced by an ion of another element. For this exchange to occur, it is necessary that the two ions have the,

- Same charge.
- Sizes differ by no more than about 5%.
- Salts must the same crystal class.

For example,

- Barium sulfate formed by adding barium chloride to a solution containing sulfate, lead, and acetate ions is found to be severely contaminated by lead sulfate.
- This contamination occurs even though acetate ions normally prevent precipitation of lead sulfate by complexing the lead.
- In this case, lead ions replace some of the barium ions in the barium sulfate crystals.

- Other examples of coprecipitation by mixed-crystal formation include $MgKPO_4$ in $MgNH_4PO_4$, $SrSO_4$ in $BaSO_4$, and MnS in CdS.

3. Occlusion: is a type of coprecipitation in which a compound is trapped within a pocket formed during rapid crystal growth.

4. Mechanical entrapment: occurs when crystals lie close together during growth.

- Several crystals grow together and in so doing trap a portion of the solution in a tiny pocket.
- Both occlusion and mechanical entrapment are at a minimum when the rate of precipitate formation is low, that is, under conditions of low supersaturation.

Precipitation from Homogeneous Solution

Homogeneous precipitation: is a process in which a precipitate is formed by slow generation of a precipitating reagent homogeneously throughout a solution.

Solids formed by homogeneous precipitation are generally purer and more easily filtered than precipitates generated by direct addition of a reagent to the analyte solution.

Urea is often used for the homogeneous generation of hydroxide ion. The reaction can be expressed by the equation

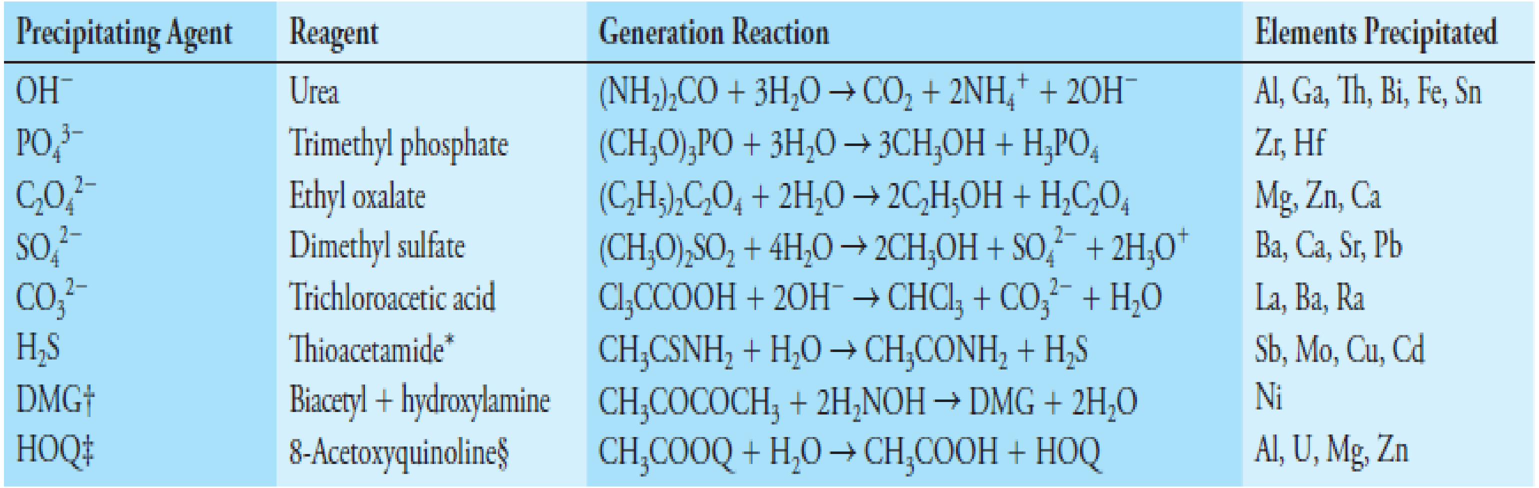
$$(H_2N)_2CO + 3H_2O \rightarrow CO_2 + 2NH_4^+ + 2OH^-$$

For example, hydrous oxides of iron(III) and aluminum, formed by direct addition of base, are bulky and gelatinous masses that are heavily contaminated and difficult to filter. In contrast, when these same products are produced by homogeneous generation of hydroxide ion, they are dense, are easily filtered, and have considerably higher purity.

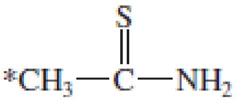
Figure: Aluminum hydroxide formed by the direct addition of ammonia (left) and the homogeneous production of hydroxide (right).

- Figure shows hydrous oxide precipitates of aluminum formed by direct addition of base and by homogeneous precipitation with urea.
- Homogeneous precipitation of crystalline precipitates also results in marked increases in crystal size as well as improvements in purity.
- Representative methods based on precipitation by homogeneously generated reagents are given in Table below.

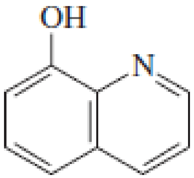
Table: Methods for Homogeneous Generation of Precipitating Agents

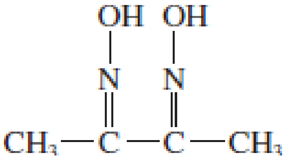


Precipitating Agent	Reagent	Generation Reaction	Elements Precipitated
OH^-	Urea	$(NH_2)_2CO + 3H_2O \rightarrow CO_2 + 2NH_4^+ + 2OH^-$	Al, Ga, Th, Bi, Fe, Sn
PO_4^{3-}	Trimethyl phosphate	$(CH_3O)_3PO + 3H_2O \rightarrow 3CH_3OH + H_3PO_4$	Zr, Hf
$C_2O_4^{2-}$	Ethyl oxalate	$(C_2H_5)_2C_2O_4 + 2H_2O \rightarrow 2C_2H_5OH + H_2C_2O_4$	Mg, Zn, Ca
SO_4^{2-}	Dimethyl sulfate	$(CH_3O)_2SO_2 + 4H_2O \rightarrow 2CH_3OH + SO_4^{2-} + 2H_3O^+$	Ba, Ca, Sr, Pb
CO_3^{2-}	Trichloroacetic acid	$Cl_3CCOOH + 2OH^- \rightarrow CHCl_3 + CO_3^{2-} + H_2O$	La, Ba, Ra
H_2S	Thioacetamide*	$CH_3CSNH_2 + H_2O \rightarrow CH_3CONH_2 + H_2S$	Sb, Mo, Cu, Cd
DMG†	Biacetyl + hydroxylamine	$CH_3COCOCH_3 + 2H_2NOH \rightarrow DMG + 2H_2O$	Ni
HOQ‡	8-Acetoxyquinoline§	$CH_3COOQ + H_2O \rightarrow CH_3COOH + HOQ$	Al, U, Mg, Zn

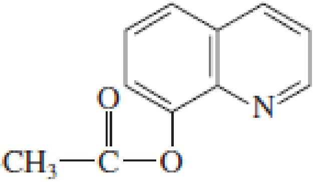
*

$CH_3—\overset{\overset{S}{\|}}{C}—NH_2$

‡HOQ = 8-Hydroxyquinoline = 

†DMG = Dimethylglyoxime = 

$CH_3—\overset{\overset{OH}{|}}{\overset{N}{\|}}{C}—\overset{\overset{OH}{|}}{\overset{N}{\|}}{C}—CH_3$

§

Drying and ignition of Precipitates

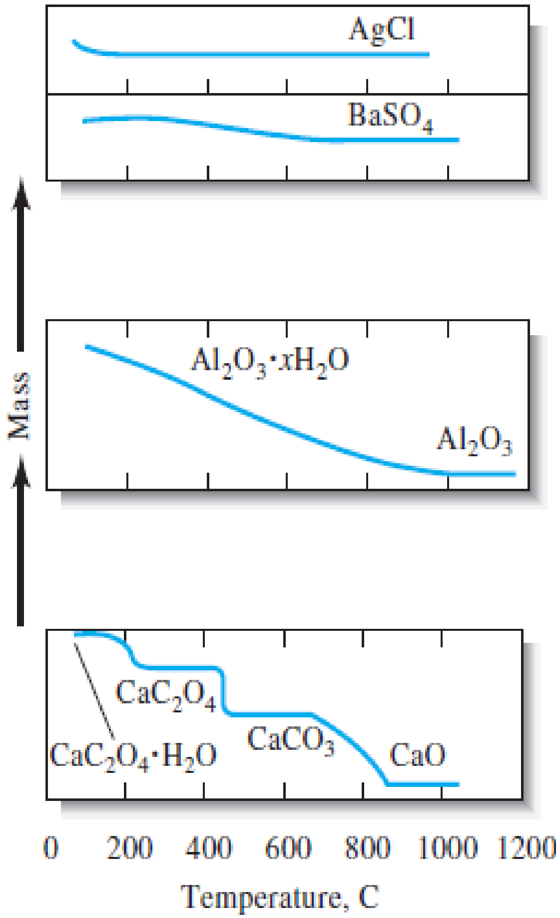


Figure : Effect of temperature on precipitate mass.

- **After filtration, a gravimetric precipitate is heated until its mass becomes constant.**
- **Heating removes the solvent and any volatile species carried down with the precipitate.**
- **Some precipitates are also ignited to decompose the solid and form a compound of known composition.**
- **This new compound is often called the weighing form.**
- **The temperature required to produce a suitable weighing form varies from precipitate to precipitate.**
- **Figure shows mass loss as a function of temperature for several common analytical precipitates.**
- **Heating three of the precipitates-silver chloride, barium sulfate, and aluminum oxide-simply causes removal of water and perhaps volatile electrolytes.**
- **Moisture is completely removed from silver chloride at temperatures higher than 110°C, but dehydration of aluminum oxide is not complete until a temperature greater than 1000°C is achieved. Aluminum oxide formed homogeneously with urea can be completely dehydrated at about 650°C.**

Calculation of Results from Gravimetric Data

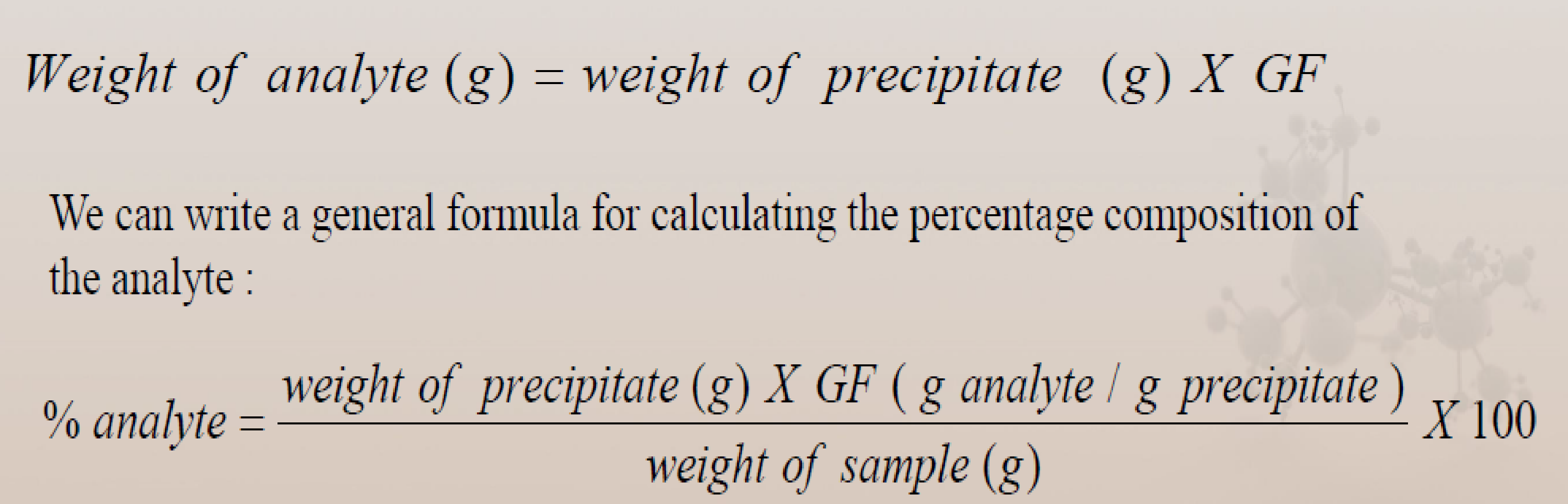
The results of a gravimetric analysis are generally computed from two experimental measurements: the mass of sample and the mass of a product of known composition.

$$GF = \frac{mw\ of\ analyte\ (g/mole)}{mw\ of\ precipitate\ (g/mole)}\ X\ R = \frac{g\ analyte}{g\ precipitate}$$

Where

GF is a gravimetric factor.

R is the number of moles of analyte in one mole of precipitate.



$$Weight\ of\ analyte\ (g) = weight\ of\ precipitate\ \ (g)\ X\ GF$$

We can write a general formula for calculating the percentage composition of the analyte :

$$\%\ analyte = \frac{weight\ of\ precipitate\ (g)\ X\ GF\ (\ g\ analyte\ /\ g\ precipitate\ )}{weight\ of\ sample\ (g)}\ X\ 100$$

Example : Calculate GF for the conversions in the table on your right :

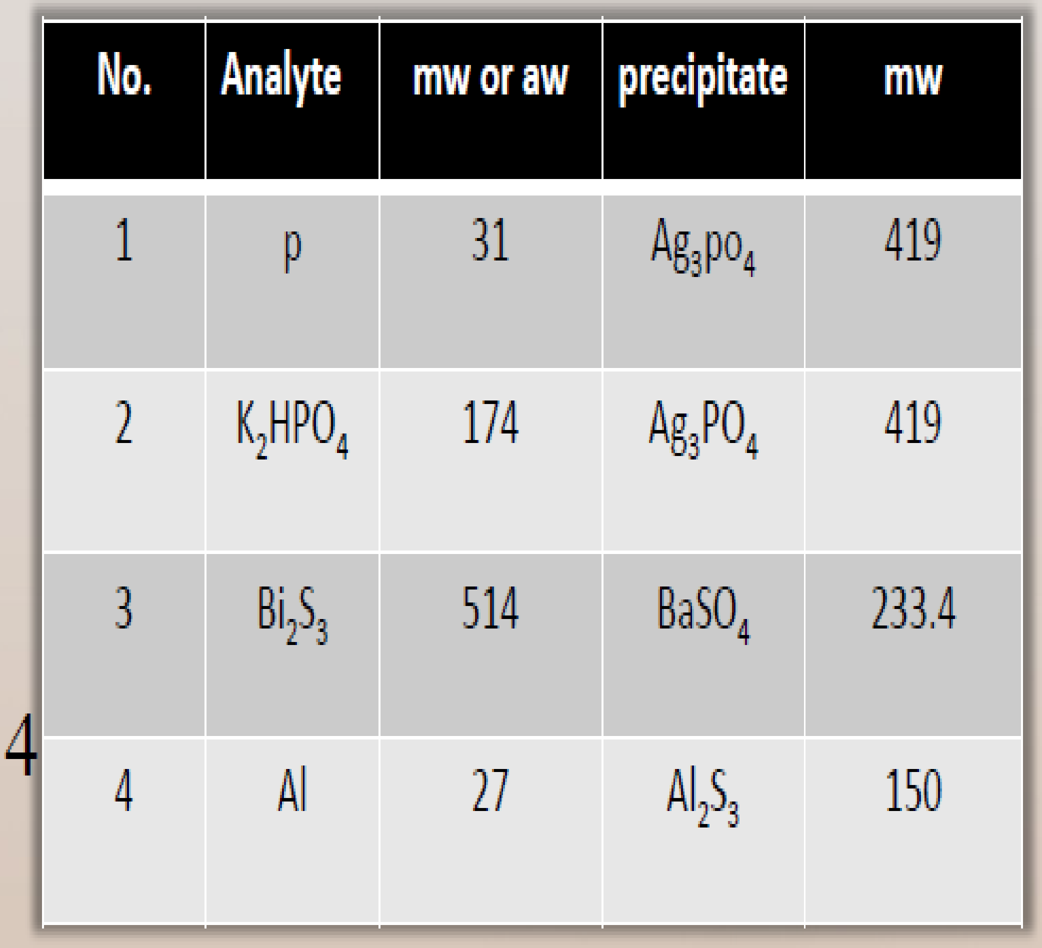
Solution :

$$(1)\ GF = \frac{31}{419}\ X\ 1 = 0.074$$

$$(2)\ GF = \frac{174}{419}\ X 1 = 0.415$$

$$(3)\ GF = \frac{514}{233.4}\ X\ \frac{1}{3} = 0.734$$

$$(4)\ GF = \frac{27}{150}\ X\ 2 = 0.54$$



No.	Analyte	mw or aw	precipitate	mw
1	p	31	Ag_3po_4	419
2	K_2HPO_4	174	Ag_3PO_4	419
3	Bi_2S_3	514	$BaSO_4$	233.4
4	Al	27	Al_2S_3	150

Example: The calcium in a 200.0-mL sample of a natural water was determined by precipitating the cation as CaC_2O_4. The precipitate was filtered, washed, and ignited in a crucible with an empty mass of 26.6002 g. The mass of the crucible plus CaO (56.077 g/mol) was 26.7134 g. Calculate the concentration of Ca (40.078 g/mol) in water in units of grams per 100 mL of the water.

Solution:

$$\text{mass of CaO} = 26.7134 - 26.6002 = 0.1132\ \text{g}$$

$$\text{moles Ca} = \text{moles CaO}$$

$$\text{amount of Ca} = \frac{0.1132\ \text{g}}{56.077\ \text{g/mol}} = 2.0186\ \text{mmol}$$

$$\frac{\text{mass Ca}}{100\ \text{mL}} = \frac{2.0186\ \text{mmol} \times 40.078\text{g/mol}}{200\ \text{mL}} \times 100\ \text{mL} = 0.04045\ \text{g}/100\ \text{mL}$$

Example: An iron ore was analyzed by dissolving a 1.1324-g sample in concentrated HCl. The resulting solution was diluted with water, and the iron(III) was precipitated as the hydrous oxide $Fe_2O_3 \cdot xH_2O$ by the addition of NH_3. After filtration and washing, the residue was ignited at a high temperature to give 0.5394 g of pure Fe_2O_3 (159.69 g/mol). Calculate (a) the % Fe (55.847 g/mol) and (b) the % Fe_3O_4 (231.54 g/mol) in the sample.

Solution:

$$\text{amount } Fe_2O_3 = \frac{0.5394\text{ g}}{159.69\text{ g/mol}} = 3.3778\text{ mmol}$$

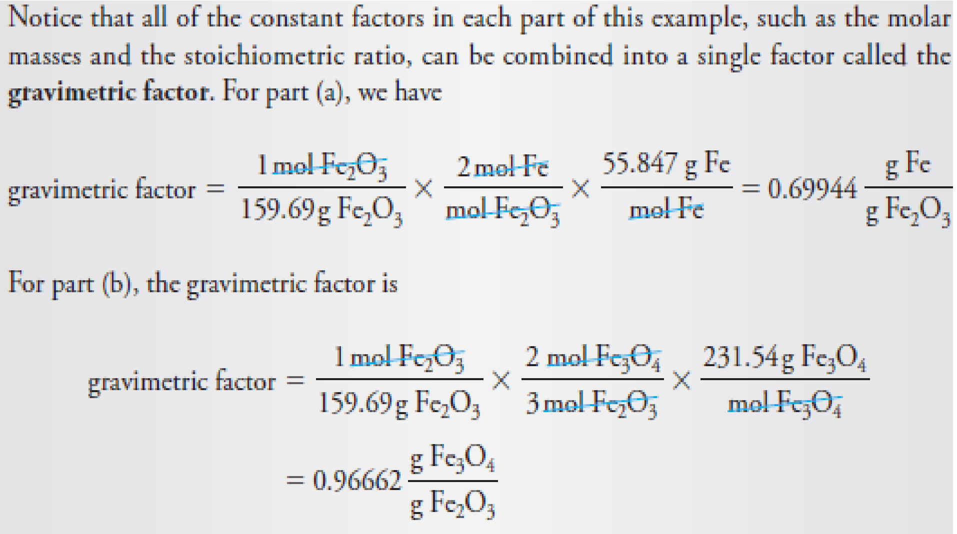
$$\text{(a) mass Fe} = 3.3778 \times 10^{-3}\text{ mol} \times 2 \times 55.847\text{ g/mol} = 0.37728\text{ g}$$

$$\%\text{ Fe} = \frac{0.37728\text{g}}{1.1324\text{g}} \times 100\% = 33.317 \approx 33.32\,\%$$

$$\text{(b)}\quad 3\,Fe_2O_3 \rightarrow 2\,Fe_3O_4 + \tfrac{1}{2}\,O_2$$

$$\text{mass } Fe_3O_4 = 3.3778\text{ mmol} \times \tfrac{2}{3} \times 231.54\text{ g/mol} = 0.52140\text{ g}$$

$$\%\,Fe_3O_4 = \frac{0.52140\text{g}}{1.1324\text{g}} \times 100\% = 46.044 \approx 46.04\,\%$$



Notice that all of the constant factors in each part of this example, such as the molar masses and the stoichiometric ratio, can be combined into a single factor called the **gravimetric factor**. For part (a), we have

$$\text{gravimetric factor} = \frac{1\,\cancel{\text{mol } Fe_2O_3}}{159.69\text{g } Fe_2O_3} \times \frac{2\,\cancel{\text{mol Fe}}}{\cancel{\text{mol } Fe_2O_3}} \times \frac{55.847\text{ g Fe}}{\cancel{\text{mol Fe}}} = 0.69944\,\frac{\text{g Fe}}{\text{g } Fe_2O_3}$$

For part (b), the gravimetric factor is

$$\text{gravimetric factor} = \frac{1\,\cancel{\text{mol } Fe_2O_3}}{159.69\text{g } Fe_2O_3} \times \frac{2\,\cancel{\text{mol } Fe_3O_4}}{3\,\cancel{\text{mol } Fe_2O_3}} \times \frac{231.54\text{g } Fe_3O_4}{\cancel{\text{mol } Fe_3O_4}}$$

$$= 0.96662\,\frac{\text{g } Fe_3O_4}{\text{g } Fe_2O_3}$$

Example: A 0.2356-g sample containing only NaCl (58.44 g/mol) and $BaCl_2$ (208.23 g/mol) yielded 0.4637 g of dried AgCl (143.32 g/mol). Calculate the percent of each halogen compound in the sample.

Solution:

$$\text{let } x = \text{mass of NaCl}, y = \text{mass of BaCl}_2 \quad \rightarrow \quad x + y = 0.2356 \text{ g}$$

$$\text{mass AgCl from NaCl } = \frac{x \text{ g} \times 143.32 \text{ g/mol}}{58.44 \text{g/mol}} = 2.4524x \text{ g}$$

$$\text{mass AgCl from BaCl}_2 \ = \frac{y \text{ g} \times 2 \times 143.32 \text{ g/mol}}{208.23 \text{ g/mol}} = 1.3766 y \text{ g}$$

$$2.4524x \text{ g} + 1.3766y \text{ g} = 2.4524x \text{ g} + 1.3766\ (0.2356 - x) \text{ g} = 0.4637 \text{ g}$$

$$1.0758x = 0.13942$$

$$x = \text{mass NaCl} = 0.12960 \text{ g NaCl}$$

$$\%\ \text{NaCl} \ = \frac{0.12956 \text{ g NaCl}}{0.2356 \text{ g}} \times 100\% = 55.01\%$$

$$\%\ \text{BaCl}_2 = 100\ \% - 55.01\% = 44.99\ \%$$

Example

Sample: $\underline{\mathrm{NaCl + NaBr + inert}}$ = 1.000 g

excess $AgNO_3$ ⇓

$\underline{\mathrm{AgCl(s) + AgBr(s)}}$ = 0.5260 g

Cl_2 treatment ⇓

$\underline{\mathrm{AgCl(s) + AgCl(s)}}$ = 0.4260 g

Ag: 107.87,
Cl: 35.45
Na: 22.99
Br: 79.90

NaCl = ? % ; NaBr = ? %

Solution if NaCl = x g, NaBr = y g

$$\text{g of AgCl(s)} = \frac{x \times 143.32}{58.44} \; ; \quad \text{g of AgBr(s)} = \frac{y \times 187.77}{102.89}$$

$$\frac{x \times 143.32}{58.44} + \frac{y \times 187.77}{102.89} = 0.5260 \text{ g}$$

$$\frac{x \times 143.32}{58.44} + \frac{y \times 143.32}{102.89} = 0.4260 \text{ g}$$

$$\%\ \text{NaCl} = \frac{x \times 100}{1.000}$$

$$\%\ \text{NaBr} = \frac{y \times 100}{1.000}$$

2- Volatilization Gravimetry

- The two most common gravimetric methods based on volatilization are those for determining water and carbon dioxide.
  - Water is quantitatively distilled from many materials by heating.
  - In direct determination, water vapor is collected on any of several solid desiccants, and its mass is determined from the mass gain of the desiccant.
- The indirect method in which the amount of water is determined by the loss of mass of the sample during heating is less satisfactory because it must be assumed that water is the only component that is volatilized.
- This assumption can present problems, however, if any component of the precipitate is volatile.
- Indirect method is widely used to determine water in items of commerce.
- An example of a gravimetric procedure involving volatilization of carbon dioxide is the determination of the sodium hydrogen carbonate content of antacid tablets. A weighed sample of the finely ground tablets is treated with dilute sulfuric acid to convert the sodium hydrogen carbonate to carbon dioxide:

$$NaHCO_3(aq) + H_2SO_4(aq) \rightarrow CO_2(g) + H_2O(l) + NaHSO_4(aq)$$

this reaction is carried out in a flask connected first to a tube containing CaSO4 that removes water vapor from the initial reaction stream to produce a stream of pure CO_2 in nitrogen. These gases then pass through a weighed absorption tube containing the absorbent Ascarite II, which consists of sodium hydroxide absorbed on a nonfibrous silicate. This material retains carbon dioxide by the reaction

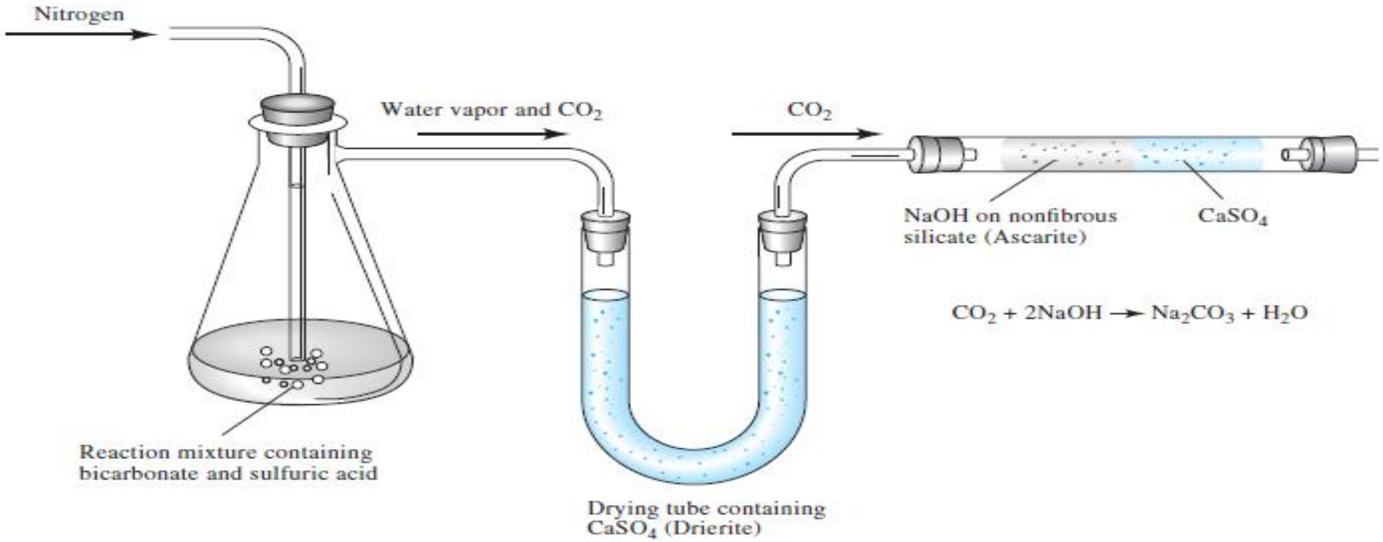


Figure: Apparatus for determining the sodium hydrogen carbonate content of antacid tablets by a gravimetric volatilization procedure.

- The absorption tube must also contain a desiccant such as $CaSO_4$ to prevent loss of the water produced by this last reaction.
- Sulfides and sulfites can also be determined by volatilization. Hydrogen sulfide or sulfur dioxide evolved from the sample after treatment with acid is collected in a suitable absorbent.
- Finally, the classical method for the determination of carbon and hydrogen in organic compounds is a gravimetric volatilization procedure in which the combustion products (H_2O and CO_2) are collected selectively on weighed absorbents. The increase in mass serves as the analytical variable.

Exercise 1 : A 0.4960 g sample of a $CaCO_3$ (100g/mol) is dissolved in an acidic solution. The calcium is precipitated as CaC_2O_4. H_2O (146 g/mol) and the dry precipitate is found to weigh 0.6186 g. What is the percentage of CaO (56g/mol) in the sample? Ans=47.78%

Exercise 2 : 0.8 g sample contains sulfur S (aw= 32) has been dissolved . The sulfur is precipitated as $BaSO_4$ (233g/mol) . If the weight of the precipitate is 0.3 g calculate the percentage of sulfur in the sample ? Ans=5.2%

Exercise 3 : 644 mg of a sample contains Mg (aw= 24) has been dissolved in water . The magnesium content of the sample is precipitated as $MgNH_4PO_4.6H_2O$ and ignited and weighed as $Mg_2P_2O_7$ (222g/mol) . If this weight is 290 mg , calculate the percentage of Mg in the sample ? Ans=9.7%

Exercise 4 : The silver content of 20 mL 0.1 M of Ag^+ solution is precipitated as Ag_2S using 0.05 M solution of S^{2-} according to the following complete reaction :

$$2\,Ag^+ + S^{2-} \rightarrow Ag_2S$$

Calculate the volume of S^{2-} solution that is required for complete precipitation of Ag^+ ? Ans=30 mL

Exercise 5 : The aluminum (aw = 27) content of a 5 g sample is determined gravimetricaly by precipitating the aluminum as Al_2S_3 (150 g/mol) . If the weight of the precipitate is 0.5 g , calculate the percentage of aluminum in the sample ? Ans=3.6%

Exercise 6 : Calculate the weight of Mn (aw = 55) in 2.5 g of Mn_3O_4 (229 g/mol) ? Ans=1.804 g

Exercise 7 : For the determination of Zn (aw = 65) gravimetricaly in a sample it is precipitated and weighed as $Zn_2Fe(CN)_6$ (342 g/mol) . (1) Calculate the weight of Zn in a sample which gives 0.35 g precipitate . (2) Calculate the weight of the precipitate which can be produced by a sample containing 0.5 g Zn ? Ans=0.133g,1.316g

Exercise 8 : 0.4 g of an impure reagent of KCl (74.5 g/mol) is dissolved and an excess of $AgNO_3$ solution is added . As a result of this 0.7332 g of AgCl (143.5 g/mol) precipitate is formed . Calculate the percentage purity of KCl reagent ? Ans=95.2%

Exercise 9 : 0.1799 g of an organic compound is burned in O_2 atmosphere . The CO_2 produced is collected in $Ba(OH)_2$ solution where 0.5613 g of $BaCO_3$ (197 g/mol) is precipitated . Calculate the percentage of carbon in the organic compound ? Ans=19%

Exercise 10 : Calculate the weight of AgI (235 g/mol) that can be precipitated from 0.24 g of a sample of MgI_2 (258 g/mol) which has a purity of 30.6 $\%_{w/w}$?

Ans.=0.1338g

Exercise 11 : Calculate the molar concentration of 25 mL of a solution of $AgNO_3$ that required to completely precipitate SCN^-as AgSCN from 0.2124 g of KSCN (89g/mol) ?

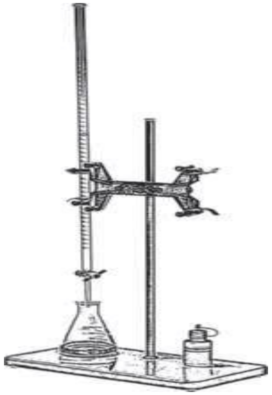
Ans.=0.1432 M

Volumetric analysis

- **Volumetric analysis is one of the most useful and accurate analytical techniques, especially for millimole amounts of analyte.**
- **They are rapid and can be manual and automated, and they can be applied to smaller amounts of analyte when combined with a sensitive instrumental technique for detecting the completion of the titration reaction, for example, pH measurement.**
- **This method based on measured the volume of reagent needed to react with analyte.**
- **Titration methods are based on determining the quantity of a reagent of known concentration that is required to react completely with the analyte. The reagent may be a standard solution of a chemical or an electric current of known magnitude.**

- A volume-based titration is shown in the Figure in which the standard solution is added from a buret, and the reaction occurs in the Erlenmeyer flask. In some titrations, known as coulometric titrations

- In coulometric titrations, the quantity of charge required to complete a reaction with the analyte is the measured quantity.



- A standard solution is a reagent of known concentration. Standard solutions are used in titrations and in many other chemical analyses.
- Back-titration is a process in which the excess of a standard solution used to consume an analyte is determined by titration with a second standard solution. Back-titrations are often required when the rate of reaction between the analyte and reagent is slow or when the standard solution lacks stability.

- **Equivalence point** is the point in a titration when the amount of added standard reagent is equivalent to the amount of analyte.

- **End point** is the point in a titration when a physical change occurs that is associated with the condition of chemical equivalence.

In volumetric methods, the titration error, E_t, is given by

$$E_t = V_{ep} - V_{eq}$$

Where

V_{ep} is the actual volume of reagent required to reach the end point.

V_{eq} is the theoretical volume necessary to reach equivalence point.

- **Indicators are often added to the analyte solution to produce an observable physical change (signaling the end point) at or near the equivalence point. Large changes in the relative concentration of analyte or titrant occur in the equivalence-point region. These concentration changes cause the indicator to change in appearance.**
- **Typical indicator changes include the appearance or disappearance of a color, a change in color, or the appearance or disappearance of turbidity.**

- **Primary standard is a highly purified compound that serves as a reference material in titrations and in other analytical methods. The accuracy of a method critically depends on the properties of the primary standard.**

1. **High purity.**
2. **Atmospheric stability.**
3. **Absence of hydrate water.**
4. **Modest cost.**
5. **Reasonable solubility in the titration medium.**
6. **Reasonably large molar mass.**

- **Secondary standard is a compound whose purity has been determined by chemical analysis. The secondary standard serves as the working standard material for titrations and for many other analyses.**

Standard solutions play a central role in all titrations. Therefore, we must consider the desirable properties for such solutions, how they are prepared, and how their concentrations are expressed.

The ***ideal*** standard solution for a titrimetric method will

1. Be sufficiently stable so that it is necessary to determine its concentration only once;
2. React rapidly with the analyte so that the time required between additions of reagent is minimized;
3. React more or less completely with the analyte so that satisfactory end points are realized;
4. Undergo a selective reaction with the analyte that can be described by a balanced equation.

Two basic methods are used to establish the concentration of such solutions.

1. **Direct method** in which a carefully determined mass of a primary standard is dissolved in a suitable solvent and diluted to a known volume in a volumetric flask.

2. **Standardization** in which the titrant to be standardized is used to titrate
   - (A) A known mass of a primary standard,
   - (B) A known mass of a secondary standard,
   - (C) Or a measured volume of another standard solution.

In a standardization, the concentration of a volumetric solution is determined by titrating it against a carefully measured quantity of a primary or secondary standard or an exactly known volume of another standard solution.

Volumetric Calculations

$$\text{amount A (mol)} = \frac{\text{mass A (g)}}{\text{molar mass A (g/mol)}}$$

$$\text{amount A (mmol)} = \frac{\text{mass A (g)}}{\text{millimolar mass A (g/mmol)}}$$

$$n_A = \frac{m_A}{\mathcal{M}_A}$$

where n_A is the amount of A, m_A is the mass of A, and $\mathcal{M}_A$ is the molar mass of A.

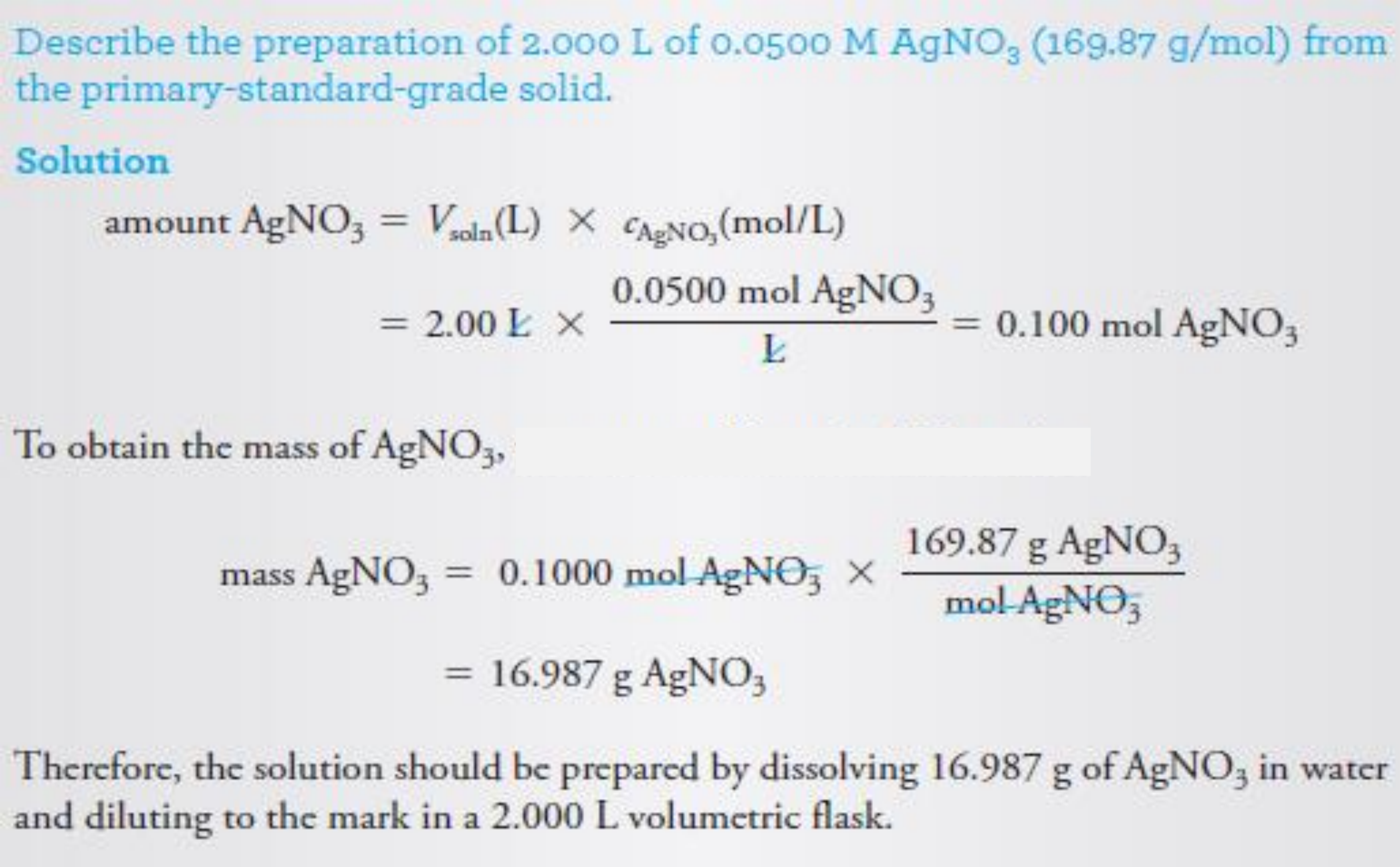
$$\text{amount A (mol)} = V\text{(L)} \times c_A\left(\frac{\text{mol A}}{\text{L}}\right)$$

$$\text{amount A (mmol)} = V\text{(mL)} \times c_A\left(\frac{\text{mmol A}}{\text{L}}\right)$$

$$c_A = \frac{n_A}{V} \quad \text{or} \quad n_A = V \times c_A$$

Calculating the Molar Concentration of Standard Solutions

The following three examples illustrate how the concentrations of volumetric reagents are calculated.



Describe the preparation of 2.000 L of 0.0500 M $AgNO_3$ (169.87 g/mol) from the primary-standard-grade solid.

Solution

$$\text{amount } AgNO_3 = V_{soln}(L) \times c_{AgNO_3}(mol/L)$$

$$= 2.00\ \cancel{L} \times \frac{0.0500\ mol\ AgNO_3}{\cancel{L}} = 0.100\ mol\ AgNO_3$$

To obtain the mass of $AgNO_3$,

$$\text{mass } AgNO_3 = 0.1000\ \cancel{mol\ AgNO_3} \times \frac{169.87\ g\ AgNO_3}{\cancel{mol\ AgNO_3}}$$

$$= 16.987\ g\ AgNO_3$$

Therefore, the solution should be prepared by dissolving 16.987 g of $AgNO_3$ in water and diluting to the mark in a 2.000 L volumetric flask.

A standard 0.0100 M solution of Na^+ is required to calibrate an ion-selective electrode method to determine sodium. Describe how 500 mL of this solution can be prepared from primary standard Na_2CO_3 (105.99 g/mL).

Solution

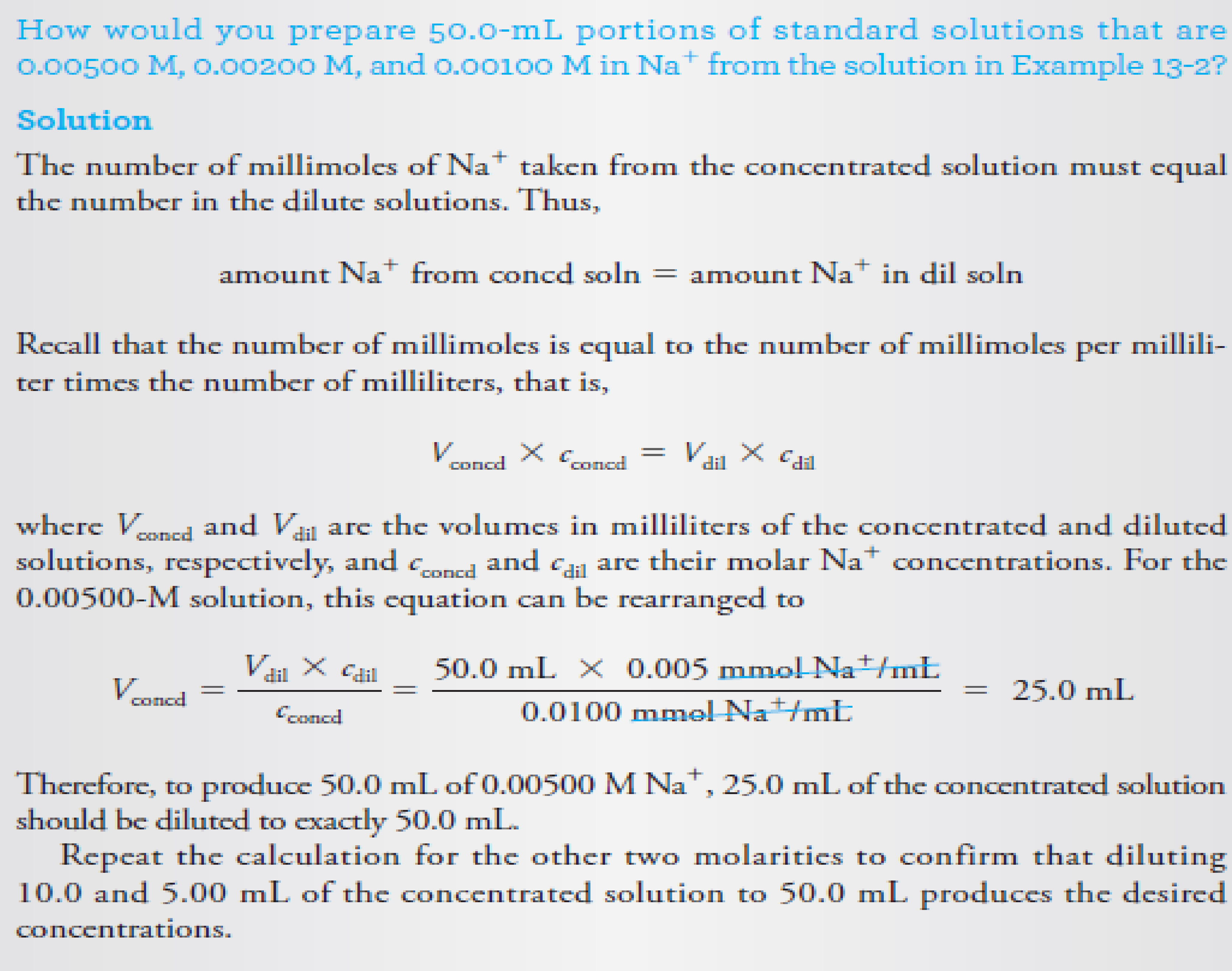
We wish to compute the mass of reagent required to produce a species concentration of 0.0100 M. In this instance, we will use millimoles since the volume is in milliliters. Because Na_2CO_3 dissociates to give two Na^+ ions, we can write that the number of millimoles of Na_2CO_3 needed is

$$\begin{aligned}\text{amount } Na_2CO_3 &= 500\ \cancel{\text{mL}} \times \frac{0.0100\ \cancel{\text{mmol Na}^+}}{\cancel{\text{mL}}} \times \frac{1\ \text{mmol Na}_2\text{CO}_3}{2\ \cancel{\text{mmol Na}^+}} \\ &= 2.50\ \text{mmol}\end{aligned}$$

From the definition of millimole, we write

$$\begin{aligned}\text{mass } Na_2CO_3 &= 2.50\ \cancel{\text{mmol Na}_2\text{CO}_3} \times 105.99\ \frac{\text{mg Na}_2\text{CO}_3}{\cancel{\text{mmol Na}_2\text{CO}_3}} \\ &= 264.975\ \text{mg Na}_2\text{CO}_3\end{aligned}$$

Since there are 1000 mg/g, or 0.001 g/mg, the solution should be prepared by dissolving 0.265 g of Na_2CO_3 in water and diluting to 500 mL.



How would you prepare 50.0-mL portions of standard solutions that are 0.00500 M, 0.00200 M, and 0.00100 M in Na^+ from the solution in Example 13-2?

Solution

The number of millimoles of Na^+ taken from the concentrated solution must equal the number in the dilute solutions. Thus,

$$\text{amount } Na^+ \text{ from concd soln} = \text{amount } Na^+ \text{ in dil soln}$$

Recall that the number of millimoles is equal to the number of millimoles per milliliter times the number of milliliters, that is,

$$V_{\text{concd}} \times c_{\text{concd}} = V_{\text{dil}} \times c_{\text{dil}}$$

where V_{concd} and V_{dil} are the volumes in milliliters of the concentrated and diluted solutions, respectively, and c_{concd} and c_{dil} are their molar Na^+ concentrations. For the 0.00500-M solution, this equation can be rearranged to

$$V_{\text{concd}} = \frac{V_{\text{dil}} \times c_{\text{dil}}}{c_{\text{concd}}} = \frac{50.0\text{ mL} \times 0.005\ \cancel{\text{mmol Na}^+/\text{mL}}}{0.0100\ \cancel{\text{mmol Na}^+/\text{mL}}} = 25.0\text{ mL}$$

Therefore, to produce 50.0 mL of 0.00500 M Na^+, 25.0 mL of the concentrated solution should be diluted to exactly 50.0 mL.

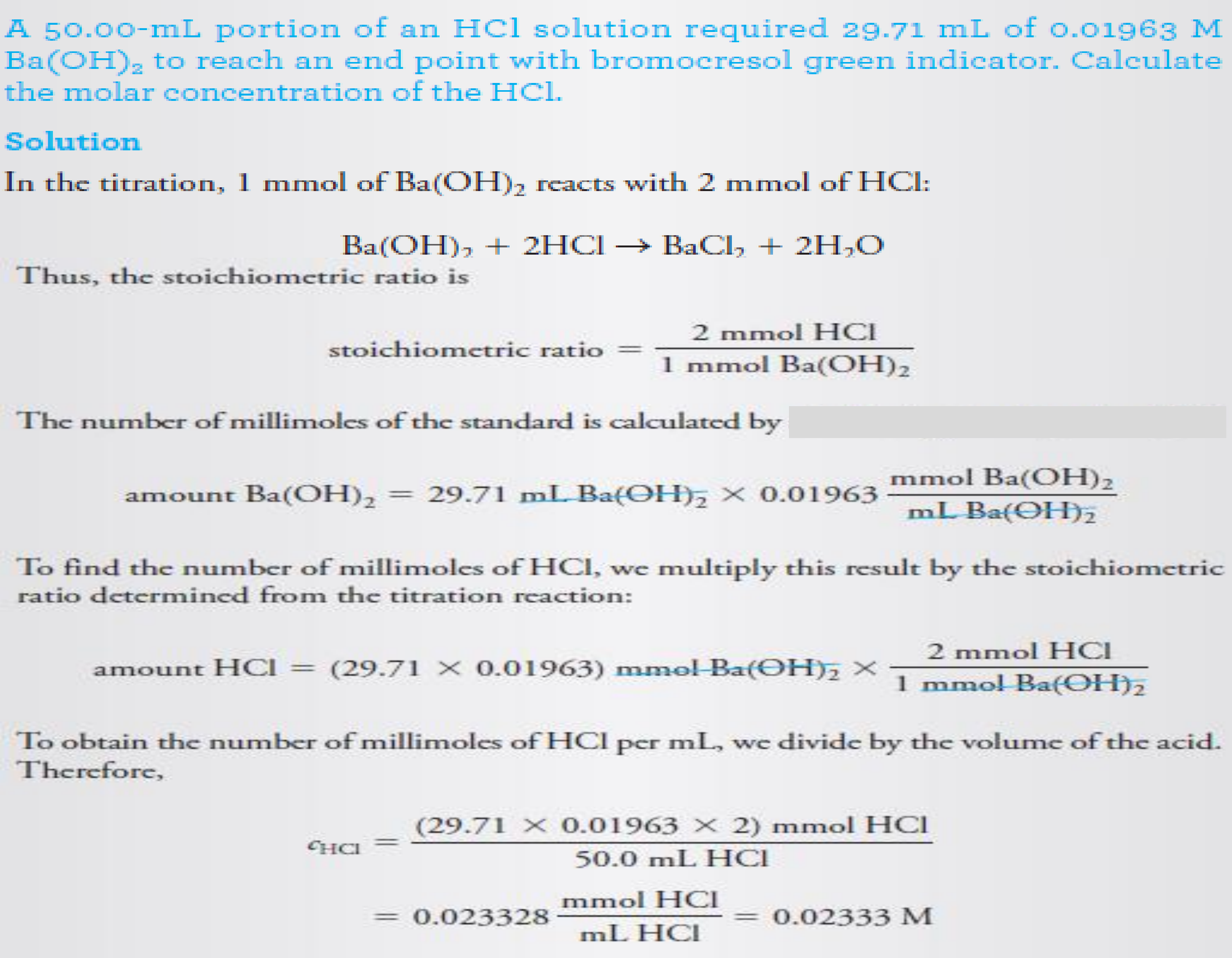
Repeat the calculation for the other two molarities to confirm that diluting 10.0 and 5.00 mL of the concentrated solution to 50.0 mL produces the desired concentrations.

Working with Titration Data

Two types of volumetric calculations we will discussed here.

- ✓ **In the first, we compute concentrations of solutions that have been standardized against either a primary standard or another standard solution.**
- ✓ **In the second, we calculate the amount of analyte in a sample from titration data.**

Calculating Molar Concentrations from Standardization Data



A 50.00-mL portion of an HCl solution required 29.71 mL of 0.01963 M $Ba(OH)_2$ to reach an end point with bromocresol green indicator. Calculate the molar concentration of the HCl.

Solution

In the titration, 1 mmol of $Ba(OH)_2$ reacts with 2 mmol of HCl:

$$Ba(OH)_2 + 2HCl \rightarrow BaCl_2 + 2H_2O$$

Thus, the stoichiometric ratio is

$$\text{stoichiometric ratio} = \frac{2 \text{ mmol HCl}}{1 \text{ mmol } Ba(OH)_2}$$

The number of millimoles of the standard is calculated by

$$\text{amount } Ba(OH)_2 = 29.71 \cancel{\text{mL } Ba(OH)_2} \times 0.01963 \frac{\text{mmol } Ba(OH)_2}{\cancel{\text{mL } Ba(OH)_2}}$$

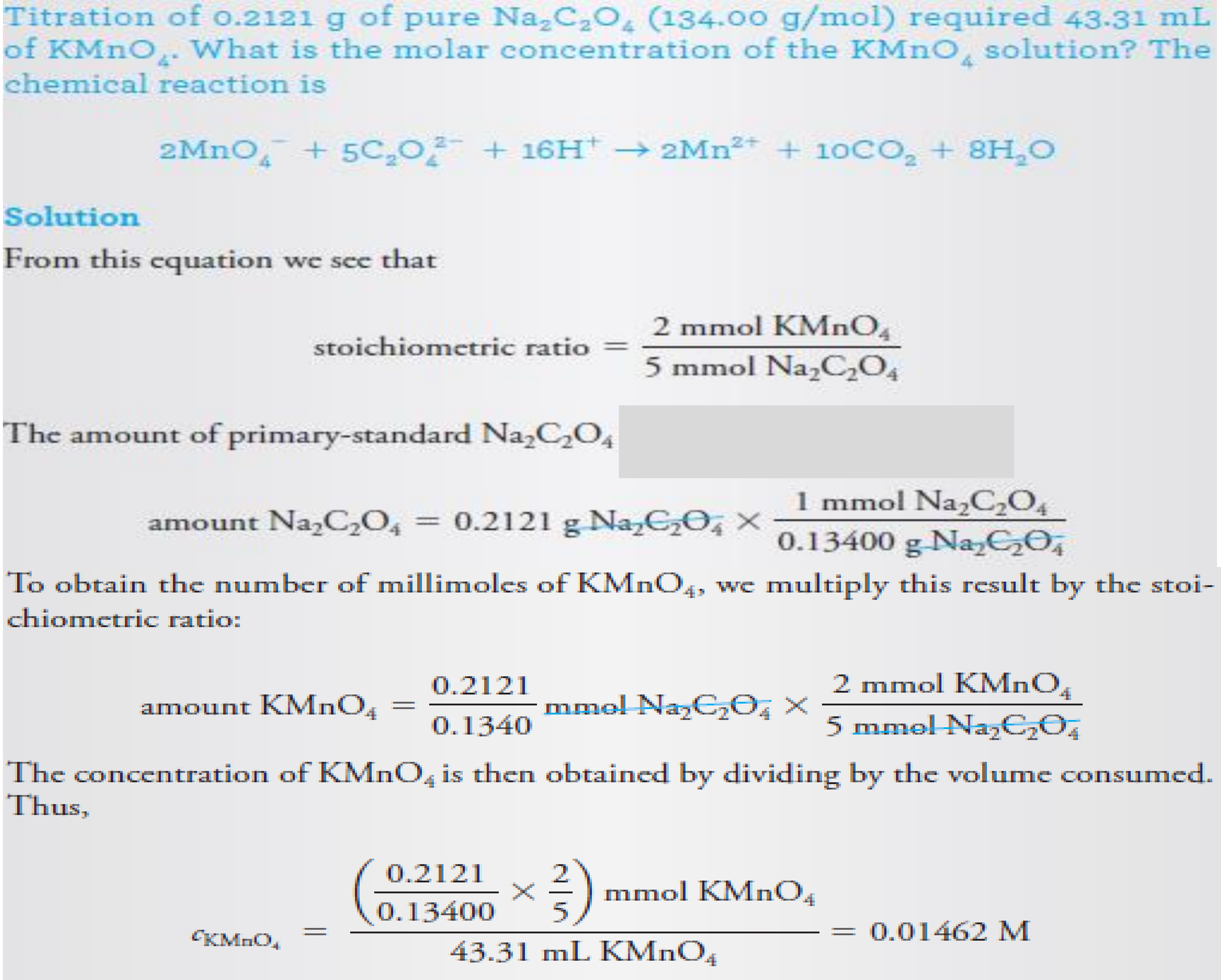
To find the number of millimoles of HCl, we multiply this result by the stoichiometric ratio determined from the titration reaction:

$$\text{amount HCl} = (29.71 \times 0.01963) \cancel{\text{mmol } Ba(OH)_2} \times \frac{2 \text{ mmol HCl}}{1 \cancel{\text{mmol } Ba(OH)_2}}$$

To obtain the number of millimoles of HCl per mL, we divide by the volume of the acid. Therefore,

$$c_{HCl} = \frac{(29.71 \times 0.01963 \times 2) \text{ mmol HCl}}{50.0 \text{ mL HCl}}$$

$$= 0.023328 \frac{\text{mmol HCl}}{\text{mL HCl}} = 0.02333 \text{ M}$$



Titration of 0.2121 g of pure $Na_2C_2O_4$ (134.00 g/mol) required 43.31 mL of $KMnO_4$. What is the molar concentration of the $KMnO_4$ solution? The chemical reaction is

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

Solution

From this equation we see that

$$\text{stoichiometric ratio} = \frac{2 \text{ mmol } KMnO_4}{5 \text{ mmol } Na_2C_2O_4}$$

The amount of primary-standard $Na_2C_2O_4$

$$\text{amount } Na_2C_2O_4 = 0.2121 \cancel{\text{g } Na_2C_2O_4} \times \frac{1 \text{ mmol } Na_2C_2O_4}{0.13400 \cancel{\text{g } Na_2C_2O_4}}$$

To obtain the number of millimoles of $KMnO_4$, we multiply this result by the stoichiometric ratio:

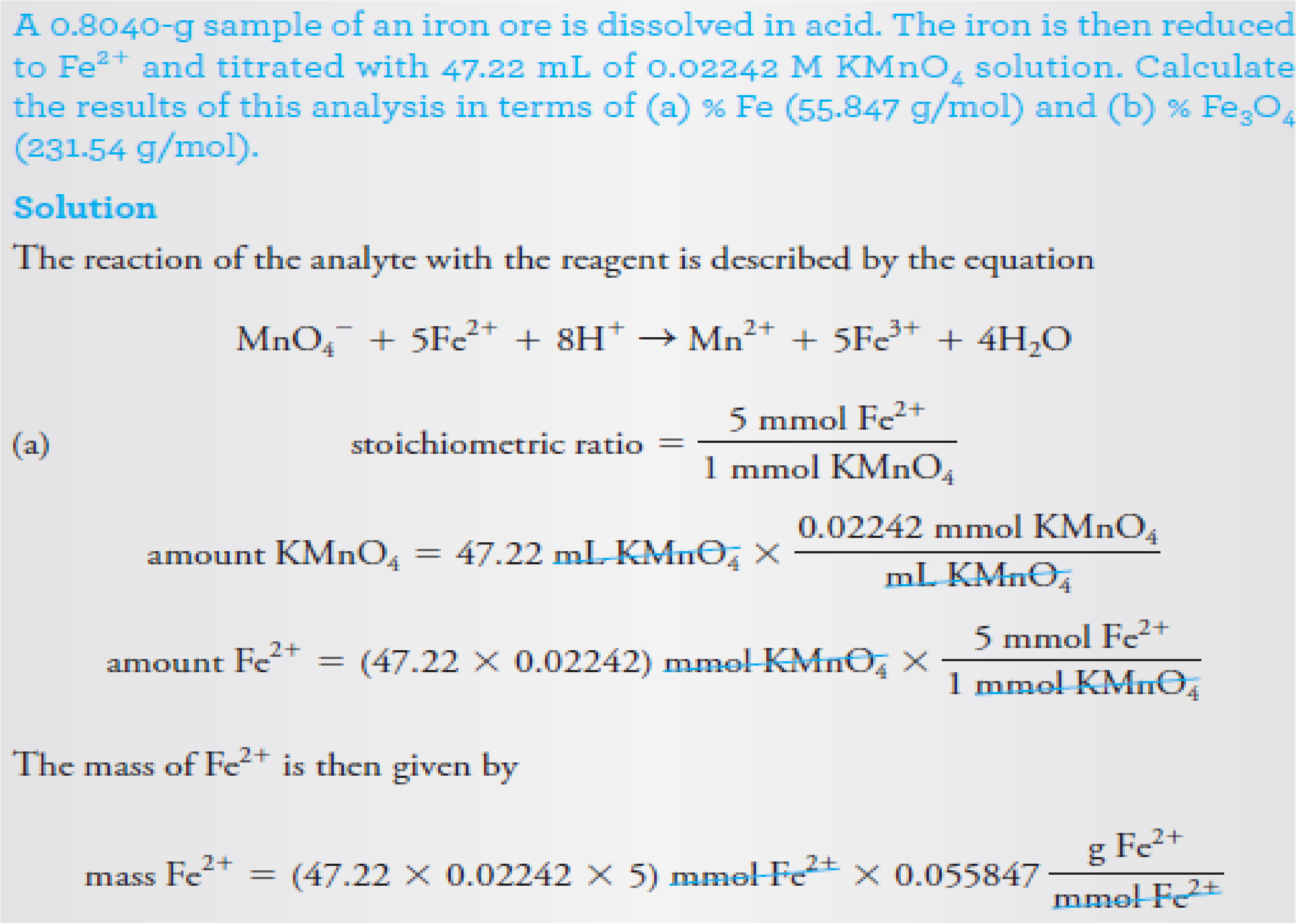
$$\text{amount } KMnO_4 = \frac{0.2121}{0.1340} \cancel{\text{mmol } Na_2C_2O_4} \times \frac{2 \text{ mmol } KMnO_4}{5 \cancel{\text{mmol } Na_2C_2O_4}}$$

The concentration of $KMnO_4$ is then obtained by dividing by the volume consumed. Thus,

$$c_{KMnO_4} = \frac{\left(\frac{0.2121}{0.13400} \times \frac{2}{5}\right) \text{mmol } KMnO_4}{43.31 \text{ mL } KMnO_4} = 0.01462 \text{ M}$$

Calculating the Quantity of Analyte from Titration Data

As shown by the examples that follow, the systematic approach just described is also used to compute analyte concentrations from titration data.



A 0.8040-g sample of an iron ore is dissolved in acid. The iron is then reduced to Fe^{2+} and titrated with 47.22 mL of 0.02242 M $KMnO_4$ solution. Calculate the results of this analysis in terms of (a) % Fe (55.847 g/mol) and (b) % Fe_3O_4 (231.54 g/mol).

Solution

The reaction of the analyte with the reagent is described by the equation

$$MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

(a)

$$\text{stoichiometric ratio} = \frac{5\ \text{mmol Fe}^{2+}}{1\ \text{mmol KMnO}_4}$$

$$\text{amount KMnO}_4 = 47.22\ \cancel{\text{mL KMnO}_4} \times \frac{0.02242\ \text{mmol KMnO}_4}{\cancel{\text{mL KMnO}_4}}$$

$$\text{amount Fe}^{2+} = (47.22 \times 0.02242)\ \cancel{\text{mmol KMnO}_4} \times \frac{5\ \text{mmol Fe}^{2+}}{1\ \cancel{\text{mmol KMnO}_4}}$$

The mass of Fe^{2+} is then given by

$$\text{mass Fe}^{2+} = (47.22 \times 0.02242 \times 5)\ \cancel{\text{mmol Fe}^{2+}} \times 0.055847\ \frac{\text{g Fe}^{2+}}{\cancel{\text{mmol Fe}^{2+}}}$$

The percent Fe^{2+} is

$$\%\ \mathrm{Fe}^{2+} = \frac{(47.22 \times 0.02242 \times 5 \times 0.055847)\ \mathrm{g\ Fe}^{2+}}{0.8040\ \mathrm{g\ sample}} \times 100\% = 36.77\%$$

(b) To determine the correct stoichiometric ratio, we note that

$$5\ \mathrm{Fe}^{2+} \equiv 1\ \mathrm{MnO_4}^-$$

Therefore,

$$5\ \mathrm{Fe_3O_4} \equiv 15\ \mathrm{Fe}^{2+} \equiv 3\ \mathrm{MnO_4}^-$$

and

$$\text{stoichiometric ratio} = \frac{5\ \mathrm{mmol\ Fe_3O_4}}{3\ \mathrm{mmol\ KMnO_4}}$$

As in part (a),

$$\text{amount KMnO}_4 = \frac{47.22\ \cancel{\mathrm{mL\ KMnO_4}} \times 0.02242\ \mathrm{mmol\ KMnO_4}}{\cancel{\mathrm{mL\ KMnO_4}}}$$

$$\text{amount Fe}_3\text{O}_4 = (47.22 \times 0.02242)\ \cancel{\mathrm{mmol\ KMnO_4}} \times \frac{5\ \mathrm{mmol\ Fe_3O_4}}{3\ \cancel{\mathrm{mmol\ KMnO_4}}}$$

$$\text{mass Fe}_3\text{O}_4 = \left(47.22 \times 0.02242 \times \frac{5}{3}\right) \cancel{\mathrm{mmol\ Fe_3O_4}} \times 0.23154\ \frac{\mathrm{g\ Fe_3O_4}}{\cancel{\mathrm{mmol\ Fe_3O_4}}}$$

$$\%\ \mathrm{Fe_3O_4} = \frac{\left(47.22 \times 0.02242 \times \frac{5}{3}\right) \times 0.23154\ \mathrm{g\ Fe_3O_4}}{0.8040\ \mathrm{g\ sample}} \times 100\% = 50.81\%$$

A 100.0-mL sample of brackish water was made ammoniacal, and the sulfide it contained was titrated with 16.47 mL of 0.02310 M $AgNO_3$. The analytical reaction is

$$2Ag^+ + S^{2-} \rightarrow Ag_2S(s)$$

Calculate the concentration of H_2S in the water in parts per million, c_{ppm}.

Solution

At the end point,

$$\text{stoichiometric ratio} = \frac{1 \text{ mmol } H_2S}{2 \text{ mmol } AgNO_3}$$

$$\text{amount } AgNO_3 = 16.47 \cancel{\text{mL } AgNO_3} \times 0.02310 \frac{\text{mmol } AgNO_3}{\cancel{\text{mL } AgNO_3}}$$

$$\text{amount } H_2S = (16.47 \times 0.02310) \cancel{\text{mmol } AgNO_3} \times \frac{1 \text{ mmol } H_2S}{2 \cancel{\text{mmol } AgNO_3}}$$

$$\text{mass } H_2S = \left(16.47 \times 0.02310 \times \frac{1}{2}\right) \cancel{\text{mmol } H_2S} \times 0.034081 \frac{\text{g } H_2S}{\cancel{\text{mmol } H_2S}}$$

$$= 6.483 \times 10^{-3} \text{ g } H_2S$$

$$c_{ppm} = \frac{6.483 \times 10^{-3} \text{ g } H_2S}{100.0 \cancel{\text{mL sample}} \times 1.00 \text{ g sample}/\cancel{\text{mL sample}}} \times 10^6 \text{ ppm}$$

$$= 64.8 \text{ ppm}$$

The phosphorus in a 4.258-g sample of a plant food was converted to PO_4^{3-} and precipitated as Ag_3PO_4 by adding 50.00 mL of 0.0820 M $AgNO_3$. The excess $AgNO_3$ was back-titrated with 4.06 mL of 0.0625 M KSCN. Express the results of this analysis in terms of % P_2O_5.

Solution

The chemical reactions are

$$\mathrm{P_2O_5 + 9H_2O \rightarrow 2PO_4^{3-} + 6H_3O^+}$$

$$\mathrm{2PO_4^{3-} + 6\ \underset{excess}{Ag^+} \rightarrow 2Ag_3PO_4(\mathit{s})}$$

$$\mathrm{Ag^+ + SCN^- \rightarrow AgSCN(\mathit{s})}$$

The stoichiometric ratios are

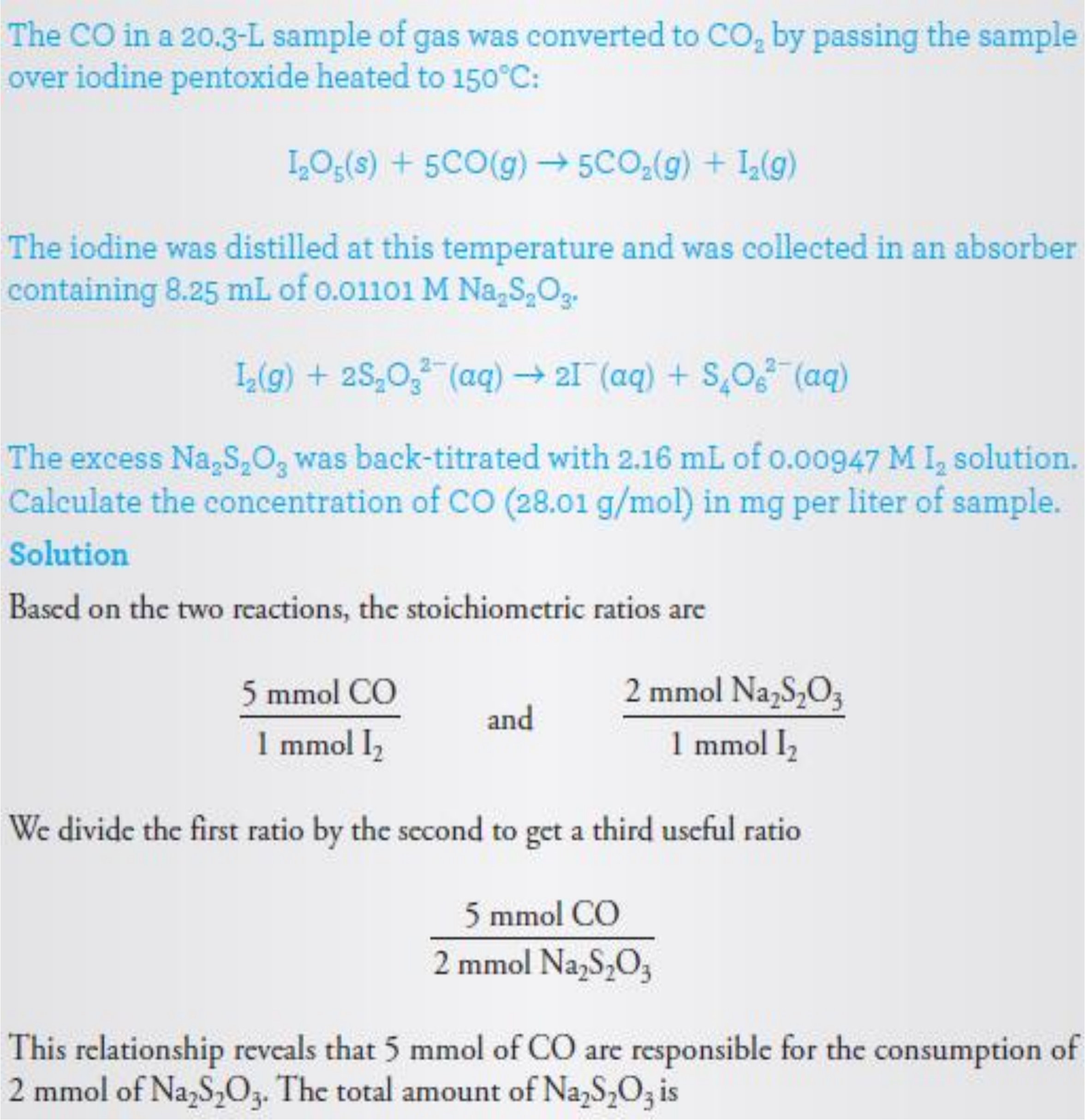
$$\frac{1\ \text{mmol P}_2\text{O}_5}{6\ \text{mmol AgNO}_3} \quad \text{and} \quad \frac{1\ \text{mmol KSCN}}{1\ \text{mmol AgNO}_3}$$

$$\text{total amount AgNO}_3 = 50.00\ \cancel{\text{mL}} \times 0.0820\ \frac{\text{mmol AgNO}_3}{\cancel{\text{mL}}} = 4.100\ \text{mmol}$$

$$\begin{aligned}\text{amount AgNO}_3\text{ consumed by KSCN} &= 4.06\ \cancel{\text{mL}} \times 0.0625\ \frac{\cancel{\text{mmol KSCN}}}{\cancel{\text{mL}}} \\ &\quad \times \frac{1\ \text{mmol AgNO}_3}{\cancel{\text{mmol KSCN}}} \\ &= 0.2538\ \text{mmol}\end{aligned}$$

$$\begin{aligned}\text{amount P}_2\text{O}_5 &= (4.100 - 0.254)\ \cancel{\text{mmol AgNO}_3} \times \frac{1\ \text{mmol P}_2\text{O}_5}{6\ \cancel{\text{mmol AgNO}_3}} \\ &= 0.6410\ \text{mmol P}_2\text{O}_5\end{aligned}$$

$$\%\ \text{P}_2\text{O}_5 = \frac{0.6410\ \cancel{\text{mmol}} \times \dfrac{0.1419\ \text{g P}_2\text{O}_5}{\cancel{\text{mmol}}}}{4.258\ \text{g sample}} \times 100\% = 2.14\%$$



The CO in a 20.3-L sample of gas was converted to CO_2 by passing the sample over iodine pentoxide heated to 150°C:

$$I_2O_5(s) + 5CO(g) \rightarrow 5CO_2(g) + I_2(g)$$

The iodine was distilled at this temperature and was collected in an absorber containing 8.25 mL of 0.01101 M $Na_2S_2O_3$.

$$I_2(g) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$$

The excess $Na_2S_2O_3$ was back-titrated with 2.16 mL of 0.00947 M I_2 solution. Calculate the concentration of CO (28.01 g/mol) in mg per liter of sample.

Solution

Based on the two reactions, the stoichiometric ratios are

$$\frac{5 \text{ mmol CO}}{1 \text{ mmol } I_2} \quad \text{and} \quad \frac{2 \text{ mmol } Na_2S_2O_3}{1 \text{ mmol } I_2}$$

We divide the first ratio by the second to get a third useful ratio

$$\frac{5 \text{ mmol CO}}{2 \text{ mmol } Na_2S_2O_3}$$

This relationship reveals that 5 mmol of CO are responsible for the consumption of 2 mmol of $Na_2S_2O_3$. The total amount of $Na_2S_2O_3$ is

$$\text{amount Na}_2\text{S}_2\text{O}_3 = 8.25\ \cancel{\text{mL Na}_2\text{S}_2\text{O}_3} \times 0.01101\ \frac{\text{mmol Na}_2\text{S}_2\text{O}_3}{\cancel{\text{mL Na}_2\text{S}_2\text{O}_3}}$$

$$= 0.09083\ \text{mmol Na}_2\text{S}_2\text{O}_3$$

The amount of $Na_2S_2O_3$ consumed in the back-titration is

$$\text{amount Na}_2\text{S}_2\text{O}_3 = 2.16\ \cancel{\text{mL I}_2} \times 0.00947\ \frac{\cancel{\text{mmol I}_2}}{\cancel{\text{mL I}_2}} \times \frac{2\ \text{mmol Na}_2\text{S}_2\text{O}_3}{\cancel{\text{mmol I}_2}}$$

$$= 0.04091\ \text{mmol Na}_2\text{S}_2\text{O}_3$$

The number of millimoles of CO can then be calculated by using the third stoichiometric ratio:

$$\text{amount CO} = (0.09083 - 0.04091)\ \cancel{\text{mmol Na}_2\text{S}_2\text{O}_3} \times \frac{5\ \text{mmol CO}}{2\ \cancel{\text{mmol Na}_2\text{S}_2\text{O}_3}}$$

$$= 0.1248\ \text{mmol CO}$$

$$\text{mass CO} = 0.1248\ \cancel{\text{mmol CO}} \times \frac{28.01\ \text{mg CO}}{\cancel{\text{mmol CO}}} = 3.4956\ \text{mg}$$

$$\frac{\text{mass CO}}{\text{vol sample}} = \frac{3.4956\ \text{mg CO}}{20.3\ \text{L sample}} = 0.172\ \frac{\text{mg CO}}{\text{L sample}}$$

Gravimetric Titrations

Mass (weight) or gravimetric titrations differ from their volumetric counterparts in that the mass of titrant is measured rather than the volume.

in a mass titration, a balance and a weighable solution dispenser are substituted for a buret and its markings.

Calculations Associated with Mass Titrations

The most common way to express concentration for mass titrations is the weight concentration, c_w, in weight molar concentration units, M_w, which is the number of moles of a reagent in one kilogram of solution or the number of millimoles in one gram of solution.

Where

n_A is the number of moles of species A and

m_{soln} is the mass of the solution

$$\text{weight molar concentration} = \frac{\text{no. mol A}}{\text{no. kg solution}} = \frac{\text{no. mmol A}}{\text{no. g solution}}$$

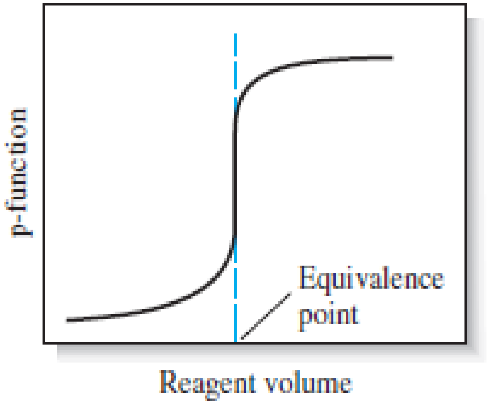
$$c_w(\mathrm{A}) = \frac{n_\mathrm{A}}{m_\mathrm{soln}}$$

Titration Curves

Titration curves are plots of a concentration-related variable versus titrant volume.

Types of Titration Curves

A sigmoidal curve in which the p-function of analyte (or sometimes the titrant) is plotted as a function of titrant volume is shown in **Figure a**.

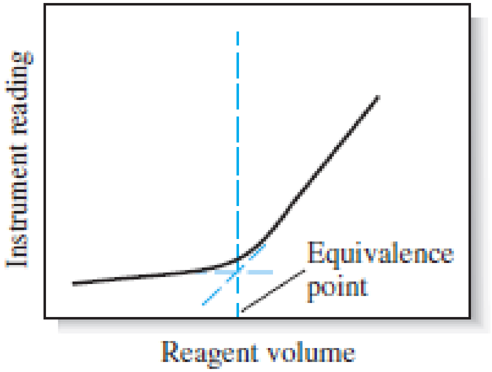


(a) Sigmoidal curve

A linear segment curve, measurements are made on both sides of, but well away from, the equivalence point.

In this type of curve, the vertical axis represents an instrument reading that is directly proportional to the concentration of the analyte or the titrant.

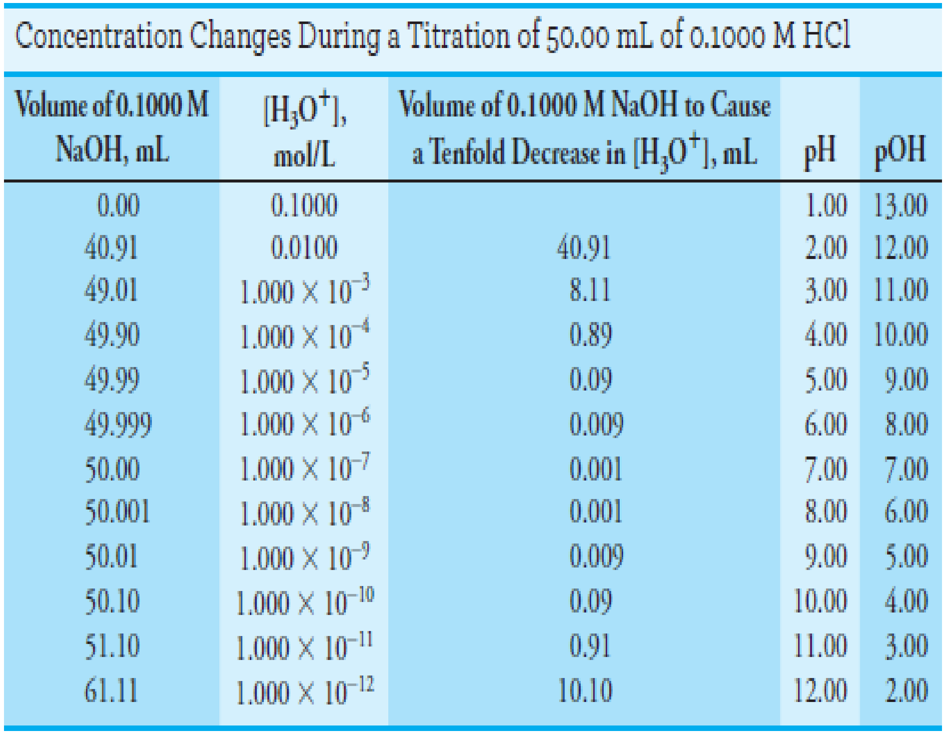
A typical linear segment curve is found in **Figure b**.



(b) Linear segment curve

Concentration Changes During Titrations

- ✓ **The equivalence point in a titration is characterized by major changes in the relative concentrations of reagent and analyte.**
- ✓ **Table below illustrates this phenomenon.**



Concentration Changes During a Titration of 50.00 mL of 0.1000 M HCl

Volume of 0.1000 M NaOH, mL	$[H_3O^+]$, mol/L	Volume of 0.1000 M NaOH to Cause a Tenfold Decrease in $[H_3O^+]$, mL	pH	pOH
0.00	0.1000		1.00	13.00
40.91	0.0100	40.91	2.00	12.00
49.01	1.000×10^{-3}	8.11	3.00	11.00
49.90	1.000×10^{-4}	0.89	4.00	10.00
49.99	1.000×10^{-5}	0.09	5.00	9.00
49.999	1.000×10^{-6}	0.009	6.00	8.00
50.00	1.000×10^{-7}	0.001	7.00	7.00
50.001	1.000×10^{-8}	0.001	8.00	6.00
50.01	1.000×10^{-9}	0.009	9.00	5.00
50.10	1.000×10^{-10}	0.09	10.00	4.00
51.10	1.000×10^{-11}	0.91	11.00	3.00
61.11	1.000×10^{-12}	10.10	12.00	2.00

- ✓ In the second column of the table show the changes in the hydronium ion concentration as a 50.00-mL aliquot of a 0.1000 M solution of hydrochloric acid is titrated with 0.1000 M sodium hydroxide. The neutralization reaction is described by the equation

$$H_3O^+ + OH^- \rightarrow 2H_2O$$

- ✓ In the third column that an addition of 40.91 mL of base is needed to decrease the concentration of H_3O+ by one order of magnitude from 0.100 M to 0.0100 M.

- ✓ Increases in OH- concentration occur at the same time.

- ✓ End-point detection then depends on this large change in the relative concentration of the analyte (or titrant) that occurs at the equivalence point for every type of titration.

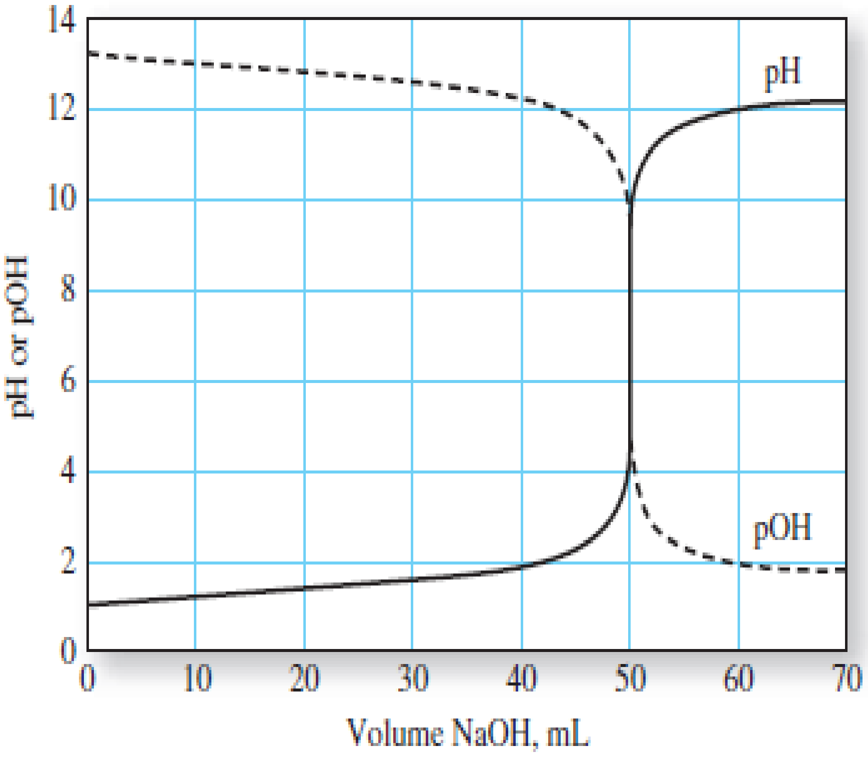


Figure :Titration curves of pH and pOH versus volume of base for the titration of 0.1000 M HCl with 0.1000 M NaOH.

- ❖ As seen in **Figure:** The large changes in relative concentration that occur in the region of chemical equivalence by plotting the negative logarithm of the analyte or the titrant concentration (the p-function) against reagent volume.

- ❖ Titration curves for reactions involving **complex formation, precipitation, and oxidation/reduction** all exhibit the same sharp increase or decrease in p-function in the equivalence-point region.

- ❖ Titration curves define the properties required of an indicator or instrument and allow us to estimate the error associated with titration methods.

References

1) Douglas A. Skoog, Donald M. West, F. James Holler and Stanley R. Crouch, “**Fundamental of Analytical Chemistry**”, ninth editions, Brooks/cole, 2014.

2) Gary D. Christian, Purnendu K. (Sandy) Dasgupta and Kevin A. Schug, “**Analytical Chemistry**”, Seventh edition, John Wiley & Sons, Inc,2014.

3) Daniel C. Harris, “**Quantitative Chemical Analysis**”, Seventh edition, W. H. Freeman and Company, 2007.