

Analytical Chemistry

Analytical chemistry is concerned with the chemical characterization of matter and the answer to two important questions: what is it (qualitative analysis) and how much is it (quantitative analysis)?

Qualitative and Quantitative analysis:

The discipline of analytical chemistry consists of qualitative analysis and quantitative analysis.

- Qualitative analysis deals with the identification of elements, ions, or compounds present in a sample.
- Quantitative analysis deals with the determination of how much of one or more constituents is present. The sample may be solid, liquid, gas, or a mixture.

Qualitative analysis tells us what chemicals are present.

Quantitative analysis tells us how much.

Qualitative tests may be performed by selective chemical reactions or with the use of instrumentation.

A clear distinction should be made between the terms selective and specific:

- A selective reaction or test is one that can occur with other substances but exhibits a degree of preference for the substance of interest.
- A specific reaction or test is one that occurs only with the substance of interest.

Simple qualitative tests are usually more rapid and less expensive than quantitative procedures. Qualitative analysis has been composed of two fields: inorganic and organic.

The Analytical Process

The general analytical process is shown in Figure 1. The analytical chemist should be involved in every step. The analyst is really a problem solver, a critical part of the team deciding what, why, and how.

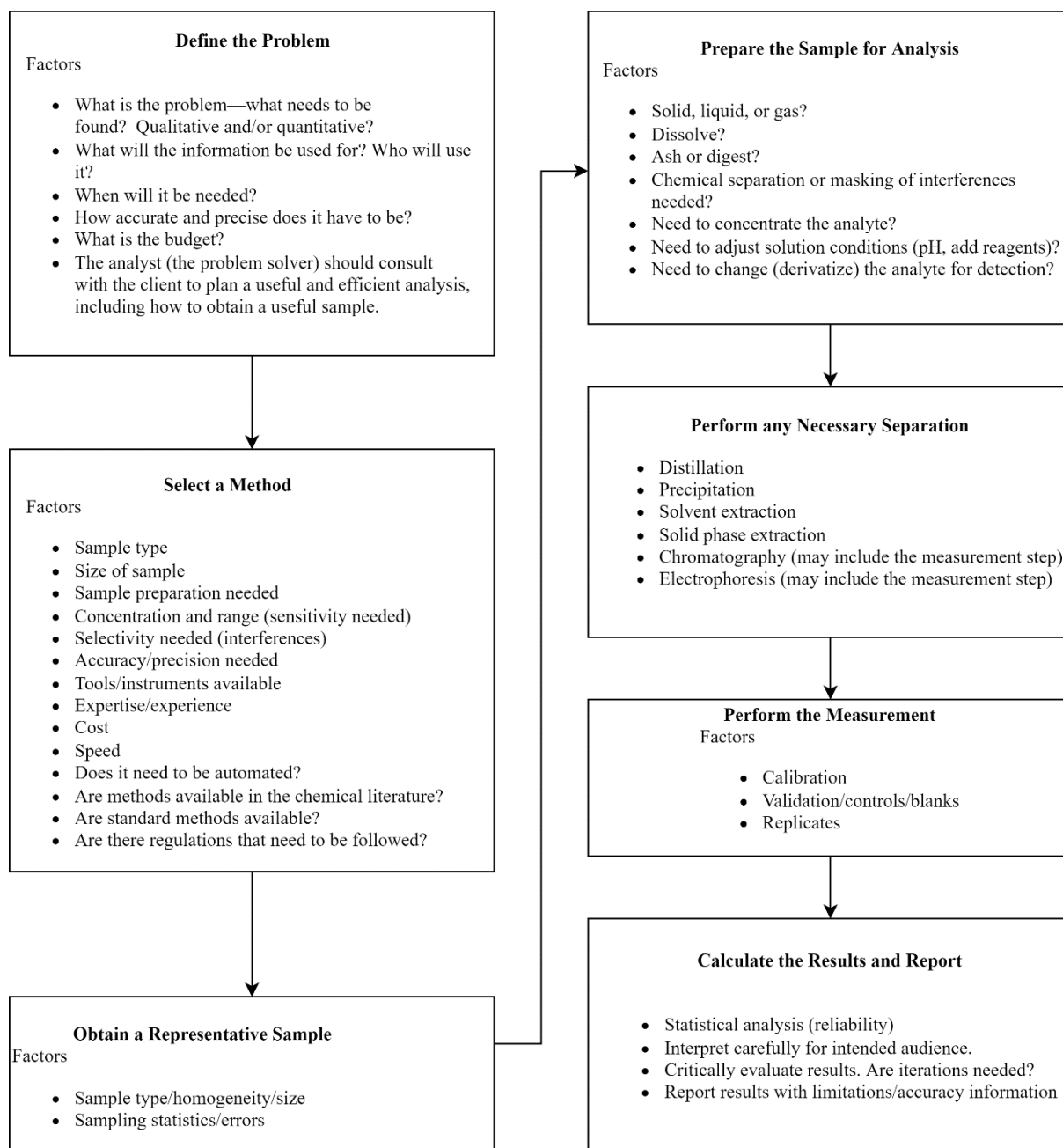


Figure 1. Steps in an analysis

Obtaining a representative sample

The material to be sampled may be solid, liquid, or gas. It may be homogeneous or heterogeneous in composition.

- **The gross sample** consists of several portions of the material to be tested.
- **The laboratory sample** is a small portion of this, taken after homogenization.
- **The analysis sample** is the sample that actually analyzed.

Handling and storing samples

Certain precautions should be taken in handling and storing samples to prevent or minimize contamination, loss, decomposition, or matrix change. In general, one must prevent contamination or alteration of the sample by (1) the container, (2) the atmosphere, (3) heat/temperature, or (4) light.

The stability of the sample must be considered. The preservative must not interfere in the analysis. Trace constituents may be lost during storage by adsorption onto the container walls.

Problems associated with obtaining gross samples

Some of the problems associated with obtaining gross samples of solids, liquids, and gases are considered below:

1. Solids

Sampling of solids is more difficult than other materials due to:

- Inhomogeneity of the material
- Variation in particle size
- Variation within the particle

The *grab sample* is the easiest but usually most unreliable way to sample a material, which is one sample taken at random and assumed to be representative. The grab sample will be satisfactory only if the material from which it is taken is homogeneous.

For most reliable results, it is best to take 1/50 to 1/100 of the total bulk for the gross sample, unless the sample is fairly homogeneous. The larger the particle size, the larger the gross sample should be.

2. Liquids

- Liquid samples tend to be homogeneous and representative samples are much easier to get.
- Liquids mix by diffusion only very slowly and must be shaken to obtain a homogeneous mixture.
- If the material is indeed homogeneous, a simple grab (single random) sample will suffice.
- If liquid samples are not homogeneous, and if they are small enough, they can be shaken and sampled immediately.

Example: there may be particles in the liquid that have tended to settle. Large bodies of liquids

are best sampled after a transfer or, if in a pipe, after passing through a pump when they have undergone thorough mixing.

3. Gases

- The usual method of sampling gases involves sampling into an evacuated container, often a specially treated stainless-steel canister or an inert polyvinyl fluoride (Tedlar) bag is commonly used.
- The sample may be collected rapidly (a grab sample) or over a long period of time, using a small orifice to slowly fill the bag.
- The volume of gross gas samples collected may or may not need to be known. Often, the concentration of a certain analyte in the gas sample is measured, rather than the amount.
- The temperature and pressure of the sample will be important in determining the volume and hence the concentration.
- Gas sampling techniques mentioned here does not concern gases dissolved in liquids, such CO₂ or O₂ in blood. These are treated as liquid samples and are then handled accordingly to measure the gas in the liquid or to release it from the liquid prior to measurement.
- Corrosive gas samples will often react with the container. It is best to analyze the gas by an in-situ analyzer that operates at a temperature in which condensation does not occur.

Preparing the sample for analysis

1. Measure the amount being analyzed (volume or weight) to the degree of precision and accuracy required for the analysis (major constituent, trace constituent and replicate).
2. Solid samples are often analyzed on a dry basis and must be dried in an oven at 110 to 120° C for 1 to 2 h and cooled in a desiccator before weighing, if the sample is stable at the drying temperatures. Some samples may require higher temperatures and longer heating time because of their great affinity for moisture.
3. Analyses may be non-destructive in nature. More often, the sample must be in solution form for measurement, and solids must be dissolved.
 - Inorganic materials may be dissolved in various acids, redox, or complexing media.
 - Acid-resistant material may require fusion with an acidic or basic flux in the molten state to render it soluble in dilute acid or water.
4. Organic materials are to be analyzed for inorganic constituents by either dry ashing (the

burning of organic matter) or wet digestion, to destroy the trace metals.

- In dry ashing, the sample is slowly combusted in a furnace at 400 to 700° C, leaving behind an inorganic residue that is soluble in dilute acid.
 - Alternatively, wet digestion (the oxidation of organic matter) destroys the organic material by heating it with oxidizing acids.
5. For organic analytes, the analyte may be extracted away from the sample or dialyzed, or the sample dissolved in an appropriate solvent. It may be possible to measure the analyte non-destructively.
 6. The solvents and reagents used for dissolution and preparation of the solution should be of high purity (reagent grade). Even so, they may contain trace impurities of the analyte.
 7. It is important to prepare and analyze replicate blanks, particularly for trace analyses. *A blank theoretically consists of all chemicals in the unknown and used in an analysis in the same amounts (including water), run through the entire analytical procedure.* The blank result is subtracted from the analytical sample result to arrive at a net analyte concentration in the sample solution.

Performing necessary chemical separations

In order to eliminate interferences, to provide suitable selectivity in the measurement, or to preconcentrate the analyte for more sensitive or accurate measurement, the analyst must often perform one or more separation steps. Separation steps may include precipitation, extraction into an immiscible solvent, chromatography, dialysis, and distillation.

Performing the measurements

Many available techniques possess varying degrees of selectivity, sensitivity, accuracy and precision, cost, and rapidity. Analytical chemistry research often deals with the optimization of one or more of these parameters, as they relate to a particular analysis or analysis technique.

- **Gravimetric analysis** usually involves the selective separation of the analyte by precipitation, followed by the very nonselective measurement of mass (of the precipitate).
- **Volumetric, or titrimetric, analysis**, the analyte reacts with a measured volume of reagent of known concentration, in a process called titration. A change in some physical or chemical property signals the completion of the reaction.

Gravimetric and volumetric analyses can provide results accurate and precise to a few parts

per thousand (tenth of 1 percent) or better. However, they require relatively large (millimole or milligram) quantities of analyte and are only suited for the measurement of major constituents, although microtitrations may be performed. Volumetric analysis is more rapid than gravimetric analysis and is therefore preferred when applicable.

Instrumental techniques: are used for many analyses and constitute the discipline of instrumental analysis. They are based on the measurement of a physical property of the sample, for example, an electrical property or the absorption of electromagnetic radiation.

Examples: spectrophotometry (ultraviolet, visible, or infrared), fluorimetry, atomic spectroscopy (absorption, emission), mass spectrometry, nuclear magnetic resonance spectrometry (NMR), X-ray spectroscopy (absorption, fluorescence), electroanalytical chemistry (potentiometric, voltametric, electrolytic), chromatography (gas, liquid), and radiochemistry.

Instrumental techniques are

- generally, more sensitive and selective than the classical techniques but are less precise, on the order of 1 to 5% or so.
- much more expensive, especially in terms of initial capital investment. But depending on the numbers of analyses, they may be less expensive when one factors in personnel costs.
- usually more rapid, may be automated, and may be capable of measuring more than one analyte at a time.
- Chromatography techniques are particularly powerful for analyzing complex mixtures. They integrate the separation and measurement steps. Constituents are separated as they are pushed through (eluted from) a column of appropriate material that interacts with the analytes to varying degrees, and these are sensed with an appropriate detector as they emerge from the column, to give a transient peak signal, proportional to the amount of each.

Table 1 compares various analytical methods to be described in this text with respect to sensitivity, precision, selectivity, speed, and cost.

Table 1. Comparison of Different Analytical Methods

Method	Approx. Range (mol/L)	Approx. Precision (%)	Selectivity	Speed	Cost	Principal Uses
Gravimetry	$10^{-1} - 10^{-2}$	0.1	Poor-moderate	Slow	Low	Inorg.
Titrimetry	$10^{-1} - 10^{-4}$	0.1 – 1	Poor-moderate	Moderate	Low	Inorg., Org.
Potentiometry	$10^{-1} - 10^{-6}$	2	Good	Fast	Low	Inorg.
Electrogravimetry, coulometry	$10^{-1} - 10^{-4}$	0.01 – 2	Moderate	Slow-moderate	Moderate	Inorg., Org.
Voltammetry	$10^{-3} - 10^{-10}$	2 – 5	Good	Moderate	Moderate	Inorg., Org.
Spectrophotometry	$10^{-3} - 10^{-6}$	2	Good-moderate	Fast-moderate	Low-moderate	Inorg., Org.
Fluorometry	$10^{-6} - 10^{-9}$	2 – 5	Moderate	Moderate	Moderate	Org.
Atomic spectroscopy	$10^{-3} - 10^{-9}$	2 – 10	Good	Fast	Moderate-high	Inorg., Multielement
Chromatography—Mass Spectrometry	$10^{-4} - 10^{-9}$	2 – 5	Good	Fast-moderate	Moderate-high	Org., multicomponent
Kinetics methods	$10^{-2} - 10^{-10}$	2 – 10	Good-moderate	Fast-moderate	Moderate	Inorg., Org., enzymes.

Instrument Standardization

A calibration curve is the instrument response as a function of concentration. Most instrumental methods of analysis are relative. Instruments register a signal due to some physical property of the solution. Instrument response may be linearly or nonlinearly related to the analyte concentration.

Calibration is accomplished by preparing a series of standard solutions of the analyte at known concentrations and measuring the instrument response to each of these (usually after treating them in the same manner as the samples) to prepare an **analytical calibration curve** of response versus concentration. Figure 2 shows examples of calibration curves obtained in a mass spectrometry experiment. The concentration of an unknown can then be determined from the response, using the calibration curve. With modern computer-controlled instruments, this is done electronically or digitally, and direct readout of concentration is obtained.

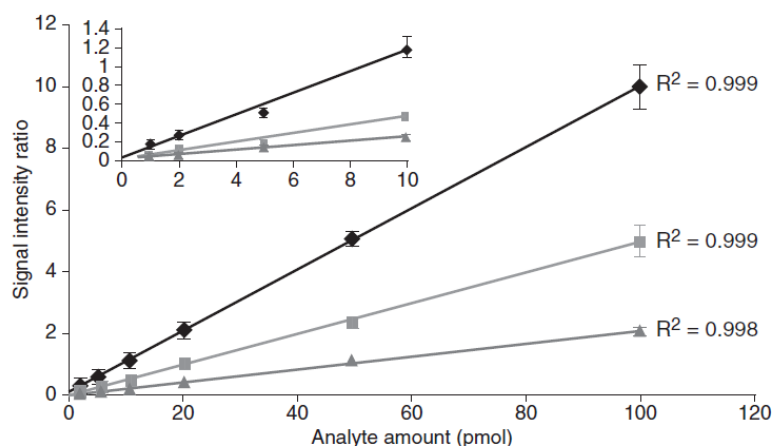


Figure 2. Calibration curves for the measurement of proteins using matrix-assisted laser desorption ionization (MALDI)—mass spectrometry and an ionic liquid matrix (Courtesy of Prof. Michael Gross, Washington University in St. Louis. Reprinted with permission).

STOICHIOMETRIC CALCULATIONS**THE BASICS: ATOMIC, MOLECULAR, AND FORMULA WEIGHTS**

The **atomic weight** for any element is the weight of a specified number of atoms of that element, and that number is the same from one element to another.

A gram-atomic weight of any element contains exactly the same number of atoms of that element as there are carbon atoms in exactly 12 g of carbon 12. This number is Avogadro's number, 6.022×10^{23} , the number of atoms present in 1 g-at wt of any element.

Molecular weight (MW) is the sum of the atomic weights of the atoms that make up a compound.

Formula weight (FW) is a more accurate description for substances that don't exist as molecules but exist as ionic compounds (strong electrolytes—acids, bases, salts). The term **molar mass** is sometimes used in place of formula weight.

MOLES

Mole is Avogadro's number (6.022×10^{23}) of atoms, molecules, ions, or other species. Numerically, it is the atomic, molecular, or formula weight of a substance expressed in **grams**.

A mole of any substance contains the same number of atoms or molecules as a mole of any other substance, atoms will react in the same mole ratio as their atom ratio in the reaction.

Example1: Calculate the weight of one mole of $\text{CaSO}_4 \cdot 7\text{H}_2\text{O}$.

Solution:

One mole is the formula weight expressed in grams. The formula weight is

Ca	40.08
S	32.06
11 O	176.00
14 H	14.11
	262.25 g/mol

$$\text{Moles} = \frac{\text{grams}}{\text{formula weight} \left(\frac{\text{g}}{\text{mol}} \right)}$$

Where the formula weight represents the atomic or molecular weight of the substance. Thus,

$$\text{Mole Na}_2\text{SO}_4 = \frac{\text{g}}{\text{FW}} = \frac{\text{g}}{142.01 \text{ g/mol}}$$

$$\text{Mole Ag}^+ = \frac{\text{g}}{\text{FW}} = \frac{\text{g}}{107.870 \text{ g/mol}}$$

For very small quantities, the formula of calculating millimoles is

$$\text{Millimoles} = \frac{\text{milligrams}}{\text{formula weight} \left(\frac{\text{mg}}{\text{mmol}} \right)}$$

Example 2: Calculate the number of moles in 500 mg Na_2WO_4 (sodium tungstate).

Solution

$$\frac{500 \text{ mg}}{293.8 \text{ mg/mmol}} \times 0.001 \text{ mol/mmol} = 0.00170 \text{ mol}$$

Example 3: What is the weight, in milligrams, of 0.250 mmol Fe_2O_3 (ferric oxide)

Solution:

$$0.250 \text{ mmol} \times 159.7 \text{ mg/mmol} = 39.9 \text{ mg}$$

CONCENTRATIONS OF SOLUTIONS**MOLARITY**

A one-**molar** solution is defined as one that contains one mole of substance in each liter of a solution. It is prepared by dissolving one mole of the substance in the solvent and diluting to a final volume of one liter in a volumetric flask; or a fraction or multiple of the mole may be dissolved and diluted to the corresponding fraction or multiple of a liter.

The **molarity** of a solution is expressed as moles per liter or as millimoles per millilitre. Molar is abbreviated as *M*.

$$\begin{aligned}\text{Moles} &= (\text{mole/liter}) \times \text{liters} \\ &= \text{molarity} \times \text{liters}\end{aligned}$$

Example 4: A solution is prepared by dissolving 1.26 g AgNO₃ in a 250-mL volumetric flask and diluting to volume. Calculate the molarity of the silver nitrate solution. How many millimoles AgNO₃ were dissolved?

Solution

$$\begin{aligned}M &= \frac{1.26\text{g}/169.9 \text{ (g/mol)}}{0.250 \text{ L}} = 0.0297 \text{ mol/L (0.0297 mmol/mL)} \\ \text{Millimoles} &= (0.0297 \text{ mmol/mL})(250 \text{ mL}) = 7.42 \text{ mmol}\end{aligned}$$

Example 5: How many grams per millilitre of NaCl are contained in a 0.250 *M* solution?

Solution:

$$\begin{aligned}0.250 \text{ mol/L} &= 0.250 \text{ mmol/mL} \\ 0.250 \text{ mmol/mL} \times 58.4 \text{ mg/mmol} \times 0.001 \text{ g/mg} &= 0.0146 \text{ g/mL}\end{aligned}$$

Example 6: How many grams Na₂SO₄ should be weighed out to prepare 500mL of a 0.100 *M*?

Solution :

$$\begin{aligned}500 \text{ mL} \times 0.100 \text{ mmol/mL} &= 50.0 \text{ mmol} \\ 50.0 \text{ mmol} \times 142 \text{ mg/mmol} \times 0.001 \text{ g/mg} &= 7.10 \text{ g}\end{aligned}$$

Example 7: Calculate the concentration of potassium ion in grams per liter after mixing 100 mL of 0.250 *M* KCl and 200 mL of 0.100 *M* K₂SO₄.

Solution

$$\text{mmol K}^+ = \text{mmol KCl} + 2 \times \text{mmol K}_2\text{SO}_4$$

$$\begin{aligned}
 &= 100 \text{ mL} \times 0.250 \text{ mmol/mL} + 2 \times 200 \text{ mL} \times 0.100 \text{ mmol/mL} \\
 &= 65.0 \text{ mmol in 300 mL} \\
 &= \frac{65.0 \text{ mmol} \times 39.1 \text{ mg/mmol} \times 0.001 \text{ g/mg} \times 1000 \text{ mL/L}}{300 \text{ mL}} \\
 &= 8.47 \text{ g/L}
 \end{aligned}$$

NORMALITY

A one-**normal** solution contains one equivalent per liter.

An **equivalent** represents the mass of material providing Avogadro's *number of reacting units*.

The number of equivalents is given by the number of moles multiplied by the number of reacting units per molecule or atom; the **equivalent weight** is the formula weight divided by the number of reacting units.

For acids and bases, the number of reacting units is based on the number of protons (i.e., hydrogen ions) an acid will furnish, or a base will react with. For oxidation–reduction reactions it is based on the number of electrons an oxidizing or reducing agent will take on or supply.

Thus, for example, sulfuric acid, H_2SO_4 , has two reacting units of protons; that is, there are two equivalents of protons in each mole. Therefore,

$$\text{Equivalent weight} = \frac{98.08 \text{ g/mol}}{2 \text{ eq/mol}} = 49.04 \text{ g/eq}$$

The mormality of sulfuric acid solution is twice its normality, that is, $N = (g/eq \text{ wt})/L$. The number of equivalents is given by

$$\text{Number of equivalents (eq)} = \frac{\text{wt (g)}}{\text{eq wt (g/eq)}} = \text{normality (eq/L)} \times \text{volume (L)}$$

MOLALITY

A one-**molal** solution contains one mole per 1000 g of **solvent**. The molal concentration is convenient in physicochemical measurements of the colligative properties of substances, such as freezing point depression, vapor pressure lowering, and osmotic pressure because colligative properties depend solely on the number of solute particles present in solution per mole of solvent. Molal concentrations are not temperature dependent as molar and normal concentrations since the solution volume in molar and normal concentrations is temperature dependent.

DENSITY CALCULATIONS

The concentrations of many fairly concentrated commercial acids and bases are usually given in terms of percent by weight. It is frequently necessary to prepare solutions of a given approximate molarity from these substances. In order to do so, we must know the density in order to calculate the molarity. **Density** is the weight per unit volume at the specified temperature, usually g/mL or g/cm³ at 20°C.

Sometimes substances list **specific gravity** rather than density. Specific gravity is defined as the ratio of the mass of a body (e.g., a solution), usually at 20°C, to the mass of an equal volume of water at 4°C (or sometimes 20°C). That is, specific gravity is the *ratio of the densities of the two substances*; it is a dimensionless quantity. Since the density of water at 4°C is 1.00000 g/mL, density and specific gravity are equal when referred to water at 4°C. But normally specific gravity is referred to water at 20°C; density is equal to specific gravity × 0.99821 (the density of water is 0.99821 g/mL at 20°C).

$$\text{Density of solution at } 20^\circ\text{C} = \text{Specific gravity of solution} * 0.99821 \text{ g/mL}$$

Example 8: How many millilitres of concentrated sulfuric acid, 94.0% (g/100 g solution), density 1.831 g/cm³, are required to prepare 1 liter of a 0.100 M solution?

Solution:

Consider 1 cm³ = 1 mL. The concentrated acid contains 0.940 g H₂SO₄ per gram of solution, and the solution weighs 1.831 g/mL. The product of these two numbers, then, gives the gram H₂SO₄ per millilitre of solution:

$$\begin{aligned} M &= \frac{(0.940 \text{ g H}_2\text{SO}_4/\text{g solution})(1.831 \text{ g/mL})}{98.1 \text{ g/mol}} \times 1000 \text{ mL/L} \\ &= 17.5 \text{ mol H}_2\text{SO}_4/\text{L solution} \end{aligned}$$

We must dilute this solution to prepare 1 L of 0.100 M solution. The same number of millimoles of H₂SO₄ must be taken as will be contained in the final solution. Since mmol = M × mL and mmol dilute acid = mmol concentrated acid,

$$\begin{aligned} \text{mmol} &= M \times 1000 \text{ mL} = 17.5 M \times \text{mL} \\ x &= 5.71 \text{ mL concentrated acid to be diluted to } 1000 \text{ mL} \end{aligned}$$

DILUTIONS

Mass is conserved:

$$M_1V_1 = M_2V_2$$

If a solution of molarity M_1 and volume V_1 is diluted to V_2 , the molarity M_2 will obey this relationship. The general equation $C_1V_1 = C_2V_2$ will hold as long as C_1 and C_2 are in the same units, regardless of the specific unit.

Example 9: You wish to prepare 500 mL of a 0.100 M $K_2Cr_2O_7$ solution from a 0.250 M solution. What volume of the 0.250 M solution must be diluted to 500 mL?

Solution

$$M_{final} \times mL_{final} = M_{original} \times mL_{original}$$

$$0.100 \text{ mmol/mL} \times 500 \text{ mL} = 0.250 \text{ mmol/mL} \times mL_{original}$$

$$mL_{original} = 200 \text{ mL}$$

Example 10: What volume of 0.40 M $Ba(OH)_2$ must be added to 50 mL of 0.30 M NaOH to give a solution 0.50 M in OH^- ?

Solution

Volumes of dilute aqueous solutions can be assumed to be additive, i.e., if x mL of $Ba(OH)_2$ is added to 50 mL NaOH, the total volume is going to be $50 + x$ mL. We can use a modified form of $C_1V_1 = C_2V_2$ where all the initial solution components are added in this manner, and these sum up to the final solution components:

$$\Sigma C_{in} \times V_{in} = C_{fin} \times V_{fin}$$

$$M_{NaOH} \times V_{NaOH} + 2 \times M_{Ba(OH)_2} \times V_{Ba(OH)_2} = M_{OH^-} \times V_{fin}$$

Note that 1 M $Ba(OH)_2$ is 2 M in OH^-

$$0.3 \text{ M} \times 50 \text{ mL} + 2 \times 0.40 \text{ M} \times x \text{ mL} = 0.50 \text{ M} \times (50 + x) \text{ mL.}$$

$$x = 33 \text{ mL.}$$

Alternatively,

Let $x = \text{mL } Ba(OH)_2$. The final volume is $(50 + x)$ mL.

$$\text{mmol } OH^- = \text{mmol NaOH} + 2 \times \text{mmol } Ba(OH)_2$$

$$0.50 \text{ M} \times (50 + x) \text{ mL} = 0.30 \text{ M NaOH} \times 50 \text{ mL} + 2 \times 0.40 \text{ M } Ba(OH)_2 \times x \text{ mL}$$

$$x = 33 \text{ mL } Ba(OH)_2$$

SOLID SAMPLES

Calculations for solid samples are based on weight. The most common way of expressing the results of macro determinations is to give the weight of analyte as a **percent** of the weight of sample (weight/weight basis). The weight units of analyte and sample are the same. For example, a limestone sample weighing 1.267 g and containing 0.3684 g iron would contain

$$0.3684 \text{ g} / 1.267 \text{ g} \times 100\% = 29.08\% \text{ Fe}$$

The general formula for calculating percent on a weight/weight basis, which is the same as parts per hundred, then is

$$\%(\text{wt/wt}) = \left[\frac{\text{wt solute (g)}}{\text{wt sample (g)}} \right] \times 10^2 \text{ (\%/g solute/g sample)}$$

Note that the grams of solute do *not* cancel the grams of sample solution; the fraction represents grams of solute per gram of sample.

Trace concentrations are usually given in smaller units, such as **parts per thousand** (ppt, ‰), **parts per million** (ppm), or **parts per billion** (ppb). These are calculated in a manner similar to parts per hundred (%):

$$\text{ppt (wt/wt)} = \left[\frac{\text{wt solute (g)}}{\text{wt sample (g)}} \right] \times 10^3 \text{ (ppt/g solute/g sample)}$$

$$\text{ppm (wt/wt)} = \left[\frac{\text{wt solute (g)}}{\text{wt sample (g)}} \right] \times 10^6 \text{ (ppm/g solute/g sample)}$$

$$\text{ppb (wt/wt)} = \left[\frac{\text{wt solute (g)}}{\text{wt sample (g)}} \right] \times 10^9 \text{ (ppb/g solute/g sample)}$$

Trace gas concentrations are also expressed in ppb, ppm, and so forth. In this case the ratio refers not to mass ratios, but to volume ratios (which for gases is the same as mole ratios). Thus, present atmospheric CO₂ concentration of 390 ppm means that each liter of air (this is a million microliters) contains 390 microliters of CO₂.

Common Units for Expressing Trace Concentrations

Unit	Abbreviation	wt/wt	wt/vol	vol/vol
Parts per million (1 ppm = 10 ⁻⁴ %)	ppm	mg/kg μg/g	mg/L μg/mL	μL/L nL/mL
Parts per billion (1 ppb = 10 ⁻⁷ % = 10 ⁻³ ppm)	ppb	μg/kg ng/g	μg/L ng/mL	nL/L pL/mL ^a
Milligram percent	mg%	mg/100 g	mg/100 mL	

Example 11: A 2.6 g sample of plant tissue was analyzed and found to contain 3.6 μg zinc.

What is the concentration of zinc in the plant in ppm? In ppb?

Solution:

$$\frac{3.6 \mu\text{g}}{2.6 \text{ g}} = 1.4 \frac{\mu\text{g}}{\text{g}} \equiv 1.4 \text{ ppm}$$

$$\frac{3.6 \times 10^3 \text{ ng}}{2.6 \text{ g}} = 1.4 \times 10^3 \text{ ng/g} \equiv 1400 \text{ ppb}$$

One ppm is equal to 1000 ppb. One ppb is equal to 10⁻⁷ %

Example 12:

(a) Show how 35 ppm CO is 40 mg/m³.

(b) What is 75 ppb SO₂ at 25°C in μg/m³?

The ideal gas laws (PV = RT, where R is the universal gas constant, 0.0821 L – atm/(mole K)) dictate that the volume of 1 mole of any gas at 1 atm pressure and 25°C is 24.5 L (at 0°C, this is 22.4 L).

Solution:

Because gas volumes change as a function of temperature and pressure, we must refer to some temperature and pressure. When this is not specified, we assume a temperature of 25°C and a pressure of 1 atm.

$$(a) \ 35 \text{ ppm} = \frac{35 \text{ mol CO}}{10^6 \text{ mol Air}} = \frac{35 \times 10^{-6} \text{ mol CO}}{\text{mol Air}} = \frac{35 \mu\text{mol CO}}{\text{mol Air}}$$

$$\text{FW CO} = 28$$

$$35 \mu\text{mol CO} / \text{mol air} \times 28 \mu\text{g}/\mu\text{mol} = 980 \mu\text{g CO} / \text{mol air} \\ = 980 \mu\text{g CO in } 24.5 \text{ L air}$$

$$\frac{980 \mu\text{g CO}}{24.5 \text{ L}} \times \frac{1 \text{ g}}{10^6 \mu\text{g}} \times \frac{1000 \text{ mg}}{1 \text{ g}} \times \frac{1000 \text{ L}}{1 \text{ m}^3} = 40 \text{ mg/m}^3$$

$$(b) \ 75 \text{ ppb} = \frac{75 \text{ mol SO}_2}{10^9 \text{ mol Air}} = \frac{75 \times 10^{-9} \text{ mol SO}_2}{\text{mol Air}} = \frac{75 \text{ nmol SO}_2}{\text{mol Air}}$$

FW of $\text{SO}_2 = 64$

$$\frac{75 \text{ nmol CO}}{24.5 \text{ L}} \times \frac{1 \text{ } \mu\text{mol}}{1000 \text{ nmol}} \times \frac{64 \text{ } \mu\text{g}}{\text{ } \mu\text{mol}} \times \frac{1000 \text{ L}}{1 \text{ m}^3} = 196 \text{ } \mu\text{g/m}^3 \approx 0.2 \text{ mg/m}^3$$

LIQUID SAMPLES

Results for liquid samples can be reported on a weight/weight basis, as above, or they may be reported on a **weight/volume basis**. The latter is more common, at least in the clinical laboratory. The calculations are similar to those above. Percent on a weight/volume basis is equal to grams of analyte per 100mL of sample, while mg% is equal to milligrams of analyte per 100mL of sample.

$$\% \text{ (wt/vol)} = \left[\frac{\text{wt solute (g)}}{\text{vol sample (mL)}} \right] \times 10^2 \text{ (\%/g solute/mL sample)}$$

$$\text{ppm (wt/vol)} = \left[\frac{\text{wt solute (g)}}{\text{vol sample (mL)}} \right] \times 10^6 \text{ (ppm/g solute/mL sample)}$$

$$\text{ppb (wt/vol)} = \left[\frac{\text{wt solute (g)}}{\text{vol sample (mL)}} \right] \times 10^9 \text{ (ppb/g solute/mL sample)}$$

$$\text{ppt (wt/vol)} = \left[\frac{\text{wt solute (g)}}{\text{vol sample (mL)}} \right] \times 10^{12} \text{ (ppt/g solute/mL sample)}$$

Example 13: A 25.0 μL serum sample was analyzed for glucose content and found to contain 26.7 μg . Calculate the concentration of glucose in $\mu\text{g/mL}$ and in mg/dL .

Solution:

$$25.0 \text{ } \mu\text{L} \times \frac{1 \text{ mL}}{1000 \text{ } \mu\text{L}} = 2.50 \times 10^{-2} \text{ mL}$$

$$26.7 \text{ } \mu\text{g} \times \frac{1 \text{ g}}{10^6 \text{ } \mu\text{g}} = 2.67 \times 10^{-6} \text{ g}$$

$$\text{glucose concentration} = \frac{2.67 \times 10^{-6} \text{ g glucose}}{2.50 \times 10^{-2} \text{ mL serum}} \times 10^6 \text{ } \mu\text{g/g} = 1.07 \times 10^2 \text{ } \mu\text{g/mL}$$

This is numerically the same in ppm units, also

$$\begin{aligned} \text{Glucose concentration} &= 1.07 \times 10^2 \frac{\text{ } \mu\text{g}}{\text{mL}} \times \frac{0.001 \text{ mg}}{1 \text{ } \mu\text{g}} \times \frac{100 \text{ mL}}{1 \text{ dL}} \\ &= 107 \text{ mg/dL} \end{aligned}$$

Note the relationship: 10 ppm (wt/vol) = 1 mg/dL

Example 14: The concentration of zinc in blood serum is about 1mg/L. Express this as meq/L.

Solution:

$$\text{meq} = \frac{\text{mg}}{\text{eq wt (mg/eq)}} = \frac{\text{mg}}{\text{FW (mg/mmol)/}n \text{ (meq/mmol)}}$$

$$n = \text{charge on ion}$$

The equivalent weight of Zn^{2+} is $65.4 \text{ (mg/mmol)}/2 \text{ (meq/mmol)} = 32.7 \text{ mg/meq}$.

Therefore,

$$\frac{1 \text{ mg Zn/L}}{32.7 \text{ mg/meq}} = 3.06 \times 10^{-2} \text{ meq/L Zn}$$

Volumetric Analysis

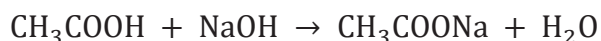
Volumetric or titrimetric analyses are among the most useful and accurate analytical techniques, especially for millimole amounts of analyte. They are rapid and can be automated, and they can be applied to smaller amounts of analyte when combined with a sensitive instrumental technique for detecting the completion of the titration reaction, for example, pH measurement.

TITRATION

In a **titration**, the test substance (analyte) reacts with an added reagent of known concentration, generally instantaneously. The reagent of known concentration is referred to as a **standard solution**. It is typically delivered from a burette; the solution delivered by the burette is called the **titrant**.

The volume of titrant required to just completely react with the analyte is measured. Since we know the reagent concentration as well as the reaction stoichiometry between the analyte and the reagent, we can calculate the amount of analyte. The requirements of a titration are as follows:

1. The reaction must be **stoichiometric**. That is, there must be a well-defined and known reaction between the analyte and the titrant. In the titration of acetic acid in vinegar with sodium hydroxide, for example, a well-defined reaction takes place:



2. The reaction should be *rapid*. Most ionic reactions, as above, are very rapid.

3. There should be *no side reactions*; the reaction should be specific. If there are interfering substances, these must be removed or independently determined and their influence subtracted from the overall signal ($C_{\text{analyte}} = C_{\text{total}} - C_{\text{interference}}$). In the above example, there should be no other acids present.
4. There should be a *marked change in some property of the solution when the reaction is complete*. This may be a change in color of the solution or in some electrical or other physical property of the solution.
5. The point at which an equivalent or stoichiometric amount of titrant is added is called the **equivalence point**. The point at which the reaction is *observed* to be complete is called the **end point**, that is, when a change in some property of the solution is detected. The end point should coincide with the equivalence point or be at a reproducible interval from it.
6. The reaction should be **quantitative**. That is, the equilibrium of the reaction should be far to the right so that a sufficiently *sharp* change will occur at the end point to obtain the desired accuracy. If the equilibrium does not lie far to the right, then there will be gradual change in the property marking the end point (e.g., pH) and this will be difficult to detect precisely.

CLASSIFICATION OF TITRATION METHODS

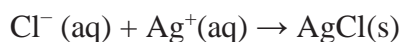
There are four general classes of volumetric or titrimetric methods.

1. *Acid–Base*: many compounds, both inorganic and organic, are either acids or bases and can be titrated, respectively, with a standard solution of a strong base or a strong acid. The end points of these titrations are easy to detect, either by means of an indicator or by following the change in pH with a pH meter.
2. *Precipitation*: the titrant forms an insoluble product with the analyte. An example is the titration of chloride ion with silver nitrate solution to form silver chloride precipitate. Again, indicators can be used to detect the end point, or the potential of the solution can be monitored electrically.
3. *Complexometric*: the titrant is a reagent that forms a water-soluble complex with the analyte, a metal ion. The titrant is often a **chelating agent**. Ethylenediaminetetraacetic acid (EDTA) is one of the most useful chelating agents used for titration. It will react with a large number of metal ions, and the reactions can be controlled by adjustment of pH. Indicators can be used to form a highly colored complex with the metal ion.
4. *Reduction–Oxidation*: These “redox” titrations involve the titration of an oxidizing agent with a reducing agent, or vice versa. An oxidizing agent gains electrons and a

reducing agent loses electrons in a reaction between them. There must be a sufficiently large difference between the oxidizing and reducing capabilities of these agents for the reaction to go to completion and give a sharp end point; that is, one should be a fairly strong oxidizing agent (strong tendency to gain electrons) and the other a fairly strong reducing agent (strong tendency to lose electrons). Appropriate indicators for these titrations are available; various electrometric means to detect the end point may also be used.

Volumetric Calculations

Assume 25.0 mL of 0.100 M AgNO₃ is required to titrate a sample containing sodium chloride. The reaction is



Since Ag⁺ and Cl⁻ react on a 1:1 molar basis, the number of millimoles of Cl⁻ is equal to the number of millimoles of Ag⁺ needed for titration. We can calculate the milligrams of NaCl as follows:

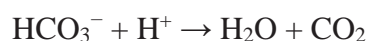
$$\begin{aligned} \text{mmol}_{\text{NaCl}} &= \text{mL}_{\text{AgNO}_3} \times M_{\text{AgNO}_3} \\ &= 25.0 \text{ mL} \times 0.100 \text{ (mmol/mL)} = 2.50 \text{ mmol} \end{aligned}$$

$$\begin{aligned} \text{mg}_{\text{NaCl}} &= \text{mmol} \times \text{FW}_{\text{NaCl}} \\ &= 2.50 \text{ mmol} \times 58.44 \text{ mg/mmol} = 146 \text{ mg} \end{aligned}$$

We can calculate the percentage of analyte A that reacts on a 1:1 mole basis with the titrant using the following general formula:

$$\begin{aligned} \% \text{Analyte} &= \text{fraction}_{\text{analyte}} \times 100\% = \frac{\text{mg}_{\text{analyte}}}{\text{mg}_{\text{sample}}} \times 100\% \\ &= \frac{\text{mmol analyte} \times \text{FW}_{\text{analyte}}(\text{mg/mol})}{\text{mg}_{\text{sample}}} \times 100 \\ &= \frac{M_{\text{titrant}}(\text{mmol/mL}) \times \text{mL}_{\text{titrant}} \times \text{FW}_{\text{analyte}}(\text{mg/mmol})}{\text{mg}_{\text{sample}}} \times 100 \end{aligned}$$

Example 15: A 0.4671-g sample containing sodium bicarbonate was dissolved and titrated with standard 0.1067 M hydrochloric acid solution, requiring 40.72 mL. The reaction is



Calculate the percent sodium bicarbonate in the sample.

Solution:

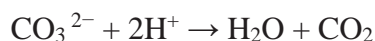
The millimoles of sodium bicarbonate are equal to the millimoles of acid used to titrate it, since they react in a 1:1 ratio.

$$\text{mmol}_{\text{HCl}} = 0.1067 \text{ mmol/mL} \times 40.72 \text{ mL} = 4.3448 \text{ mmol}_{\text{HCl}} \equiv \text{mmol NaHCO}_3$$

$$\text{mg}_{\text{NaHCO}_3} = 4.3448 \text{ mmol} \times 84.01 \text{ mg/mmol} = 365.01 \text{ mg NaHCO}_3$$

$$\% \text{NaHCO}_3 = \frac{365.01 \text{ mg NaHCO}_3}{467.1 \text{ mg}_{\text{sample}}} \times 100\% = 78.14\% \text{ NaHCO}_3$$

Example 16: A 0.2638-g soda ash sample is analyzed by titrating the sodium carbonate with the standard 0.1288 M hydrochloride solution, requiring 38.27 mL. The reaction is



Calculate the percent sodium carbonate in the sample.

Solution:

The millimoles of sodium carbonate is equal to one-half the millimoles of acid used to titrate it, since they react in a 1:2 ratio ($a/t = \frac{1}{2}$).

$$\text{mmol}_{\text{HCl}} = 0.1288 \text{ mmol/mL} \times 38.27 \text{ mL} = 4.929 \text{ mmol HCl}$$

$$\text{mmol}_{\text{Na}_2\text{CO}_3} = 4.929 \text{ mmol HCl} \times \frac{1}{2} \left(\frac{\text{mmol Na}_2\text{CO}_3}{\text{mmol HCl}} \right) = 2.4645 \text{ mmol Na}_2\text{CO}_3$$

$$\text{mg}_{\text{Na}_2\text{CO}_3} = 2.4645 \text{ mmol} \times 105.99 \frac{\text{mg Na}_2\text{CO}_3}{\text{mmol}} = 261.21 \text{ mg Na}_2\text{CO}_3$$

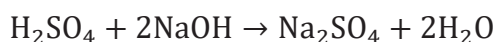
$$\% \text{Na}_2\text{CO}_3 = \frac{261.21 \text{ mg Na}_2\text{CO}_3}{263.8 \text{ mg}_{\text{sample}}} \times 100\% = 99.02\% \text{ Na}_2\text{CO}_3$$

Or, combining all the steps at once,

$$\begin{aligned} \% \text{Na}_2\text{CO}_3 &= \frac{M_{\text{HCl}} \times mL_{\text{HCl}} \times \frac{1}{2} (\text{mmol Na}_2\text{CO}_3/\text{mmol HCl}) \times FW_{\text{Na}_2\text{CO}_3}}{\text{mg}_{\text{sample}}} \times 100 \\ &= \frac{0.1288 \text{ mmol HCl} \times 38.27 \text{ mL HCl} \times \frac{1}{2} (\text{mmol Na}_2\text{CO}_3/\text{mmol HCl}) \times 105.99 (\text{mg Na}_2\text{CO}_3/\text{mmol})}{263.8 \text{ mg}_{\text{sample}}} \\ &\times 100\% = 99.02\% \text{ Na}_2\text{CO}_3 \end{aligned}$$

Example 17: How many millilitres of 0.25 M Solution H₂SO₄ will react with 10 mL of a 0.25 M solution of NaOH?

Solution:



One half as many millimoles of H_2SO_4 as of NaOH will react, or

$$M_{\text{H}_2\text{SO}_4} \times \text{mL}_{\text{H}_2\text{SO}_4} = M_{\text{NaOH}} \times \text{mL}_{\text{NaOH}} \times \frac{1}{2} (\text{mmol H}_2\text{SO}_4 / \text{mmol NaOH})$$

Therefore,

$$\begin{aligned} \text{mL}_{\text{H}_2\text{SO}_4} &= \frac{0.25 \text{ mmol NaOH/mL} \times 10 \text{ mL NaOH} \times \frac{1}{2} (\text{mmol H}_2\text{SO}_4 / \text{mmol NaOH})}{0.25 \text{ mmol H}_2\text{SO}_4 / \text{mL}} \\ &= 5.0 \text{ mL H}_2\text{SO}_4 \end{aligned}$$

Example 18: A sample of impure salicylic acid, $\text{C}_6\text{H}_4(\text{OH})\text{COOH}$ (one titratable proton), is analyzed by titration. What size sample should be taken so that the percent purity is equal to five times the milliliters of 0.0500 M NaOH used to titrate it?

Solution:

Let $x = \text{mL NaOH}$, % salicylic acid (HA) = $5x$:

$$\% \text{HA} = \frac{M_{\text{NaOH}} \times \text{mL}_{\text{NaOH}} \times (1 \text{ mmol HA/mmole NaOH}) \times \text{FW}_{\text{HA}} (\text{mg/mmole})}{\text{mg}_{\text{sample}}} \times 100\%$$

$$5x \% = \frac{0.0500 \text{ M} \times x \text{ mL NaOH} \times 1 \times 138 \text{ mg HA/mmole}}{\text{mg}_{\text{sample}}} \times 100\%$$

$$\text{mg}_{\text{sample}} = 138 \text{ mg}$$

STANDARDIZATION AND TITRATION CALCULATIONS

$$\text{mmol}_{\text{standard}} = \frac{\text{mg}_{\text{standard}}}{\text{FW}_{\text{standard}} (\text{mg/mmole})}$$

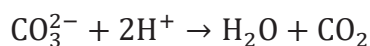
$$\begin{aligned} \text{mmol}_{\text{titrant}} &= M_{\text{titrant}} (\text{mmol/mL}) \times \text{mL}_{\text{titrant}} \\ &= \text{mmol}_{\text{standard}} \times t/a (\text{mmol}_{\text{titrant}} / \text{mmol}_{\text{standard}}) \end{aligned}$$

$$M_{\text{titrant}} (\text{mmol/mL}) = \frac{\text{mmol}_{\text{standard}} \times t/a (\text{mmol}_{\text{titrant}} / \text{mmol}_{\text{standard}})}{\text{mL}_{\text{titrant}}}$$

Or, combining all steps at once,

$$\begin{aligned} M_{\text{titrant}} (\text{mmol/mL}) \\ &= \frac{\text{mg}_{\text{standard}} / \text{FW}_{\text{standard}} (\text{mg/mmole}) \times t/a (\text{mmol}_{\text{titrant}} / \text{mmol}_{\text{standard}})}{\text{mL}_{\text{titrant}}} \end{aligned}$$

Example 19: An approximate 0.1 M hydrochloric acid solution is prepared by 120-fold dilution of concentrated hydrochloric acid. It is standardized by titrating 0.1876 g of dried primary standard sodium carbonate:



The titration required 35.86 mL acid. Calculate the molar concentration of the hydrochloric acid.

Solution

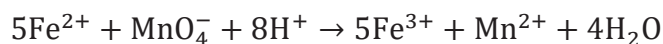
The millimoles of Hydrochloric acid are equal to twice the millimoles of sodium carbonate titrated.

$$\text{mmol}_{\text{Na}_2\text{CO}_3} = 187.6 \text{ mg Na}_2\text{CO}_3 / 105.99 \text{ (mg Na}_2\text{CO}_3/\text{mmol)} = 1.770 \text{ mmol Na}_2\text{CO}_3$$

$$\text{mmol}_{\text{HCl}} = M_{\text{HCl}}(\text{mmol/mL}) \times 35.86 \text{ mL HCl} = 1.770 \text{ mmol Na}_2\text{CO}_3 \\ \times 2(\text{mmol HCl}/\text{mmol Na}_2\text{CO}_3)$$

$$M_{\text{HCl}} = \frac{1.770 \text{ mmol Na}_2\text{CO}_3 \times 2(\text{mmol HCl}/\text{mmol Na}_2\text{CO}_3)}{35.86 \text{ mL HCl}} = 0.09872 \text{ M}$$

Example 20: The iron (II) in an acidified solution is titrated with 0.0206 M solution of potassium permanganate:



If the titration required 40.2 mL, how many milligrams iron are in the solution?

Solution:

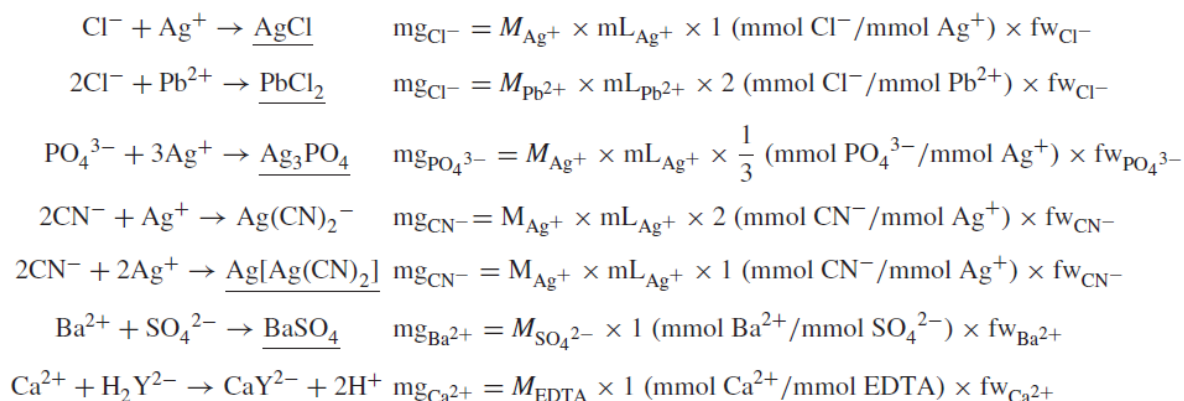
There are five times as many millimoles of iron as there are of permanganate that react with it, so

$$\text{mmol}_{\text{Fe}} = \frac{\text{mg}_{\text{Fe}}}{\text{FW}_{\text{Fe}}} = M_{\text{KMnO}_4} \times \text{mL}_{\text{KMnO}_4} \times \frac{5}{1} (\text{mmol Fe}/\text{mmol KMnO}_4)$$

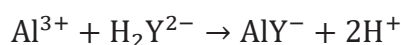
$$\text{mg}_{\text{Fe}} = 0.0206 \text{ mmol KMnO}_4/\text{mL} \times 40.2 \text{ mL KMnO}_4 \times 5(\text{mmol Fe}/\text{mmol MnO}_4^-) \\ \times 55.8 \text{ mg Fe}/\text{mmol} \\ = 231 \text{ mg Fe}$$

PRECIPITATION AND COMPLEXOMETRIC TITRATION REACTIONS

Following is a list of typical precipitation and complexometric titration reactions and the factors for calculating the milligrams of analyte from millimoles of titrant.



Example 21: Aluminium is determined by titrating with EDTA:



A 1.00 g sample requires 20.5 mL EDTA for titration. The EDTA was standardized by titrating 25.0 mL of a 0.100 M CaCl₂ Solution, requiring 30.0 mL EDTA. Calculate the percent Al₂O₃ in the sample.

Solution:

Since Ca²⁺ and EDTA react on a 1:1 mole ratio:

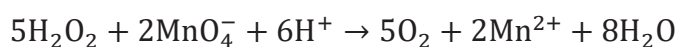
$$M_{\text{EDTA}} = \frac{0.100 \text{ mmol CaCl}_2/\text{mL} \times 25.0 \text{ mL CaCl}_2}{30.0 \text{ mL EDTA}}$$

The millimoles of Al³⁺ are equal to the millimoles EDTA used in the sample titration, but there are one-half this number of millimoles of Al₂O₃ (since 1 Al³⁺ → $\frac{1}{2}$ Al₂O₃).

Therefore,

$$\begin{aligned} \% \text{Al}_2\text{O}_3 &= \frac{M_{\text{EDTA}} \times \text{mL}_{\text{EDTA}} \times \frac{1}{2} \text{ (mmol Al}_2\text{O}_3/\text{mmol EDTA}) \times \text{FW}_{\text{Al}_2\text{O}_3}}{\text{mg}_{\text{Sample}}} \times 100\% \\ \% \text{Al}_2\text{O}_3 &= \frac{0.0833 \text{ mmol EDTA/mL} \times 20.5 \text{ mL EDTA} \times \frac{1}{2} \times 101.96 \text{ mg Al}_2\text{O}_3/\text{mmol}}{1000 \text{ mg sample}} \\ &\times 100\% = 8.71 \% \text{Al}_2\text{O}_3 \end{aligned}$$

Example 22: In acid solution, potassium permanganate reacts with H₂O₂ to form Mn²⁺:



In neutral solution, it reacts with MnSO₄ to form MnO₂:



Calculate the number of millilitres of 0.100 M KMnO_4 that will react with 50.0 mL of 0.200 M H_2O_2 and with 50.0 mL of 0.200 M MnSO_4 .

Solution

The number of millimoles of MnO_4^- will be equal to two-fifth of the number of millimoles of H_2O_2 reduced:

$$M_{\text{MnO}_4^-} \times \text{mL}_{\text{MnO}_4^-} = M_{\text{H}_2\text{O}_2} \times \text{mL}_{\text{H}_2\text{O}_2} \times \frac{2}{5} (\text{mmol MnO}_4^- / \text{mmol H}_2\text{O}_2)$$

$$\text{mL}_{\text{MnO}_4^-} = \frac{0.200 \text{ mmol H}_2\text{O}_2 / \text{mL} \times 50.0 \text{ mL H}_2\text{O}_2 \times \frac{2}{5}}{0.100 \text{ mmol MnO}_4^- / \text{mL}} = 40.0 \text{ mL kMnO}_4$$

The number of millimoles of MnO_4^- reacting with Mn^{2+} will be equal to two-thirds of the number of millimoles of Mn^{2+} :

$$M_{\text{MnO}_4^-} \times \text{mL}_{\text{MnO}_4^-} = M_{\text{Mn}^{2+}} \times \frac{2}{3} (\text{mmol MnO}_4^- / \text{mmol Mn}^{2+})$$

$$\text{mL}_{\text{MnO}_4^-} = \frac{0.200 \text{ mmol Mn}^{2+} / \text{mL} \times 50.0 \text{ mL Mn}^{2+} \times \frac{2}{3}}{0.100 \text{ mmol MnO}_4^- / \text{mL}} = 66.7 \text{ mL kMnO}_4$$

BACK-TITRATION

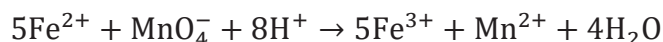
In this technique, a measured amount of the reagent, which would normally be the titrant, is added to the sample so that there is a slight excess. After the reaction with the analyte is allowed to go to completion, the amount of excess (unreacted) reagent is determined by titration with another standard solution; the kinetics of the analyte reaction may be increased in the presence of excess reagent. So by knowing the number of millimoles of reagent taken and by measuring the number of millimoles remaining unreacted, we can calculate the number of millimoles of sample that reacted with the reagent:

$$\begin{aligned} \text{mmol reagent reacted} &= \text{mmol taken} - \text{mmol back-titrated} \\ \text{mg analyte} &= \text{mmol reagent reacted} \times \text{factor (mmol analyte/mmole reagent)} \\ &\quad \times \text{FW analyte (mg/mmole)} \end{aligned}$$

Example 23: A 0.200 g sample of pyrolusite is analyzed for manganese content as follows. Add 50.0 mL of a 0.100 M solution of ferrous ammonium sulfate to reduce the MnO_2 to Mn^{2+} . After reduction is complete, the excess ferrous ion is titrated in acid solution with 0.0200 M KMnO_4 , requiring 15.0 mL. Calculate the percentage of manganese in the sample as Mn_3O_4 (the manganese may or may not exist in this form, but we can make the calculations on the assumption that it does).

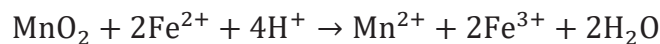
Solution:

The reaction between Fe^{2+} and MnO_4^- is



and so there are five times as many millimoles of excess Fe^{2+} as of MnO_4^- that reacted with it.

The reaction between Fe^{2+} and MnO_2 is



and there are one-half as many millimoles of MnO_2 as millimoles of Fe^{2+} that react with it.

There are one-third as many millimoles of Mn_3O_4 as of MnO_2 ($1\text{MnO}_2 \rightarrow \frac{1}{3}\text{Mn}_3\text{O}_4$). Therefore,

mmol Fe^{2+} reacted

$$= 0.100 \text{ mmol Fe}^{2+}/\text{mL} \times 50.0 \text{ mL Fe}^{2+}$$

$$- 0.0200 \text{ mmol MnO}_4^-/\text{mL} \times 15.0 \text{ mL MnO}_4^- \times 5 \text{ mmol Fe}^{2+}/\text{mmol MnO}_4^-$$

$$= 3.5 \text{ mmol Fe}^{2+} \text{ reacted}$$

$$\text{mmol MnO}_2 = 3.5 \text{ mmol} \times \frac{1}{2} (\text{mmol MnO}_2/\text{mmol Fe}^{2+}) = 1.75 \text{ mmol MnO}_2$$

$$\text{mmol Mn}_3\text{O}_4 = 1.756 \text{ mmol MnO}_2 \times \frac{1}{3} (\text{mmol Mn}_3\text{O}_4/\text{mmol MnO}_2)$$

$$= 0.583 \text{ mmol Mn}_3\text{O}_4$$

$$\% \text{Mn}_3\text{O}_4 = \frac{0.583 \text{ mmol Mn}_3\text{O}_4 \times 228.8 (\text{mg Mn}_3\text{O}_4/\text{mmol})}{200 \text{ mg sample}} \times 100\%$$

$$= 66.7 \% \text{ Mn}_3\text{O}_4$$

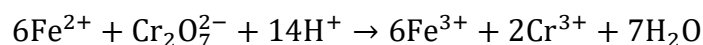
TITER

For routine titrations, it is often convenient to calculate the **titer** of the titrant. The titer Titer = milligrams analyte that is the weight of analyte that is chemically equivalent to 1mL of the titrant, usually react with 1mL of titrant, expressed in milligrams.

Example 24: A standard solution of potassium dichromate contains 5.442 g/L. What is its titer in terms of milligrams Fe_3O_4 ?

Solution:

The iron titrated as Fe^{2+} and each $\text{Cr}_2\text{O}_7^{2-}$ will react with 6Fe^{2+} (or the iron from $2\text{Fe}_3\text{O}_4$):



The molarity of the $\text{K}_2\text{Cr}_2\text{O}_7$, solution is:

$$M_{\text{Cr}_2\text{O}_7^{2-}} = \frac{g/L}{FW_{\text{Cr}_2\text{O}_7^{2-}}} = \frac{5.442 g/L}{294.19 g/mol} = 0.01850 mol/L$$

Therefore, the titer is

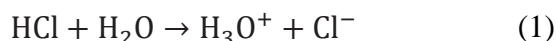
$$\begin{aligned} 0.01850 \left(\frac{\text{mol K}_2\text{Cr}_2\text{O}_7}{\text{mL}} \right) \times \frac{2}{1} \left(\frac{\text{mol Fe}_3\text{O}_4}{\text{mmol K}_2\text{Cr}_2\text{O}_7} \right) \times 231.54 \left(\frac{\text{mg Fe}_3\text{O}_4}{\text{mmol Fe}_3\text{O}_4} \right) \\ = 8.567 \text{ mg Fe}_3\text{O}_4/\text{mL K}_2\text{Cr}_2\text{O}_7 \end{aligned}$$

ACID–BASE EQUILIBRIA

Acid–Base Equilibria in Water

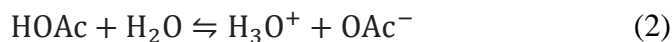
When an acid or base is dissolved in water, it will dissociate, or **ionize**, the amount of ionization being dependent on the strength of the acid or the base. A “strong” electrolyte is completely dissociated, while a “weak” electrolyte is partially dissociated. Table 3.2 lists some common electrolytes, some strong and some weak.

Hydrochloric acid is a strong acid, and in water, its ionization is complete:



An equilibrium constant for Equation 1 would have a value of infinity. The proton H^+ exists in water as a hydrated ion, the **hydronium ion**, H_3O^+ . Higher hydrates probably exist, particularly H_9O_4^+ . The hydronium ion is written as H_3O^+ for convenience and to emphasize Brønsted behavior.

Acetic acid is a weak acid, which ionizes only partially in water (a few percent):



Simplified equations for the above reactions are



We can write an **equilibrium constant** for this reaction:

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

We will use H^+ in place of H_3O^+ , Also, molar concentrations will generally be used instead of activities.

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

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 , to a smaller number of significant figures, it is still accurately represented as 1.0×10^{-14} . The product of the hydrogen ion concentration and

the hydroxide ion concentration in aqueous solution is always equal to 1.0×10^{-14} at room temperature:

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

Table 3.2 Some Strong Electrolytes and Some Weak Electrolytes

Strong	Weak
HCl	CH ₃ COOH (Acetic acid)
HClO ₄	NH ₃
H ₂ SO ₄	C ₆ H ₅ OH (phenol)
HNO ₃	HCHO ₂ (formic acid)
NaOH	C ₆ H ₅ NH ₂ (aniline)
	CH ₃ COONa

In pure water, then, the concentrations of these two species are equal since there are no other sources of H⁺ or OH⁻ except H₂O dissociation:

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

Therefore,

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

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

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 1: 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,

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

$$[\text{OH}^-] = 1.0 \times 10^{-11} \text{ M}$$

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. The **pH** of a solution was defined by Sørensen as

$$\text{pH} = -\log[\text{H}^+]$$

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:

$$\text{pOH} = -\log[\text{OH}^-]$$

Example 1: Calculate the pH of a 2.0×10^{-3} M solution of HCl.

Solution

HCl is completely ionized, so

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

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

If the hydrogen ion concentration is known, we can calculate the hydroxyl ion concentration, and vice versa. The equation in logarithm form for a more direct calculation of pH or pOH is

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

$$\text{p}K_w = \text{pH} + \text{pOH}$$

at 25°C

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

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

Solution

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

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

$$\text{pH} + 1.30 = 14.00$$

$$\text{pH} = 12.70$$

or

$$[\text{H}^+] = (1.0 \times 10^{-14}) / (5.0 \times 10^{-2})$$

$$= 2.0 \times 10^{-13} \text{ M}$$

$$\text{pH} = -\log(2.0 \times 10^{-13}) = 13 - \log 2.0 = 13 - 0.30 = 12.70$$

Example 3: Calculate the pH of a solution prepared by mixing 2.0 mL of a strong acid solution of pH 3.00 and 3.0 mL of a strong base of pH 10.00.

Solution

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

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

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

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

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

There is an excess of acid.

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

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

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

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

Example 4: The pH of a solution is 9.67. Calculate the hydrogen ion concentration in the solution.

Solution

$$-\log[\text{H}^+] = 9.67$$

$$[\text{H}^+] = 10^{-9.67} = 10^{-10} \times 10^{0.33}$$

$$[\text{H}^+] = 2.1 \times 10^{-10} \text{ M}$$

Remember, this answer is reported to two significant figures ($2.1 \times 10^{-10} \text{ M}$) because the mantissa of the pH value (9.67) has two significant figures.

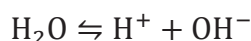
- When $[\text{H}^+] = [\text{OH}^-]$, then a solution is said to be **neutral**. If $[\text{H}^+] > [\text{OH}^-]$, then the solution is **acidic**.
- When $[\text{H}^+] < [\text{OH}^-]$, the solution is **alkaline**.

The hydrogen ion and hydroxide ion concentrations in pure water at 25°C are each 10^{-7} M, and the pH of water is 7. A pH of 7 is therefore neutral. Values of pH that are greater than this are alkaline, and pH values less than this are acidic.

Example 5: Calculate the pH and pOH of a 1.0×10^{-7} M solution of HCl.

Solution

Equilibria:



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

$$[\text{H}^+]_{\text{H}_2\text{O diss}} = [\text{OH}^-]_{\text{H}_2\text{O diss}} = x$$

Since the hydrogen ions contributed from the ionization of water are not negligible compared to the HCl added,

$$[\text{H}^+] = C_{\text{HCl}} + [\text{H}^+]_{\text{H}_2\text{O diss}}$$

Then,

$$([\text{H}^+]_{\text{HCl}} + x)(x) = 1.0 \times 10^{-14}$$

$$(1.0 \times 10^{-7} + x)(x) = 1.0 \times 10^{-14}$$

$$x^2 + 1.00 \times 10^{-7}x - 1.0 \times 10^{-14} = 0$$

Using the quadratic equation to solve

$$x = \frac{-1.00 \times 10^{-7} \mp \sqrt{1.0 \times 10^{-14} + 4(1.0 \times 10^{-14})}}{2} = 6.2 \times 10^{-8} \text{ M}$$

Therefore, the total H^+ concentration = $(1.00 \times 10^{-7} + 6.2 \times 10^{-8}) = 1.62 \times 10^{-7} \text{ M}$:

$$\text{pH} = -\log 1.62 \times 10^{-7} = 7 - 0.21 = 6.79$$

$$\text{pOH} = 14.00 - 6.79 = 7.21$$

or, since $[\text{OH}^-] = x$,

$$\text{pOH} = -\log(6.2 \times 10^{-8}) = 8 - 0.79 = 7.21$$

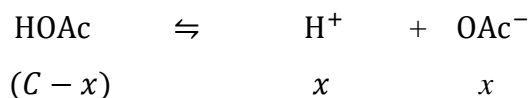
Weak Acids and Bases

weak acids (or bases) are only partially ionized. While mineral (inorganic) acids and bases such as HCl, HClO₄, HNO₃, 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 the Equation will always be equal to 1.75×10^{-5} .

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



Example 6: Calculate the pH and pOH of a $1.00 \times 10^{-3} M$ solution of acetic acid.

Solution



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 ($x = \text{mmol/mL HOAc ionized}$)	$-x$	$+x$	$+x$
Equilibrium	$1.00 \times 10^{-3} - x$	x	x

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

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

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

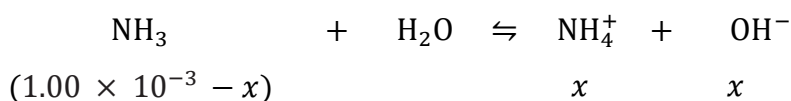
Therefore,

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

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

Example 7: The basicity constant K_b for ammonia is 1.75×10^{-5} at 25°C . (It is only coincidental that this is equal to K_a for acetic acid.) Calculate the pH and pOH for a $1.00 \times 10^{-3}\text{M}$ solution of ammonia.

Solution



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

The same rule applies for the approximation applied for a weak acid. Thus,

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

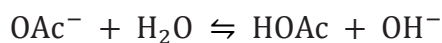
$$x = 1.32 \times 10^{-4} \text{ M} = [\text{OH}^-]$$

$$\text{pOH} = -\log 1.32 \times 10^{-4} = 3.88$$

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

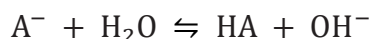
Salts of Weak Acids and Bases

The salt of a weak acid, for example, NaOAc, is a strong electrolyte, like (almost) all salts, and completely ionizes. In addition, the anion of the salt of a weak acid is a **Brønsted base**, which will accept protons. It partially hydrolyzes in water to form hydroxide ion and the corresponding undissociated acid. For example,



The HOAc here is undissociated and therefore does not contribute to the pH. This ionization is also known as **hydrolysis** of the salt ion. Because it hydrolyzes, sodium acetate is a weak base (the conjugate base of acetic acid). The ionization constant is equal to the basicity constant of the salt anion. The weaker the conjugate acid, the stronger the conjugate base, that is, the more strongly the salt will combine with a proton, as from the water, to shift the ionization in the Equation above to the right. *Equilibria for these Brønsted bases are treated identically to the weak bases we have just considered.*

For any salt of a weak acid HA that hydrolyzes in water,



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

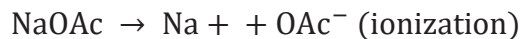
We will use K_b to emphasize that these salts are treated the same as for any other weak base.

$$[OH^-] = \sqrt{\frac{K_w}{K_a} \cdot C_{A^-}} = \sqrt{K_b C_{A^-}}$$

Example 8: Calculate the pH of a 0.10 M solution of sodium acetate.

Solution

Write the equilibria



Write the equilibrium constant

$$\frac{[HOAc][OH^-]}{[OAc^-]} = K_b = \frac{K_w}{K_a} = \frac{1.00 \times 10^{-14}}{1.75 \times 10^{-5}} = 5.7 \times 10^{-10}$$

Let x represent the concentration of HOAc and OH^- at equilibrium. Then, at equilibrium,

$$[HOAc] = [OH^-] = x$$

$$[OAc^-] = C_{OAc^-} - x = 0.10 - x$$

Since $C_{OAc^-} \gg K_b$, neglect x compared to C_{OAc^-} . Then,

$$\frac{(x)(x)}{0.10} = 5.7 \times 10^{-10}$$

$$x = \sqrt{5.7 \times 10^{-10} \times 0.10} = 7.6 \times 10^{-6} M$$

Compare this last step with Equation

$$[OH^-] = \sqrt{\frac{K_w}{K_a} \cdot C_{A^-}} = \sqrt{K_b C_{A^-}}$$

Also, compare the entire setup and solution with those in Example 7. The HOAc formed is undissociated and does not contribute to the pH:

$$[OH^-] = 7.6 \times 10^{-6} M$$

$$[H^+] = \frac{1.0 \times 10^{-14}}{7.6 \times 10^{-6}} = 1.3 \times 10^{-9} M$$

$$pH = -\log 1.3 \times 10^{-9} = 9 - 0.11 = 8.89$$

Buffers

A **buffer** is defined as a solution that resists change in pH when a small amount of an acid or base is added or when the solution is diluted. While carrying out a reaction, this is very useful for maintaining the pH within an optimum range. A buffer solution consists of a mixture of a weak acid and its conjugate base, or a weak base, and its conjugate acid at predetermined concentrations or ratios. That is, we have a mixture of a weak acid and its salt or a weak base and its salt. Consider an acetic acid–acetate buffer. The equilibrium that governs this system is



But now, since we have added a supply of acetate ions to the system, the hydrogen ion concentration is no longer equal to the acetate ion concentration. The hydrogen ion concentration is

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

This form of the ionization constant equation is useful for calculating the pH of a weak acid solution containing its salt. A general form can be written for a weak acid HA that ionizes to its salt, A⁻, and [H⁺]:



$$\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

$$\text{pH} = \text{p}K_a + \log \frac{[\text{conjugate base}]}{[\text{acid}]}$$

$$\text{pH} = \text{p}K_a + \log \frac{[\text{proton acceptor}]}{[\text{proton donor}]}$$

The **buffering mechanism** for a mixture of a weak acid and its salt can be explained as follows: The pH is governed by the logarithm of the ratio of the salt and acid:

$$\text{pH} = \text{constant} + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

Example: Calculate the pH of a buffer prepared by adding 10 mL of 0.10 *M* acetic acid to 20 mL of 0.10 *M* sodium acetate.

Solution

We need to calculate the concentration of the acid and salt in the solution. The final volume is 30 mL:

$$M1 \times mL1 = M2 \times mL2$$

For HOAc,

$$0.10 \text{ mmol/mL} \times 10 \text{ mL} = M_{\text{HOAc}} \times 30 \text{ mL}$$

$$M_{\text{HOAc}} = 0.033 \text{ mmol/mL}$$

For OAc⁻,

$$0.10 \text{ mmol/mL} \times 20 \text{ mL} = M_{\text{OAc}^-} \times 30 \text{ mL}$$

$$M_{\text{OAc}^-} = 0.067 \text{ mmol/mL}$$

The ionization of the acid is suppressed by the salt and can be neglected.

$$\text{pH} = -\log K_a + \log \frac{[\text{proton acceptor}]}{[\text{proton donor}]}$$

$$\text{pH} = -\log (1.75 \times 10^{-5}) + \log \frac{0.067 \text{ mmol/mL}}{0.033 \text{ mmol/mL}}$$

$$= 4.76 + \log 2.0$$

$$= 5.06$$

We could have shortened the calculation by recognizing that in the log term the volumes cancel.

So, we can take the ratio of millimoles only:

$$\text{mmol}_{\text{HOAc}} = 0.10 \text{ mmol/mL} \times 10 \text{ mL} = 1.0 \text{ mmol}$$

$$\text{mmol}_{\text{OAc}^-} = 0.10 \text{ mmol/mL} \times 20 \text{ mL} = 2.0 \text{ mmol}$$

$$\text{pH} = 4.76 + \log \frac{2.0 \text{ mmol}}{1.0 \text{ mmol}} = 5.06$$

HomeWorks:

- Calculate the pH of a solution prepared by adding 25mL of 0.10 *M* sodium hydroxide to 30mL of 0.20 *M* acetic acid (this would actually be a step in a typical titration). *Ans. 4.61*

- Suppose you have 100mL of a buffer containing 0.100M acetic acid and 0.0500M sodium acetate. Calculate the pH of the buffer when 3.00mL of 1.00M HCl is added to it. *Ans.* 4.22
- Calculate the volume of concentrated ammonia and the weight of ammonium chloride you would have to take to prepare 100mL of a buffer at pH 10.00 if the final concentration of salt is to be 0.200 M. *Ans.* 7.8 mL
- How many grams ammonium chloride and how many milliliters 3.0 M sodium hydroxide should be added to 200 mL water and diluted to 500mL to prepare a buffer of pH 9.50 with a salt concentration of 0.10 M? *Ans.* 30mL
- Calculate the pH of a 0.100 M H_3PO_4 solution. *Ans.* 1.55

ACID-BASE TITRATIONS

An acid-base titration involves a **neutralization** reaction in which an acid is reacted with an equivalent amount of base. By constructing a **titration curve**, we can easily explain how the **end points** of these titrations can be detected. The end point signals the completion of the reaction. A titration curve is constructed by plotting the pH of the solution as a function of the volume of titrant added. *The titrant is always a strong acid or a strong base.* The analyte may be either a strong base or acid or a weak base or acid.

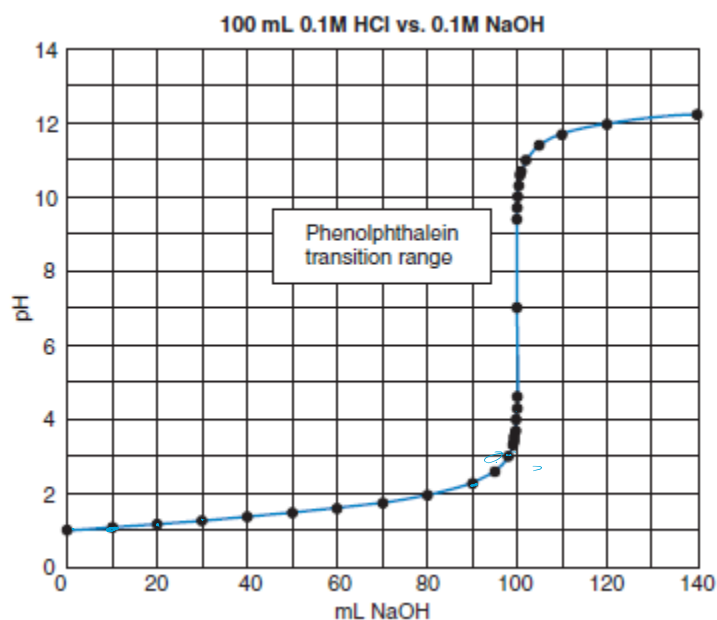


Fig 1. Titration curve for 100 mL of 0.1 M HCl versus 0.1 M NaOH

Example: Calculate the pH at 0, 10, 90, 100, and 110% titration (% of the equivalence point volume) for the titration of 50.0 mL of 0.100 M HCl with 0.100 M NaOH.

Solution

At 0%, $\text{pH} = -\log 0.100 = 1.00$

At 10%, 5.0 mL NaOH is added. We start with $0.100 \text{ M} \times 50.0 \text{ mL} = 5.00 \text{ mmol H}^+$.

Calculate the concentration of H^+ after adding the NaOH:

$$\begin{array}{r} \text{mmol H}^+ \text{ at start} \\ \text{mmol OH}^- \text{ added} = 0.100 \times 5.0 \text{ mL} \\ \text{mmol H}^+ \text{ left} \end{array} \qquad \begin{array}{r} = 5.00 \text{ mmol H}^+ \\ = 0.500 \text{ mmol OH}^- \\ \hline = 4.50 \text{ mmol H}^+ \text{ in } 55.0 \text{ mL} \end{array}$$

$$[\text{H}^+] = 4.50 \text{ mmol}/55.0 \text{ mL} = 0.0818 \text{ M}$$

$$\text{pH} = -\log 0.0818 = 1.09$$

At 90%,

$$\begin{array}{r} \text{mmol H}^+ \text{ at start} \\ \text{mmol OH}^- \text{ added} = 0.100 \times 45.0 \text{ mL} \\ \text{mmol H}^+ \text{ left} \end{array} \qquad \begin{array}{r} = 5.00 \text{ mmol H}^+ \\ = 4.50 \text{ mmol OH}^- \\ \hline = 0.50 \text{ mmol H}^+ \text{ in } 95.0 \text{ mL} \end{array}$$

$$[\text{H}^+] = 0.00526 \text{ M}$$

$$\text{pH} = -\log 0.00526 = 2.28$$

At 100%: All the H^+ has been reacted with OH^- , and we have a 0.0500 M solution of NaCl. Therefore, the pH is 7.00.

At 110%: We now have a solution consisting of NaCl and excess added NaOH.

$$\text{mmol OH}^- = 0.100 \text{ M} \times 5.00 \text{ mL} = 0.50 \text{ mmol OH}^- \text{ in } 105 \text{ mL}$$

$$[\text{OH}^-] = 0.00476 \text{ M}$$

$$\text{pOH} = -\log 0.00476 = 2.32; \text{ pH} = 11.68$$

Note that prior to the equivalence point, when there is excess acid, the relationship is

$$[\text{H}^+] = (M_{\text{acid}} \times V_{\text{acid}} - M_{\text{base}} \times V_{\text{base}})/V_{\text{total}}, \text{ where } V \text{ is the volume.}$$

You can simply apply this to calculate $[H^+]$ once you understand the solution to Example 1. Likewise, beyond the equivalence point when there is excess base, $[OH^-] = (M_{base} \times V_{base} - M_{acid} \times V_{acid})/V_{total}$.

where V_{total} is always $V_{acid} + V_{base}$

The magnitude of the break will depend on both the concentration of the acid and the concentration of the base. Titration curves at different concentrations are shown in Figure 2. The reverse titration gives the mirror image of these curves. The titration of 0.1 M NaOH with 0.1 M HCl is shown in Figure 3.

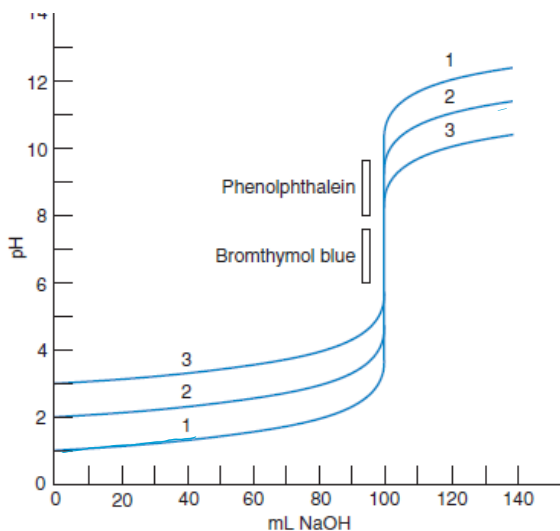


Fig. 2. Dependence of the magnitude of end-point break on concentration. Curve 1: 100mL of 0.1 M HCl versus 0.1 M NaOH. Curve 2: 100mL of 0.01 M HCl versus 0.01 M NaOH. Curve 3: 100mL of 0.001 M HCl versus 0.0001 M NaOH. The equivalence point pH is 7.00 in all cases.

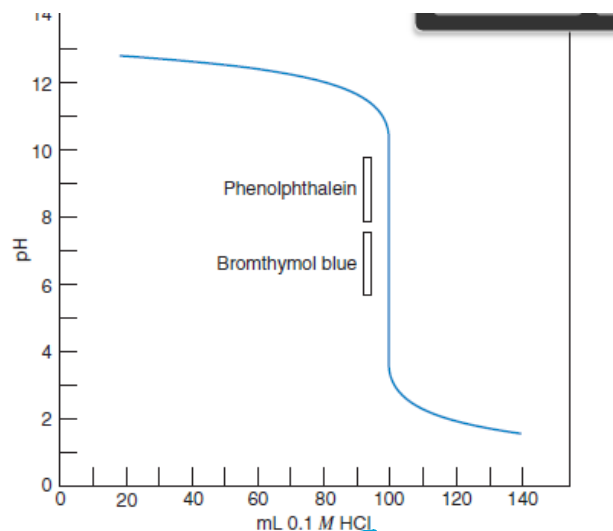


Fig. 3. Titration curve for 100mL 0.1 M NaOH versus 0.1 M HCl. The equivalence point pH is 7.00.

Weak Acid versus Strong Base

Example: Calculate the pH at 0, 10.0, 25.0, 50.0, and 60.0 mL titrant in the titration of 50.0 mL of 0.100 M acetic acid with 0.100 M NaOH.

Solution

At 0 mL, we have a solution of only 0.100 M HOAc:

$$\frac{(x)(x)}{0.100 - x} = 1.75 \times 10^{-5}$$

$$[\text{H}^+] = x = 1.32 \times 10^{-3} \text{ M}$$

At 10.0 mL, we started with $0.100\text{M} \times 50.0 \text{ mL} = 5.00 \text{ mmol HOAc}$; part has reacted with OH^- and has been converted to OAc^- :

mmol HOAc at start = 5.00 mmol HOAc

$$\begin{aligned} \text{mmol OH}^- \text{ added} &= 0.100\text{M} \times 10.0 \text{ mL} = 1.00 \text{ mmol OH}^- \\ &= \text{mmol OAc}^- \text{ formed in } 60.0 \text{ mL} \end{aligned}$$

$$\text{mmol OH}^- \text{ left} = 4.00 \text{ mmol HOAc in } 60.0 \text{ mL}$$

We have a buffer. Since volumes cancel, use millimoles:

$$\text{pH} = \text{p}K_a + \log \frac{[\text{OAc}^-]}{[\text{HOAc}]}$$

$$\text{pH} = 4.76 + \log \frac{1.00}{4.00} = 4.16$$

At 25.0 mL, one-half the HOAc has been converted to OAc^- , so $\text{pH} = \text{p}K_a$:

$$\text{mmol HOAc at start} = 5.00 \text{ mmol HOAc}$$

$$\text{mmol OH}^- = 0.100 \text{ M} \times 25.0 \text{ mL} = 2.50 \text{ mmol OAc}^- \text{ formed}$$

$$\text{mmol HOAc left} = 2.5 \text{ mmol HOAc}$$

$$\text{pH} = 4.76 + \log \frac{2.50}{2.50} = 4.76$$

At 50.0 mL, all the HOAc has been converted to OAc^- (5.00 mmol in 100 mL, or 0.0500 M):

$$\begin{aligned} [\text{OH}^-] &= \sqrt{\frac{K_w}{K_a} [\text{OAc}^-]} \\ &= \sqrt{\frac{1.0 \times 10^{-14}}{1.75 \times 10^{-5}} \times 0.0500} = 5.35 \times 10^{-6} \text{ M} \end{aligned}$$

$$\text{pOH} = 5.27, \quad \text{pH} = 8.73$$

At 60.0 mL, we have a solution of NaOAc and excess added NaOH. The hydrolysis of the acetate is negligible in the presence of added OH^- . So, the pH is determined by the concentration of excess OH^- :

$$\text{mmol OH}^- = 0.100 \text{ M} \times 10.0 \text{ mL} = 1.00 \text{ mmol in 110 mL}$$

$$[\text{OH}^-] = 0.00909 \text{ M}$$

$$\text{pOH} = -2.04; \text{pH} = 11.96$$