



Analytical Chemistry

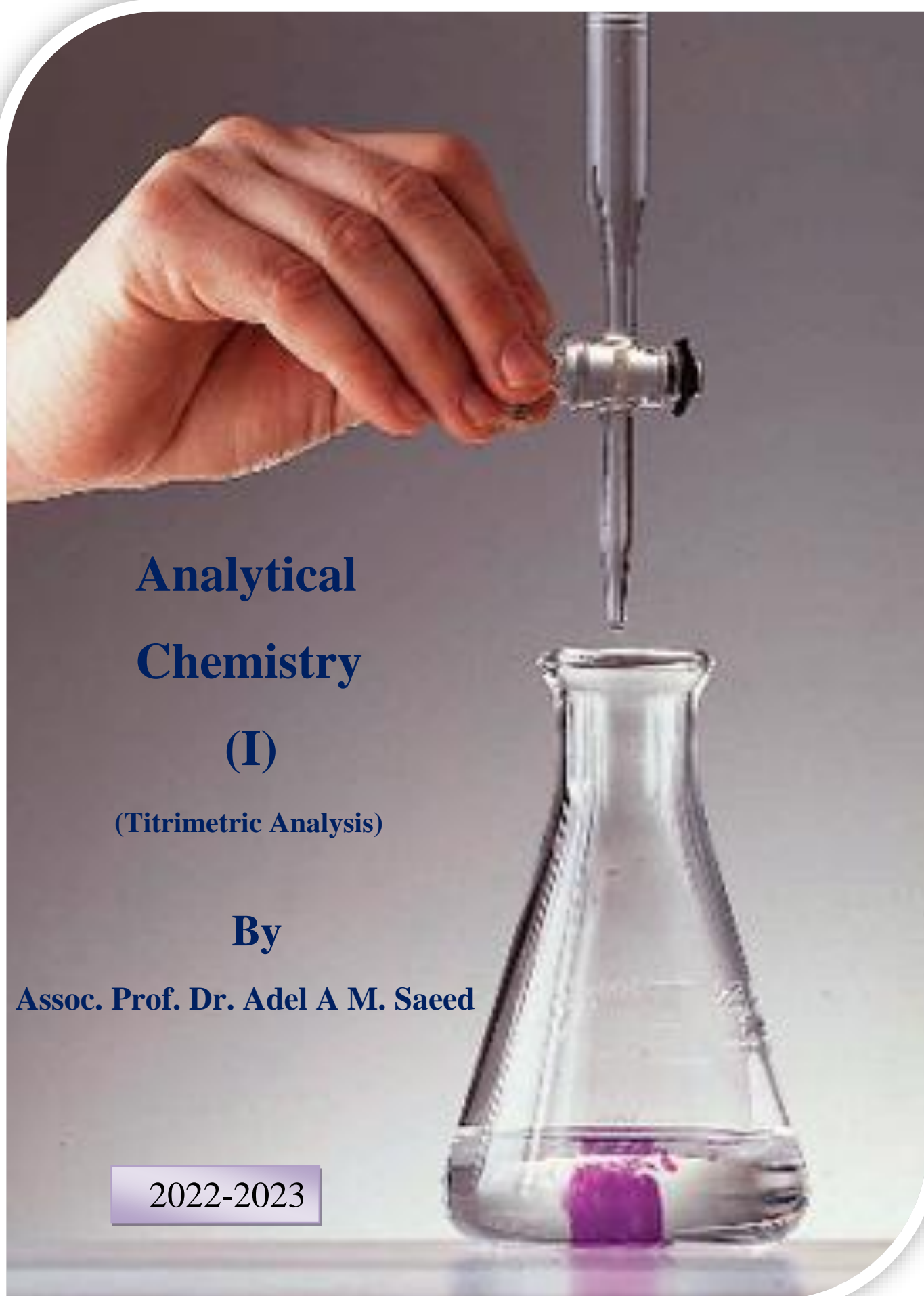
(I)

(Titrimetric Analysis)

By

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**Learning Outcomes:**

- To understand the concepts, rules & laws, ideas & apparatus used in volumetric analysis.
- To understand the correct titrimetric procedures.
- To learn how to do accurate measurements.
- To learn how to do statistical calculations.
- To learn how to draw titrimetry curves.

Students should know the following keywords:

Volumetric Analysis, Titration, Standard & Non-Standard Solutions, Indicator

1. INTRODUCTION

Chemistry is the study of matter, including its composition, structure, physical properties, and reactivity. It is divided into five major fields: organic, inorganic, physical, biochemical, and analytical.

What Is Analytical Chemistry?

"Analytical chemistry is what analytical chemists do."

Analytical chemistry is often described as the area of chemistry responsible for characterizing the composition of matter, both qualitatively and quantitatively. It was dealing with the identification and determination of compounds. It is convenient for our purposes to treat it as a five-step process:

1. Identify and define the problem.
2. Design the experimental procedure.
3. Conduct an experiment, and gather data.
4. Analyze the experimental data.
5. Propose a solution to the problem.

Typical problems on which analytical chemists work include qualitative analyses (what is present?), quantitative analyses (how much is present?), characterization analyses (what are the material's chemical and physical properties?), and fundamental analyses (how does this method work and how can it be improved?).

Analytical chemistry consists of:

Qualitative analysis deals with the identification of elements, ions, or compounds present in a sample (tells us what chemicals are present in a sample). **Quantitative analysis, which** is dealing with the determination of how much of one or more constituents is present (tells how much amounts of chemicals are present in a sample).

This analysis can be divided into three branches:



Volumetric analysis (Titrimetric analysis):

-The analyte reacts with a measured volume of reagent of known concentration, in a process called **titration**.

- Any method of quantitative chemical **analysis** in which the amount of a substance is determined by measuring the volume that it occupies or, in broader usage, the volume of a second substance that combines with the first in known proportions, more correctly called **titrimetric analysis**.

Gravimetric analysis: usually involves the selective separation of the analyte by precipitation, followed by the very non-selective measurement of mass (of the precipitate).

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.

Volumetric analysis was divided to:

A: Titration analysis.

B: Gas analysis.

Well, we are speaking about the volumetric analysis, we shall consider, what the solutions are:

Solution: Homogeneous mixture of two or more substances produces from dissolved (disappeared) solute particles (ions, atoms, molecules) (lesser amount) between solvent particles (larger amount).

Solute (lesser amount) + Solvent (larger amount) = Solution

e.g. $\text{NaCl}_{(s)} + \text{H}_2\text{O}_{(l)} = \text{NaCl}_{(aq)}$

Concentrated Solution has a large amount of solute, and **Dilute Solution** has a small amount of solute.

Classification of solutions according to the amount of solute:

Unsaturated solution: if the amount of solute dissolved is less than the solubility limit, or if the amount of solute is less than the capacity of the solvent.

Saturated solution: is one in which no more solute can dissolve in a given amount of solvent at a given temperature, or if the amount of solute is equal to the capacity of solvent.

Supersaturated solution: solution that contains a dissolved amount of solute that exceeds the normal solubility limit (saturated solution). Or a solution contains a larger amount of solute than the capacity of solvent at high temperatures.

Classification of solution based on solute particle size:

True solution.

Suspension solution: heterogeneous mixture which settles on standing and their components can be separated by filtrating (Amoxicillin, Antibiotics), particles of solute visible to the naked eye.

Colloidal solution: homogeneous mixture which does not settle nor are its components filterable, solute particle visible with an electron microscope (milk).

We are now considered the standard solution which was defined as:

Standard solution: It is a reagent of known concentration that is used to carry out a titrimetric analysis.

The properties of the standard solution are:

- 1 - Be sufficiently stable so that it is only necessary to determine its concentration once.
- 2 - React rapidly with the analyte so that the time required to complete the analysis is minimized.
- 3 - React completely with the analyte so that a satisfactory endpoint is realized.



4 - Undergo a selective reaction with the analyte.

5 - The reaction with the analyte can be described by a balanced equation.

A titration was performed by adding a standard solution from a burette or other liquid-dispensing device to a solution of the analyte until the reaction between the two solutions is judged complete. The volume of the reagent needed to complete the titration is determined by the difference between the initial and final volume. Titrimetric methods include a large and powerful group of quantitative procedures based on measuring the amount of a reagent of known concentration that is consumed by an analyte.

Classification of volumetric or titrimetric methods:

(1) Neutralization (acid-base) titrations.

(2) Precipitation titrations.

(3) Complexation titrations.

(4) Reduction-Oxidation titrations.

Equivalent point: The point in titration in which the amount of added standard reagent is equivalent to the amount of the analyte (theoretical point). That means the amounts are chemically equivalent.

Endpoint: The point in titration in which the physical change occurs, that is associated with the condition of the chemical.

The difference in volume or mass between equivalent and endpoints is called the titration error.

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

where, E_t = titration error, V_{eq} = theoretical volume (volume at an equivalent point) V_{ed} = actual volume (volume at endpoint)

Primary standard material:

It is a highly purified compound that serves as a reference material in all volumetric and mass titrimetric methods.

The most important requirements for the primary standard materials are:

1 - High purity.

2 - Atmospheric stability.

3 - Absence of hydrated water so that the composition of the solid does not change with variations in relative humidity.

4 - Ready availability at a modest cost.

5 - Reasonable solubility in the titration medium.

6 - Reasonable large molar mass, so that the relative error associated with weighing the standard is minimized.

Back titration: - sometimes a reaction is slow to go to completion, and a sharp endpoint cannot be obtained. A back titration will often yield useful results. 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. In back-titration, a known number of millimoles



of reaction is taken, in excess of the analyte. The unreacted portion is titrated.

mmol reagent reacted = mmol took - mmol back-titrated

mg analyte = mmol reagent reacted x factor (mmol analyte/mmol reagent)

Volumetric Titrimetry (Volumetric Analysis)

Volumetric Titrimetry or volumetric analysis is a widely-used quantitative analytical method. As the name implies, this method involves the measurement of the volume of a solution of known concentration which is used to determine the concentration of the analyte.

1. Prepare a solution from an accurately weighed sample to ± 0.0001 g of the material to be analyzed.
2. Choose a substance that will react rapidly and completely with the analyte and prepare a standard solution for this substance. The concentration of the standard solution should be known to ± 0.0001 M.
3. Place the standard solution in a burette and add it slowly to the unknown. This process is called titration and the solution in the burette is called the titrant. Continue the titration until the reaction is complete; that is until the amount of reactant added is exactly the amount required to react with all the constituents being analyzed. This point is called the equivalence point and can be detected by adding an indicator to the unknown solution before beginning the titration. An indicator is a substance that gives a color change at or near the equivalence point. The point at which the color change occurs is the end point of the titration.
4. Measure the exact volume of standard solution required from burette readings before and after the titration. Since the molarity of the standard solution is known, the number of moles of titrant can be calculated. From a knowledge of the equation for the reaction, the number of moles of constituent present in the sample can also be calculated.

How to prepare a standard solution?

1. The most accurate and convenient way of preparing a standard solution is to weigh the reagent, dissolve it, and dilute the solution to a definite volume in a volumetric flask. This method can only be used if the reagent is a primary standard.
2. In order for a reagent to be a primary standard, it must be obtainable in pure form (generally at least 99.98% pure), stable both in pure form and in solution, easy to dry and keep dry, and soluble in a suitable solvent.
3. Many useful reagents do not meet those requirements, so the reagent is dissolved and diluted approximately to the concentration desired. The solution is then standardized by titrating it against a primary solution. This standardized solution is called a **secondary standard**.

Classical titration procedures

1. Clean the burette before use and rinse with water. If any drops of water collect on the walls, the burette is not clean. Once the burette is clean, rinse it with the titrant solution before filling it. Pour



about 5 mL of the titrant into the burette and, holding the burette almost horizontally, rotate it slowly so that the titrant cleans the entire burette. Do this three times.

2. Place the burette in a burette clamp attached to a large ring stand. Using a funnel, fill the burette with titrant to a level above the zero mark. Place a beaker under the burette and open the stopcock for a few seconds to remove all air from the tip and fill it. The top of the solution should now be below the zero mark.
3. Read the burette to ± 0.01 mL with the meniscus level with the eye to minimize parallax (see Fig.1.1). Parallax is the varying of the apparent position of the meniscus due to eye level. If you are looking down on the meniscus, the reading will be low. If you are looking up at it, the reading will be high.



Figure 1.1. Place a black strip behind the burette to make the meniscus easier to see and the volume easier to read.

4. Place the solution that is to be titrated in an Erlenmeyer flask and add 3-5 drops of the appropriate indicator. Position the flask under the burette.
5. Add the titrant slowly from the burette while swirling the contents of the flask to assure adequate mixing (see Fig. 1.2). As the endpoint is approached, the titrant must be added very slowly - a drop at a time. Usually, there is an indication as the endpoint is approached. If the endpoint is a color change, the change is produced momentarily where the reagent drops into the solution, but fades with stirring into the solution. This fading occurs more slowly as the endpoint is approached.



Figure 1.2. The proper handling of the stopcock of the burette. This allows for maximum control of the rate at which the titrant is added.

6. When the endpoint has been reached, allow the solution to sit for 10 seconds so the liquid in the burette can settle, then read the burette. Subtract the initial burette reading from the final reading to obtain the volume of titrant used.

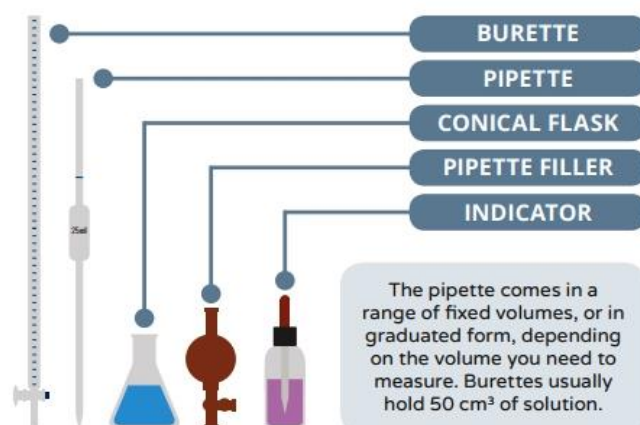
Indicators are used to determine the endpoint of the titration. An indicator is used in classical titrations. The color change of the indicator should be near the equivalence point of the reaction.



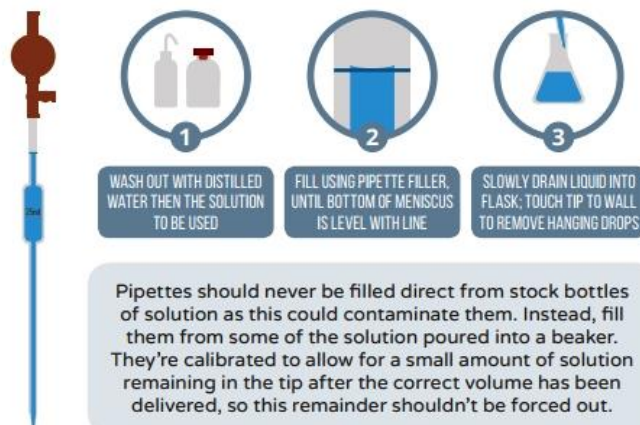
CHEMISTRY TECHNIQUES: TITRATION

Used to determine the concentration of a particular solution, by measuring how much of a solution of known concentration reacts with a known volume of it.

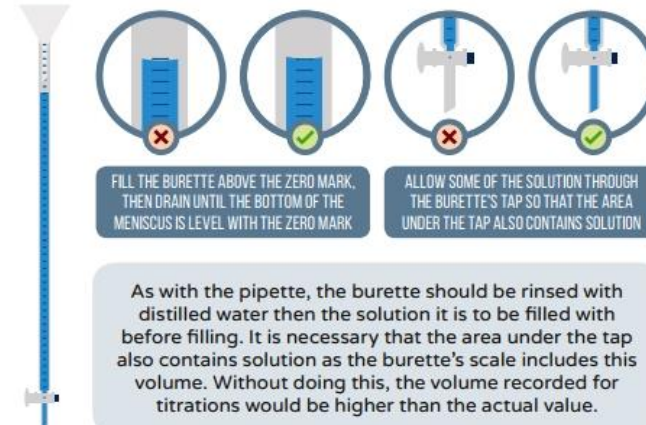
EQUIPMENT



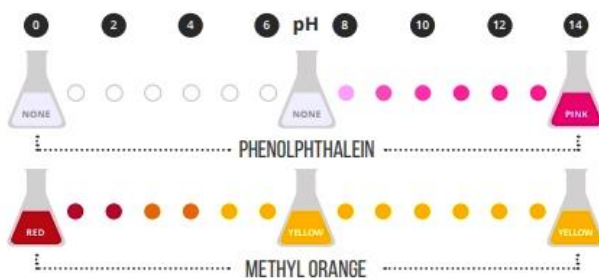
USING A PIPETTE



FILLING THE BURETTE



USING INDICATORS



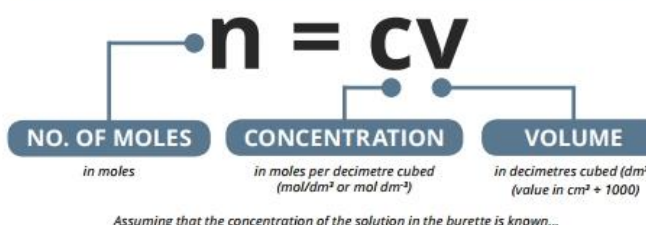
In acid-base titrations, a range of indicators can be used. These are solutions which change colour at a specific pH, and can be used to precisely identify when the neutralisation reaction is complete (the end point). Different indicators are suitable for different acid-base combinations.

CARRYING OUT THE TITRATION



To carry out the titration, the tap of the burette is opened to allow the solution inside to flow into a known volume of the solution in the conical flask. The amount of solution from the burette required to reach the end point is recorded. A rough titration is usually followed by more accurate runs. Multiple titrations are carried out until concordant titres are obtained (within 0.10 cm³ of each other).

CARRYING OUT CALCULATIONS



- 1 Calculate number of moles of solution added from the burette.
- 2 Determine the number of moles of solution in the conical flask using the equation for the reaction and reacting ratios.
- 2 Calculate the concentration of the solution in the conical flask by rearranging the equation ($c = n \div v$).



2. CONCENTRATION EXPRESSIONS & CALCULATIONS

Most of the substances we encounter in daily life are mixtures: Wood, milk, gasoline, seawater, shampoo, steel, and air are common examples. When the components of a mixture are uniformly **intermingled**—that is, when a mixture is homogeneous—it is called a solution. Solutions can be gases, liquids, or solids, as shown in Table 2.1. However, we will be concerned at this level with the properties of liquid solutions, particularly those containing water. As you saw in your first-level study, many essential chemical reactions occur in aqueous solutions because water is capable of dissolving so many substances.

Chemical Concentrations

A solution is a homogeneous mixture of two or more substances. A minor species in a solution is called the solute, and the major species is the solvent. **Concentration** states how much solute is contained in a given volume or mass of solution or solvent.

Table 2.1 Various Types of Solutions			
State of Solute	State of Solvent	State of Solution	Example
Gas	Gas	Gas	Air, natural gas
Liquid	Liquid	Liquid	Antifreeze
Solid	Solid	Solid	Brass
Gas	Liquid	Liquid	Carbonated water (soda)
Solid	Liquid	Liquid	Seawater, sugar solution
Gas	Solid	Solid	Hydrogen in platinum

Expressing Amount of solute:

A **mole** (mol) is **Avogadro's number** (6.022×10^{23}) of particles (atoms, molecules, ions, or anything else).

The **atomic mass (or molar mass)** of an element is the number of grams containing Avogadro's number of atoms.

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

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

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

The number of moles of a substance is calculated from

$$\text{Moles (n)} = \frac{\text{grams}}{\text{molecular mass } \left(\frac{\text{g}}{\text{mol}}\right)} = \dots \text{ mol} \quad (1)$$

where **molecular mass (M.wt.)** (sometimes called molecular weight, **formula weight (F.wt.)**, or **formula mass**) represents the sum of atomic masses of the atoms in the molecule of a strong electrolyte even though there are very few molecules with that formula. Molecular mass is the number of grams containing Avogadro's number of molecules.

Thus,

Moles $\text{Na}_2\text{SO}_4 = \text{g} / \text{F.wt.} = \text{g} / 142.04 \text{ g/mol}$

Moles $\text{Ag}^+ = \text{g} / \text{M.wt.} = \text{g} / 107.870 \text{ g/mol}$



Units for Expressing Concentration

Concentration is a general measurement unit stating the amount of solute present in a known amount of solution

$$\text{Concentration} = \frac{\text{amount of solute}}{\text{amount of solution}} \quad (2)$$

Molarity, Formality, and Molality

Molarity (symbolized by M): the number of moles of a substance per liter of solution. A **liter (L)** is the volume of a cube that is 10 cm on each edge. Because $10 \text{ cm} = 0.1 \text{ m}$, $1 \text{ L} = (0.1 \text{ m})^3 = 10^{-3} \text{ m}^3$. Chemical concentrations, denoted with square brackets, are usually expressed in moles per liter (M). Thus “[H⁺]” means “the concentration of H⁺”.

An electrolyte is a substance that dissociates into ions in a solution. In general, electrolytes are more dissociated in water than in other solvents. We refer to a compound that is mostly dissociated into ions as a strong electrolyte. One that is partially dissociated is called a weak electrolyte.

Magnesium chloride is a strong electrolyte. In 0.44 M MgCl₂ solution, 70% of the magnesium is free Mg²⁺ and 30% is MgCl⁺. The concentration of MgCl₂ molecules is close to 0.

$$\frac{\text{Weight}}{\text{M. wt.}} = n = \text{M} \times \text{V (L)} \quad (3)$$

and

$$\text{wt. (g)} = \text{M} \times \text{V (L)} \times \text{F.wt. (M.wt.)}$$

$$\text{wt. (mg)} = \text{M} \times \text{V (ml)} \times \text{F.wt. (M. wt.)}$$

Sometimes the molarity of a strong electrolyte is called the **formal concentration or Formality**, to emphasize that the substance is really converted into other species in solution.

Formality (symbolized by F): number of formula weights in a liter of solution, is a substance's total concentration in solution without regard to its specific chemical form. There is no difference between a substance's molarity and formality if it dissolves without dissociating into ions. The molar concentration of a solution of glucose, for example, is the same as its formality. For substances that ionize in solution, such as NaCl, and MgCl₂ molarity and formality are different. For example, dissolving 0.1 mol of NaCl in 1 L of water gives a solution containing 0.1 mol of Na⁺ and 0.1 mol of Cl⁻. The molarity of NaCl, therefore, is zero since there is essentially no undissociated NaCl in the solution. The solution instead, is 0.1 M in Na⁺ and 0.1 M in Cl⁻. The formality of NaCl, however, is 0.1 F because it represents the total amount of NaCl in the solution. When we say that the “concentration” of MgCl₂ is 0.054 M in seawater, we are really speaking of its formal concentration (0.054 F). We are going to use the abbreviation M.wt. for both molecular mass and formula mass.

Normality (N): it is the number of equivalent weights of a substance in solution has a one-liter volume.

The normality of a solution gives the number of gram equivalents of the solute present in one liter of the solution.

$$\text{Normality (N)} = \frac{\text{Number of grams equivalents of solute}}{\text{Volume of Solution in L}} = \text{Eq./L} = \dots (\text{wt./E.wt.})/\text{L} \quad (4)$$

Number of gram equivalent of solute = Mass of solute in gram/ equivalent weight of solute



Equivalent weight of solute (E.wt.) = Molar mass of solute/ Valence factor (V. f)

Valence factor for base = acidity of the base.

Valence factor for acid = basicity of acid.

Valence factor for element = valency.

Thus, if one gram equivalent of a solute is present in one liter of the solution, the concentration of the solution is said to be *one normal*.

1N = Normal = One gram equivalent of the solute per liter of solution = Normality is 1

N/2 = Seminormal = 0.5 g equivalent of the solute per liter of solution = Normality is 0.5

N/10 = Decinormal = 0.1 g equivalent of the solute per liter of solution = Normality is 0.1

N/100 = Centinormal = 0.01 g equivalent of the solute per liter of solution = Normality is 0.01

N/1000 = Millinormal = 0.001 g equivalent of the solute per liter of solution = Normality is 0.001

Relationship between normality and molarity:

If

$$\text{Molarity} \times \text{Molecular mass} = \text{Strength of solution (g/L)} \quad (5)$$

Similarly,

$$\text{Normality} \times \text{Equivalent mass} = \text{Strength of solution (g/L)} \quad (6)$$

Hence,

$$\text{Molarity} \times \text{Molecular mass} = \text{Normality} \times \text{Equivalent mass} \quad (7)$$

So,

$$\text{Normality} = \text{Number of reacting units (Valance)} \times \text{Molarity} \quad (8)$$

or

$$\text{Normality} = \text{V. f} \times \text{Molarity}, \quad (\text{V. f} = \text{M.wt./E.wt.}) \quad (9)$$

Let 'd' be the density of the solution in g/mL (density = mass/volume)

and

p is the percentage of the solute by mass.

Then,

$$N = \frac{p \times d \times 10}{\text{Equivalent Mass of Solute (E.wt.)}} \quad (10) \quad \& \quad M = \frac{p \times d \times 10}{\text{Molecular Mass of Solute (M.wt.)}} \quad (11)$$

Also,

Normality:

$$N = \frac{\text{No. Eq.}}{V(L)}$$

$$\text{No. Eq.} = \frac{\text{mass (g)}}{\text{Eq. wt.}}$$

$$\text{No. Eq.} = \frac{m(g)}{\text{Eq. wt.}}$$

$$\text{Eq. wt.} = \frac{\text{M.wt.}}{x}$$

$$\therefore N = x \cdot \frac{m}{\text{M.wt.}} \cdot \frac{1}{V}$$

Molarity:

$$\text{Molarity} = \frac{\text{No. moles}}{V(L)}$$

$$M = \frac{\text{No. moles}}{V(L)}$$

$$M = \frac{n}{V(L)}$$

$$M = \frac{m}{\text{M.wt.}} \cdot \frac{1}{V(L)}$$

$$\therefore N = (x) \cdot (M)$$

Molarity, formality, and normality are based on the volume of the solution in which the solute is dissolved. Since density is a temperature-dependent property of a solution's volume, and thus its molar, formal and



normal concentrations will change as a function of its temperature. By using the solvent's mass in place of its volume, the resulting concentration becomes independent of temperature.

Molality (symbolized by m), the number of moles of solute per kilogram of solvent: is used in thermodynamic calculations where a temperature-independent unit of concentration is needed.

$$\text{Molality} = \frac{\text{moles of solute}}{\text{kilogram of solvent}} \quad (12)$$

Relationship between Molality and Molarity (Fig.2.1):

$$\begin{aligned} \frac{\text{Molarity}}{\text{Molality}} &= \frac{\text{No. of moles of solute}}{\text{Volume of solution in L}} \times \frac{\text{Mass of solvent in Kg}}{\text{Number of moles of solute}} \\ &= \frac{\text{Mass of solvent in Kg}}{\text{Volume of solution in L}} = \frac{W}{V} \end{aligned} \quad (13)$$

Let the density of the solution be d . (Unit= g mL^{-1} or Kg L^{-1})

Mass of solution = $V \times d$

Mass of solute = number of moles (n) \times molecular mass of solute ($M_{\text{wt.A}}$) = $n M_{\text{wt.A}}$

Mass of solvent (W) = mass of solution ($V \times d$) – mass of solute = $V \times d - (n M_{\text{wt.A}})$

Thus,

$$\frac{\text{Molarity}}{\text{Molality}} = \frac{M}{m} = \frac{V \times d - (n M_{\text{wt.A}})}{V} \quad (14)$$

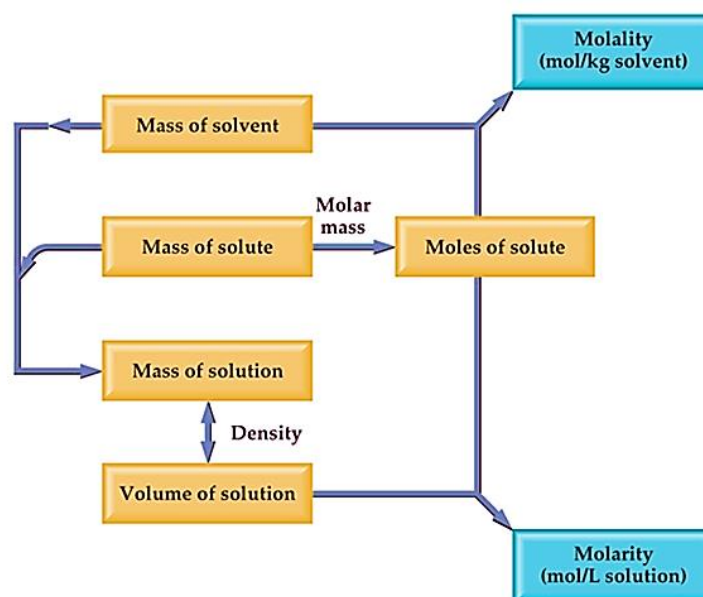


Figure 2.1. Relationship between Molality and Molarity

Weight, Volume, Weight-to-Volume, and Volume-to-Weight Ratios:

Mass percent (sometimes called weight percent) (% w/w), **volume percent** (% v/v), **weight-to-volume percent** (% w/v) and **volume-to-weight percent** (% v/w) (less common) express concentration as units of solute per 100 units of sample.

$$\text{Mass percent} \left(\% \frac{w}{w} \right) = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100\% \quad (15)$$



$$\text{Volume percent } \left(\% \frac{v}{v} \right) = \frac{\text{volume of solute}}{\text{volume of solution}} \times 100\% \quad (16)$$

$$\text{Weight – to – volume percent } \left(\% \frac{w}{v} \right) = \frac{\text{mass of solute}}{\text{volume of solution}} \times 100\% \quad (17)$$

$$\text{Volume – to – weight percent } \left(\% \frac{v}{w} \right) = \frac{\text{volume of solute}}{\text{mass of solution}} \times 100\% \quad (18)$$

A solution in which a solute has a concentration of 23% w/v contains 23 g of solute per 100 ml of solution. Another way of describing solution composition is the **mole fraction** (symbolized by the Greek lowercase letter chi, χ), the ratio of the number of moles of a given component to the total number of moles in solution. For a two-component solution, where n_A and n_B represent the number of moles of the two components,

$$\text{Mole fraction of component A} = \chi_A = \frac{n_A}{n_A + n_B} \quad (19)$$

$$\text{Mole fraction of component B} = \chi_B = \frac{n_B}{n_A + n_B} \quad (20)$$

where the total number of mole fraction of components $\chi_A + \chi_B = 1$.

Relation between mole fraction and Molality:

$$\frac{\chi_A}{1 - \chi_A} \times 1000 = m \quad (21)$$

Parts per million and parts per billion:

Parts per million (ppm) and parts per billion (ppb) are mass ratios of grams of solute to one million or one billion grams of sample, respectively or the number of milligrams of solute per kg of solution = one ppm, since $1 \text{ mg} = 10^{-3} \text{ g}$ and $1 \text{ kg} = 10^3 \text{ g}$.

Assuming the density of water is 1.00 g/mL, 1 liter of solution = is 1 kg and hence, $1 \text{ mg/L} = 1 \text{ ppm}$. This is generally true for freshwater and other dilute aqueous solutions.

Parts per million concentrations are essentially mass ratios (solute to solution) \times a million (10^6). In this sense, they are similar to wt%, which could be thought of as parts per hundred (although nobody uses this term). A steel that is 450 ppm in Mn contains 450 μg of Mn for every gram of steel. If we approximate the density of an aqueous solution as 1.00 g/ml, then solution concentrations can be expressed in parts per million or parts per billion using the following relationships.

$$\text{ppm} = \frac{\text{mg}}{\text{Kg}} = \frac{\mu\text{g}}{\text{g}} \quad (\text{for solid sample}) \quad \text{or} \quad \text{ppm} = \frac{\text{mg}}{\text{L}} = \frac{\mu\text{g}}{\text{mL}} \quad (\text{for solution}) \quad (22)$$

$$\text{ppb} = \frac{\mu\text{g}}{\text{Kg}} = \frac{\text{ng}}{\text{g}} \quad (\text{for solid sample}) \quad \text{or} \quad \text{ppb} = \frac{\mu\text{g}}{\text{L}} = \frac{\text{ng}}{\text{mL}} \quad (\text{for solution}) \quad (23)$$



For **gases**, a part per million usually is a **volume ratio**. Thus, a helium concentration of 6.3 ppm means that one liter of air contains 6.3 ml of He.

The relationship between ppm with M and N is as follows:

$$\text{ppm} = M \times \text{M.wt.} \times 1000 \quad (24)$$

$$\text{ppm} = N \times \text{Eq.wt.} \times 1000 \quad (25)$$

$$\text{ppm (wt./vol)} = \left[\frac{\text{wt. solute (g)}}{\text{Vol sample (mL)}} \right] \times 10^6 (\text{ppm/g solute/mL sample}) \quad (26)$$

$$\text{ppb (wt./vol)} = \left[\frac{\text{wt. solute (g)}}{\text{Vol sample (mL)}} \right] \times 10^9 (\text{ppb/g solute/mL sample}) \quad (27)$$

for E.wt.:

$$\text{no. of meq} = \frac{\text{mg}}{\text{Eq wt. (mg/meq)}} = \frac{\text{mg}}{\text{F. wt. (mg/mmol)/n (meq/mmol)}} \quad (28)$$

where n = charge on the ion.

Other expressions to find concentration are related to physical methods such as:

1- Osmotic pressure, π expression

$$\pi = MRT \quad (29)$$

where M = molarity of solution and R = gas constant (R = 0.082 L atm/mol K, or: 8.314 J/mol K).

2- Boiling point, ΔT_b , expression

$$\Delta T_b = K_b m \quad (30)$$

where K_b = molal boiling point elevation constant, m = molality of solute particles.

3- Freezing point depression expression

$$\Delta T_f = K_f m \quad (31)$$

where K_f = molal freeze-point depression constant, m = molality of solute particles.

Dilutions

When we concentrate or dilute a solution the amount of solute in the solution does not change (only the concentration changes).

We can say that;

$$\text{Amount of solute before dilution} = \text{Amount of solute after dilution} \quad (32)$$

We know that concentration is a ratio of the amount of solute to the amount of solution; See Example 1.

$$\text{Concentration} = \frac{\text{Amount of solute}}{\text{Amount of solution}} \quad (33)$$

The concentration formula can be re-arranged to find the amount of solute in the solution;

$$\text{Amount of Solute} = \text{Concentration} * \text{Amount of solvent} \quad (34)$$

$$X = C_1 * V_1$$



We can then combine these formulae to allow the amount of solute, dilutions, and concentrations to be found;

$$\begin{array}{ccccccc} \text{Amount of solute} & = & \text{Concentration} & * & \text{Volume} & = & \text{Concentration} & * & \text{Volume} \\ & & \text{(before)} & & \text{(before)} & & \text{(after)} & & \text{(after)} \\ \mathbf{X} & & \mathbf{C_1} & * & \mathbf{V_1} & = & \mathbf{C_2} & * & \mathbf{V_2} \end{array} \quad (35)$$

- The form of the concentration does not matter since all concentrations are a ratio of the amount of solute to solution
- The units for volume must be the same, however.

√NOTE: It is critical that you report units for concentrations, amounts and volumes. When you make calculations for dilutions you must not mix up the units. Eg: it doesn't work to write,

$$V_1 (160 \text{ milliliters}) * C_1 (160 \text{ milligrams/liter}) = V_2 (\text{unknown}) * C_2 (\text{desired- grams/liter})$$

Units

As concentration represents a proportional relationship, you can select from a variety of units. For example, 1 milligram/milliliter is the same as 1 gram/liter, 1 microgram/microlitre, or 1 nanogram/nanolitre. It is also the same as 1000 milligrams/liter!

Always try to select units that simplify your expressions.

Terminology & Unit Definitions

- Molecular weight (M.wt.) = weight in grams of one mole of compound
 - g/mole = mg/mole
- Valence = amount of charge of an ion
- Equivalent (Eq) = number of univalent counter ions needed to react with each molecule of substance
 - HCl has 1 equivalent per mole in that one mole of H⁺ reacts with one mole of Cl⁻
- milligram = mg = 1/1000 of a g or 10⁻³ g
- gram = g = 1000 mg
- kilogram = kg = 1000 g or 10³ g
- milliliter = 1/1000 of a liter or 10⁻³ l
- liter = l = 1000 mL
- ppt = parts per thousand = g/L (0.01ppt = 10 ppm)
- ppm = parts per million = mg/L (1ppm = 0.001ppt)
- ppb = parts per billion = ug/L (1 ppb = 0.001ppm)
- ppm = ppt * 1000
- ppt = ppm/1000
- w/v = weight (of solute) per final solution volume
- v/v = volume (of reagent) per final solution volume
- mole = 6.023 x 10²³ molecules (Avogadro's Number)
- molarity = moles per liter
- molar = M = term used to discuss the molarity of solutions (e.g., 2.5 M means 2.5 moles of solute dissolved up to one liter of solution using a desired solvent)
- millimole = 1/1000 of a mole
- millimolar = mM = term used to discuss molarity in thousandths of a mole (e.g., a 20 mM solution contains 20/1000 = 0.02 moles per liter)
- normality = equivalent per liter
- normal = N = term used to discuss the normality of solutions (e.g., 2.5 N means 2.5 equivalent of solute dissolved up to one liter of solution using a desired solvent)
- milliequivalent = 1/1000 of an equivalent
- formality = formal per liter
- formal = F = term used to discuss the formality of solutions (e.g., 2.5 F means 2.5 formal of solute dissolved up to one liter of solution using a desired solvent)
- mole fraction, χ = moles of solute/total moles



EXAMPLES

Example 2.1: You have 10 grams of sucrose and dissolve this in water up to 200 milliliters. What is the concentration of sucrose in the solution?

Solution:

Information given; Amount of solution = 0.2litre, Amount of solute = 10g

Information required; Concentration = ?

Concentration=10 grams / 0.2 liter

Concentration = 50 grams/liter.

Example 2.2: Prepare a 3 % w/v NaCl solution.

Solution:

To make a 3 % w/v NaCl solution 3.0 g NaCl is dissolved up to 100 mL solution (or the equivalent for whatever volume you needed). If you want to make up less or more than 100 mL of solution, the proper amount of solute can be determined by multiplying the number of grams in a 1% w/v solution by the desired final volume divided by 100.

Example 2.3: Prepare 350 mL of 12% w/v NaCl.

Solution:

To make 350 mL of 12% w/v NaCl in water, substitute values into the percentage concentration formula and use algebra to solve.

Information given; Concentration = 12%, Amount of solution = 350mL

Information required; Amount of solute

$12/100 = \text{Amount of solute}/350\text{mL}$

$(12/100) * 350 = \text{Amount of solute} = 42 \text{ g}$

So, dissolve 42 g of NaCl in 350mL water

Example 2.4: Make up 15 mL of 0.05% w/v NaCl

Solution:

Information given; Concentration = 0.05%, Amount of solution =15mL

Information required; Amount of solute

$(0.05/100) = \text{Amount of solute}/15$

$(0.05/100) * 15 = \text{Amount of solute} = 0.0075\text{g} = 7.5\text{mg}$

So dissolve 0.0075 g NaCl in 15mL water

Example 2.5: If you want to make 100mL of 70% v/v ethanol you would mix 70 mL of 100% ethanol with 30 mL of water. How to prepare 60 mL and 130 mL of 70% v/v ethanol.

Solution:

Making up volumes less or more than 100 mL is handled the same way as for solutions prepared from solids.

Example 2.6: How to make up 912 mL of 21.5% v/v AquaX.

Solution:

Information given; Concentration = 21.5%, Amount of solution =912mL

Information required; Amount of solute



$$(21.5 / 100 \text{ mL}) = \text{Amount of solute} / 912$$

$$(21.5/100)*912 = \text{Amount of solute} = 196.1 \text{ mL}$$

The amount of solvent used is based upon the final volume, you must subtract the starting volume from the final to calculate it.

$$912 - 196.1 = 715.9 \text{ mL}$$

So, mix 196.1 mL of AquaX with 715.9 mL of water and you'll have a 21.5% v/v solution

Example 2.7: How many milligrams of methanol (CH_3OH) are in one gallon (3800mL) with 10 ppm concentration?

Solution:

$$10 \text{ ppm} = 10 \text{ mg} / 1000 \text{ g} = 10 \text{ mg} / 1000 \text{ mL}$$

$$\text{wt. (mg)} = 10 \text{ mg} / 1000 \text{ mL} \times 3800 \text{ mL}$$

$$\text{wt.} = 38 \text{ mg.}$$

Example 2.8: Calculate the mass in grams of magnesium in a body (solute) if the body weighs 50 Kg and the concentration is 4.0 ppm.

Solution:

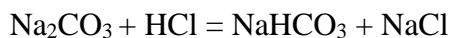
Information given; Concentration = 4.0 ppm, Amount of solution = 50 kg = 50,000g

Information required; Amount of solute (mass of magnesium in grams)

$$4 / 1,000,000 = \text{Amount of Solute} / 50,000$$

$$(4 / 1,000,000) * 50,000 = \text{Amount of Solute} = 0.2 \text{ grams of magnesium}$$

Example 2.9: convert 0.1 N Na_2CO_3 to M & F if:



Solution:

$$N = \text{no. of eq.} \times M$$

$$0.1 \text{ N} = 1 \times M$$

$$M = 0.1 / 1 = 0.1$$

But for F; Na_2CO_3 has 2 equivalents. So;

$$0.1 \text{ N} = 2 \times F$$

$$F = 0.1 / 2 = 0.05$$

Example 2.10: Find F for HCl if; sp.gr. = 1.188g/mL and contains 37.50% by mass HCl.

(Atomic weight: H = 1, Cl = 35.5 g/mol)

Solution:

$$F = M = \text{sp.gr.} \times \% / \text{M.wt.}$$

$$= \frac{1.188 \text{ g/mL}}{\frac{1}{1000} \text{ L/mL}} \times \frac{37.5}{36.5 \text{ g/mol}}$$

$$= 12.22 \text{ F}$$



Example 2.11: How many grams of Na_2SO_4 (M.wt.= 142.0, E. wt.= 71.0) is required to prepare 0.5N of this compound in a 250 mL volumetric flask?

Solution:

$$N = \frac{\text{no.eq.}}{V}$$

no. eq. = $N \times V = 0.5 \text{ eq/L} \times 0.25 \text{ L} = 0.125 \text{ eq.}$ &

wt. = no. eq. \times E.wt. = $0.125 \text{ eq.} \times 71.0 \text{ g/eq.} = 8.875 \text{ g.}$

Example 2.12: A solution of sucrose (in water) with volume V_1 of 200mL and concentration C_1 of 50grams/liter. What is the total amount of sucrose in your solution?

Solution:

Information given; Concentration = 50 g/l, Amount of solution = .2litre = 200mL
Information required; Amount of solute (mass of sucrose in grams)

$$X = C_1 * V_1$$

$$X = 50 \text{ grams/liter} * 0.2 \text{ liter}$$

$$X = 10 \text{ grams sucrose.}$$

Example 2.13: A NaCl solution with a concentration of 50g/l and a volume of 200mL is diluted to a total volume of 2 liters. What is the concentration of the new solution?

Solution:

Information given; Concentration before dilution(C_1) = 50 g/l, Amount of solution before dilution(V_1) = 0.2litre, Amount of solution after dilution(V_2) = 2litre

Information required; Concentration after dilution (C_2)

$$C_2 * 2 = 50 * 0.2$$

$$C_2 = (50 * 0.2) / 2$$

$$C_2 = 5 \text{ grams per liter}$$

Example 2.14: A NaCl solution with a concentration of 50g/l and a volume of 100mL is diluted to a total volume of 2.5 liters. What is the concentration of the new solution?

Solution:

Information given; Concentration before dilution(C_1) = 50 g/l, Amount of solvent before dilution(V_1) = 0.1litre, Amount of solvent after dilution(V_2) = 2.5litre

Information required; Concentration after dilution (C_2)

$$C_2 * 2.5 = 50 * 0.1$$

$$C_2 = (50 * 0.1) / 2.5$$

$$C_2 = 2.5 \text{ grams per liter}$$

Example 2.15: You have a stock solution of known concentration(50g/l), and you wish to know how much additional solvent and original solution are required to reach a predetermined concentration (30g/l) and volume (2L).

Solution:

Information given; Concentration before dilution(C_1) = 50 g/l, Amount of solution after dilution(V_2) = 2litre, Concentration after dilution (C_2) = 30g/l

Information required; Amount of solution before dilution(V_1) = ?, Additional solvent required = ($V_2 - V_1$)

$$50 \text{ grams/liter} * V_1 \text{ liter} = 30 \text{ grams/liter} * 2 \text{ liter}$$

$$V_1 = (30 * 2) / 50$$



$V_1 = 1.2$ liters, this is the amount of stock solution required

$V_2 - V_1 =$ Additional solvent required

$2 - 1.2 = 0.8$ liter, this is the amount of additional solvent required to reach given concentration.

Example 2.16: Calculate the concentration in ppm of a solution of chlorine bleach created by diluting 500 mL of a 4.0 ppm solution with 300 mL of water.

Solution:

Information given; Concentration before dilution (C_1) = 4ppm, Amount of solution after dilution (V_2) = 800mL, Amount of solution before dilution (V_1) = 500mL

Information required; Concentration after dilution (C_2) = ?

$C_1 = 4.0$ ppm ; $V_1 = 500$ mL; $C_2 = ?$ ppm; $V_2 = 800$ mL;

$$4 * 500 = C_2 * 800$$

$$C_2 = (4 * 500) / 800 = 2.5 \text{ ppm}$$

Example 2.17: Calculate the mass of nickel (II) sulfate, NiSO_4 , contained in 200 g of a 60 % (w/w) solution of NiSO_4 .

Solution:

Mass of soln. = 200 g, percent of solute (w/w) = 60 % (w/w), m. solute = ?

$$\text{Percent of NiSO}_4 \text{ (w/w)} = \frac{\text{mass of NiSO}_4 \text{ (g)}}{\text{mass of NiSO}_4 \text{ soln. (g)}} \times 100 \%$$

$$60 \% = \frac{\text{mass of NiSO}_4 \text{ (g)}}{200 \text{ g}} \times 100 \%$$

$$\text{Mass of NiSO}_4 = \frac{200 \times 60}{100}$$

$$\therefore \text{Mass of NiSO}_4 = 120 \text{ g NiSO}_4$$

Example 2.18: Calculate the percent by mass (w/w) of NaCl, when 6.0 g of NaCl was dissolved in 60.0 g of H_2O .

Solution:

M. solute = 6.0 g , M. solvent = 60.0 g , percent solute (w/w) = ?

$$\text{Percent of NaCl (w/w)} = \frac{\text{mass of NaCl (g)}}{\text{mass of NaCl soln (g)}} \times 100 \%$$

$$\begin{aligned} \text{Mass of solution} &= \text{mass of NaCl} + \text{mass of H}_2\text{O} \\ &= 6.0 \text{ g} + 60.0 \text{ g} \\ &= 66.0 \text{ g} \end{aligned}$$

$$\text{Percent of NaCl (w/w)} = \frac{6.0 \text{ g}}{66.0 \text{ g}} \times 100 \%$$

$$\therefore \text{Percent of NaCl (w/w)} = 9.1 \% \text{ (w/w)}$$

This means, in 100 g of solution containing 9.1 g of NaCl.

Example 2.19: A 12.7 g of NiSO_4 was dissolved in 199.3 g of H_2O . The density of NiSO_4 solution is 1.06g/mL at 25°C. What is the percent of NiSO_4 in unit (w/v)?

Solution:

Mass of solute = 12.7 g , mass of solvent = 199.3 g, percent NiSO_4 (w/v) = ?

$$\text{Percent of NiSO}_4 \text{ (w/v)} = \frac{\text{mass of NiSO}_4 \text{ (g)}}{\text{vol. of NiSO}_4 \text{ soln. (mL)}} \times 100 \%$$

$$\begin{aligned} \text{Mass of NiSO}_4 \text{ solution} &= \text{mass of NiSO}_4 + \text{mass of H}_2\text{O} \\ &= 12.7 \text{ g} + 199.3 \text{ g} \\ &= 212 \text{ g} \end{aligned}$$

By using the law of density, we can be calculating the volume of the solution:



$$\text{density} = \frac{\text{mass(g)}}{\text{volume(mL)}} \longrightarrow \text{volume(mL)} = \frac{\text{mass(g)}}{\text{density(g/mL)}}$$

$$\begin{aligned} \text{volume(mL)} &= \frac{212 \text{ g}}{1.06 \text{ g/mL}} \\ &= 200 \text{ mL} \end{aligned}$$

$$\text{Percent of NiSO}_4 \text{ (w/v)} = \frac{12.7 \text{ g}}{200 \text{ mL}} \times 100\%$$

$$\therefore \text{Percent of NiSO}_4 \text{ (w/v)} = 6.35\% \text{ (wt/v)}$$

This means, in 100 mL of solution contained 6.35 g of NiSO₄.

Example 2.20: Calculate the percent by volume (v/v) of ethanol, when 20.0 mL of ethanol was dissolved in 60.0 mL of H₂O.

Solution:

Vol. solute (ethanol) = 20.0 mL , Vol. solvent (H₂O) = 60.0 mL ,
Percent of ethanol (v/v) = ?

$$\text{Percent of solute (v/v)} = \frac{\text{vol. of solute(mL)}}{\text{vol. of solution(mL)}} \times 100\%$$

$$\begin{aligned} \text{Volume of ethanol soln.} &= \text{vol. of ethanol} + \text{vol. of H}_2\text{O} \\ &= 20.0 \text{ mL} + 60.0 \text{ mL} \\ &= 80.0 \text{ mL} \end{aligned}$$

$$\text{Percent of ethanol (v/v)} = \frac{20.0 \text{ mL}}{80.0 \text{ mL}} \times 100\%$$

$$\therefore \text{Percent of ethanol (v/v)} = 25.0\% \text{ (v/v)}$$

This means, in 100 mL of solution contained 25 mL of ethanol.

Example 2.21: A mixture of gases contains 4.46 mol of neon (Ne), 0.74 mol of argon (Ar), and 2.15 mol of xenon (Xe). What is the mole fraction of each gas in the mixture?

Solution:

The number of moles of Ne = 4.46 mol

The number of moles of Ar = 0.74 mol

The number of moles of Xe = 2.15 mol

$$\begin{aligned} \text{The total number of moles (n}_t\text{)} &= \text{No. mol of Ne} + \text{No. mol of Ar} + \text{No. mol of Xe} \\ &= 4.46 \text{ mol} + 0.94 \text{ mol} + 2.15 \text{ mol} \\ &= 7.35 \text{ mol} \end{aligned}$$

$$\begin{aligned} \text{Mole fraction of Ne} = X_{\text{Ne}} &= \frac{\text{moles of Ne}}{n_t} \\ &= \frac{4.46 \text{ mol}}{7.35 \text{ mol}} = 0.607 \end{aligned}$$

$$\begin{aligned} \text{Mole fraction of Ar} = X_{\text{Ar}} &= \frac{\text{moles of Ar}}{n_t} \\ &= \frac{0.74 \text{ mol}}{7.35 \text{ mol}} = 0.100 \end{aligned}$$

$$\begin{aligned} \text{Mole fraction of Xe} = X_{\text{Xe}} &= \frac{\text{moles of Xe}}{n_t} \\ &= \frac{2.15 \text{ mol}}{7.35 \text{ mol}} = 0.293 \end{aligned}$$

$$\begin{aligned} \text{The sum of mole fraction of all gases} &= X_{\text{Ne}} + X_{\text{Ar}} + X_{\text{Xe}} \\ &= 0.607 + 0.100 + 0.293 \\ &= 1.00 \end{aligned}$$

Example 2.22: Calculate the molality of sulfuric acid solution (H₂SO₄) containing 24.4 g of H₂SO₄ (M.wt. = 98 g/mol) in 198 g of H₂O.

Solution:

Mass of H₂SO₄ = 24.4 g , Mass of H₂O = 198 g

$$\text{Molality of H}_2\text{SO}_4 \text{ solution} = \frac{\text{moles of solute(mol)}}{\text{mass of solvent(g)}} \times 1000$$



$$\begin{aligned}\text{Number of moles of H}_2\text{SO}_4 &= \frac{\text{mass of sulfuric acid (g)}}{\text{M.wt. of sulfuric acid (g/mol)}} \\ &= \frac{24.4 \text{ g}}{98 \text{ g/mol}} = 0.249 \text{ mol H}_2\text{SO}_4 \\ \text{Molality of H}_2\text{SO}_4 \text{ solution} &= \frac{0.249 \text{ mol}}{198 \text{ g}} \times 1000 \\ &= 1.26 \text{ mol/kg} \\ &= 1.26 \text{ m}\end{aligned}$$

Example 2.23: A 2.5 g sample of groundwater was found to contain 5.4 μg of zinc ion (Zn^{2+}). What is the concentration of Zn^{2+} in ppm?

Solution:

$$\text{Mass of sample} = 2.5 \text{ g}, \quad \text{mass of Zn}^{2+} = 5.4 \mu\text{g}$$

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

$$\begin{aligned}\text{Mass of Zn}^{2+} \text{ in gram} &= 5.4 \mu\text{g} \times \frac{1 \text{ g}}{10^6 \mu\text{g}} \\ &= 5.4 \times 10^{-6} \text{ g}\end{aligned}$$

$$\begin{aligned}C_{\text{ppm}} &= \frac{5.4 \times 10^{-6} \text{ g}}{2.5 \text{ g}} \times 10^6 \text{ ppm} \\ &= 2.2 \text{ ppm}\end{aligned}$$

This means 2.2 mg of Zn^{2+} per 1 kg of groundwater.

Example 2.24: Calculate the molarity of a solution that contains 3.65 g of HCl in 2.00 L.

Solution:

$$\begin{aligned}\text{Mass of solute (HCl)} &= 3.65 \text{ g}, & \text{M.wt of HCl} &= 36.5 \text{ g/mol} \\ \text{Vol. of HCl solution} &= 2.00 \text{ L}, & \text{Molarity of HCl solution} &= ?\end{aligned}$$

$$\text{Molarity of HCl soln.} = \frac{n \text{ (mol)}}{\text{vol. of HCl solution (L)}}$$

$$\text{The number of moles of HCl} = n = \frac{\text{mass (g)}}{\text{M.wt (g/mol)}}$$

$$\therefore n = \frac{3.65 \text{ g}}{36.5 \text{ g/mol}} = 0.1 \text{ mol}$$

$$\text{Molarity of HCl soln.} = \frac{0.1 \text{ mol}}{2.00 \text{ L}}$$

$$\therefore \text{Molarity of HCl solution} = 0.05 \text{ M}$$

Example 2.25: Find formality (F) of HCl if sp.gr. = 1.188 g/mL, & contents 37.50 by mass HCl.

Solution:

$$\begin{aligned}F = M &= \frac{\text{sp.gr} \times \%}{\text{M.wt}} = \frac{1.188 \times 37.50 \times 10}{36.5} \\ &= 12.22 \text{ F}\end{aligned}$$

Example 2.26: Calculate (a) the number of moles of H_2SO_4 (b) the number of grams of H_2SO_4 in 500 mL of 0.324 M H_2SO_4 solution. (H = 1, S = 32.1, O = 16 g/mol)

Solution:

$$\text{Volume of H}_2\text{SO}_4 \text{ solution} = 500 \text{ mL}, \quad \text{Molarity of H}_2\text{SO}_4 \text{ solution} = 0.324 \text{ M}$$

1. The number of moles of H_2SO_4 :

From the law of molarity:

$$\text{Molarity of H}_2\text{SO}_4 \text{ solution} = \frac{n \text{ (mol)}}{\text{vol. of solution (mL)}} \times 1000$$



$$\begin{aligned} \text{Number of H}_2\text{SO}_4 \text{ of moles (n)} &= \frac{M (\text{mol/L}) \times V (\text{mL})}{1000} \\ &= \frac{(0.324 \text{ mol/L}) \times 500 \text{ mL}}{1000} \end{aligned}$$

$$\therefore \text{Number of moles of H}_2\text{SO}_4 = 0.162 \text{ mol}$$

2. The number of grams of H₂SO₄:

To calculate the mass of H₂SO₄ in the solution:

$$n = \frac{\text{mass (g)}}{\text{M.wt (g/mol)}} \longrightarrow \text{mass (g)} = n (\text{mol}) \times \text{M.wt (g/mol)}$$

$$\text{The number of grams} = (0.162 \text{ mol}) \times (98.1 \text{ g/mol})$$

$$\therefore \text{The number of grams of H}_2\text{SO}_4 = 15.9 \text{ g}$$

Worked Problems:

2.1- What is the weight percentage of urea solution in which 5 gm of urea is dissolved in 95 gm water.

Answer

$$\text{Weight percentage of urea} = (\text{weight of urea} / \text{weight of solution}) \times 100$$

$$= 5 / (95 + 5) \times 100 = 5\% \text{ urea solution (w/W).}$$

2.2- 3.65 g of HCl gas is present in 100 mL of its aqueous solution. What is the molarity?

Answer

$$\text{Molarity} = \frac{\text{wt}}{\text{M.wt}} \times \frac{1000}{V (\text{mL})} = (3.65 / 36.5) \times 1000 / 100 = 1\text{M}$$

2.3- The density of a 3M sodium thiosulphate solution is 1.25 gm cm⁻³. Calculate

i) the molalities of Na⁺ and S₂O₃²⁻ ions.

ii) percentage of weight of solution.

Answer

3M Na₂S₂O₃ (Sodium thiosulphate) solution means

3 moles Na₂S₂O₃ is present in 1 L or, 1000 ml solution

$$\text{Wt. of solute Na}_2\text{S}_2\text{O}_3 = 3 \times 158$$

$$\text{wt. of solution} = v \times d$$

$$= 1000 \text{ ml} \times 1.25 \text{ g/ml}$$

$$= 1000 \times 1.25 \text{ g}$$

$$\text{Wt. of solvent} = (1000 \times 1.25 - 3 \times 158) \text{ g H}_2\text{O}$$

Molality = no. of moles of solute per 1000 g solvent

$$= 3 \times \frac{1000}{1000 \times 1.25 - (3 \times 158)}$$

$$= 3.865 \text{ mol kg}^{-1} \text{ solvent}$$

$$\text{Now, Na}_2\text{S}_2\text{O}_3 = 2\text{Na}^+ + \text{S}_2\text{O}_3^{2-}$$



a) Hence molality of $\text{Na}^+ = 2 \times 3.865 \text{ mol kg}^{-1}$

$$= 7.73 \text{ mol kg}^{-1}$$

Hence molality of $\text{S}_2\text{O}_3^{2-} = 1 \times 3.865 \text{ mol kg}^{-1}$

$$= 3.865 \text{ mole/kg}$$

b) % of wt. of solution

1 L i.e. 1000 ml solution containing 3 moles $\text{Na}_2\text{S}_2\text{O}_3$

1000 \times 1.25 g solution containing 3 \times 158 g $\text{Na}_2\text{S}_2\text{O}_3$

$$\therefore 100 \text{ g solution containing } \frac{3 \times 158}{1000} \times \frac{100}{1.25}$$

$$= 37.92\%$$

2.4- CH_3COOH exists as a dimer in benzene. 1.2 g of the acid was dissolved and the volume was made up to one liter using benzene. What is the formality?

Answer

The molar mass of $\text{CH}_3\text{COOH} = 60$

Formula weight of the associated molecule of the acid = $2 \times 60 = 120$

Weight of $\text{CH}_3\text{COOH} = 1.2 \text{ g}$

Volume of solution = 1L

$$\text{Formality} = 1.2/120 \times 1/1 = 0.01 \text{ F}$$

2.5- The concentration of zinc ion in blood serum is about 1 ppm. Express this as meq/L.

Answer

$$1 \text{ ppm} = 1 \mu\text{g/mL} = 1 \text{ mg/L}$$

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

Therefore,

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

This unit is actually used for the major electrolytes.



3. STATISTICAL DATA TREATMENT IN CHEMICAL ANALYSES AND EVALUATION

Statistics is a tool to answer questions:

- How accurate are the analyses?
- How many analyses do I have to make to overcome problems of inhomogeneity or imprecision?
- Does the product meet the specification?
- With what confidence is the limit exceeded?

Data Treatment (Data Analysis)

Most data quantitative - is derived from measurements.

Never really know the error.

With more measurements, you get a better idea of what it might be.

The Factor–Label Method (Dimensional Analysis)

Many chemical and physical processes can be described by numerical relationships. In fact, many of the most useful ideas in science must be treated mathematically.

The units must *always* accompany the numeric value of a measurement, whether we are writing about the quantity, talking about it, or using it in calculations.

Multiplication by unity (by one) does not change the value of an expression. If we represent “one” in a useful way, we can do many conversions by just “multiplying by one.”

This method of performing calculations is known as the **factor-label method, dimensional analysis**, or the **unit factor method**. Regardless of the name chosen, it is a powerful mathematical tool that is almost foolproof.

In this method, a quantity described in one unit is converted into an equivalent quantity with a different unit by using a **conversion factor** to express the relationship between units:

$$\text{Original quantity} \times \text{Conversion factor} = \text{Equivalent quantity}$$

Significant Figures (significant digits)

All measurements involve uncertainty. One source of this uncertainty is the measuring device itself. Another source is your ability to perceive and interpret a reading. You cannot measure anything with complete certainty. The last (farthest right) digit in any measurement is always an estimate.

The digits that you record when you measure something are called **significant figures** (or **significant digits**). Significant digits include the digits that you are certain about and a final, uncertain digit that you estimate. For example, 3.17 g has three significant digits. The first two digits, the 3 and the 1, are certain. The last digit, the 7, is an estimate. Therefore, it is uncertain.

The value 2.4 has two significant digits. The 2 is certain, and the 4 is uncertain.

How can you tell which digits are significant?

You can identify the number of significant digits in any value. Table 3.1 lists some rules to help you do this.



Table 3.1 Rules for Determining Significant Figures

Rules	Examples
1. All non-zero numbers are significant.	6.776 has four significant digits. 27.2 has three significant digits. 515.366 993 has nine significant digits.
2. All zeros that are located between two non-zero numbers are significant.	709 has three significant digits. 55 064 has five significant digits.
3. Zeros that are located to the left of a value are not significant.	0.0907 has three significant digits. They are the 9, the third 0 to the right, and the 7. The function of the 0.0 at the beginning is only to locate the decimal. 0.000 000 000 06 has one significant digit.
4. Zeros that are located to the right of a value may or may not be significant. If a number is greater than 1, then all zeros to the right of the decimal point are significant If a number is less than 1, then only the zeros that are at the end and in the middle of the number are significant	0.08 L 1 significant figure 2.0 mg (equal or greater than 1) 2 significant figures 0.00420 g (less than 1) 3 significant figures 12000 may have two significant digits, or it may have five significant digits. E.g. 12000 ???? Answer: using a scientific notation 12 x 10 ³ means 2 significant figures or 12.000 x 10 ³ means 5 significant figures.
5. Rounding off Rules The final answer should only contain figures that are certain, plus the first uncertain number. -Round a 5 to the nearest even number. Carry an extra figure all through calculations Just round off at the end of calculations.	45.2%. Error less than 1% or we would only write 45%. Error larger than 0.05% or would write 45.23%. 4.55 to 4.6 and 4.45 to 4.4 but 4.54 to 4.5 and 4.56 to 4.6
6. Addition & Subtraction Rules The absolute uncertainty of the answer must not exceed that of the most uncertain number. Simple rule: Decimal places in answer = decimal places in number with the fewest places -When errors are known: $R \pm r = (A \pm a) + (B \pm b) + (C \pm c)$ where $r^2 = a^2 + b^2 + c^2$	12.2 +00.365 <u>+01.04</u> 13.605 goes to 13.6 Calculate the error in the M.wt. of FeS from the following atomic weights: Fe:55.847 ±0.004, S:32.064 ±0.003 Answer: $r = (0.004^2 + 0.003^2)^{1/2} = 0.005$ then, M.wt. = 87.911 ± 0.005
7. Multiplication and Division Rules Simplest rule: Sig figs in answer = smallest number of sig figs in any value used.	1.07400 x 0.993 = 1.07 1.07400 x 1.002 = 1.076
8. Logarithms (logs) Rules Only figures in the mantissa (after the decimal point) are significant figures Use as many places in mantissa as there are significant figures in the corresponding number.	pH = 3.85 has 2 sig figs



Errors in Chemical Analysis

Trueness: the closeness of agreement between the true value and the sample mean.

Error: the difference between one measurement and the true value.

It is impossible to eliminate errors. The analytical results are impossible to be free of errors or uncertainties, but

It is possible to minimize these errors and estimate their size with acceptable accuracy.

Q. How reliable are our data?

Answer:

Carry out replicate measurements.

Analyze accurately known standards.

Perform statistical tests on data.

Notes:

-Data of unknown quality are worthless!

-The true value of a measurement is never known exactly.

Reliability can be assessed in several ways:

- 1- Standards of known composition can be analyzed and the results compared with the known composition.
- 2- Calibrating equipment enhances the quality of data.

Classification of Errors

The errors which affect an experimental result may conveniently be divided into 'systematic' and 'random' errors.

Systematic (determinate) errors: These are errors which can be avoided, or whose magnitude can be determined. The most important of them are:

1. Operational and personal errors. These are due to factors for which the individual analyst is responsible and are not connected with the method or procedure: they form part of the 'personal equation' of an observer. The errors are mostly physical in nature and occur when sound analytical technique is not followed. Examples are: mechanical loss of materials in various steps of an analysis; under washing or overwashing of precipitates; ignition of precipitates at incorrect temperatures; insufficient cooling of crucibles before weighing; allowing hygroscopic materials to absorb moisture before or during weighing; and use of reagents containing harmful impurities.

Personal errors may arise from the constitutional inability of an individual to make certain observations accurately. Thus some persons are unable to judge color changes sharply in visual titrations, which may result in a slight overstepping of the endpoint.

2. Instrumental and reagent errors. These arise from the faulty construction of balances, the use of uncalibrated or improperly calibrated weights, graduated glassware, and other instruments; the attack of reagents upon glassware, porcelain, etc., resulting in the introduction of foreign materials; volatilization of platinum at very high temperatures; and the use of reagents containing impurities.

3. Errors of method. These originate from incorrect sampling and from incompleteness of a reaction. In gravimetric analysis, errors may arise owing to appreciable solubility of precipitates, co-precipitation, and post-precipitation, decomposition, or volatilization of weighing forms on ignition, and precipitation of substances other than the intended ones. In titrimetric analysis errors may occur owing to the failure of



reactions to proceed to completion, occurrence of induced and side reactions, reaction of substances other than the constituent being determined, and a difference between the observed endpoint and the stoichiometric equivalence point of a reaction.

4. Additive and proportional errors. The absolute value of an additive error is independent of the amount of the constituent present in the determination. Examples of additive errors are loss in weight of a crucible in which a precipitate is ignited, and errors in weights. The presence of this error is revealed by taking samples of different weights.

The absolute value of a proportional error depends upon the amount of the constituent. Thus a proportional error may arise from an impurity in a standard substance, which leads to an incorrect value for the molarity of a standard solution. Other proportional errors may not vary linearly with the amount of the constituent, but will at least exhibit an increase with the amount of constituent present. One example is the ignition of aluminum oxide: at 1200 °C the aluminum oxide is anhydrous and virtually non-hygroscopic; ignition of various weights at an appreciably lower temperature will show a proportional type of error.

Random (indeterminate) errors: These errors manifest themselves by the slight variations that occur in successive measurements made by the same observer with the greatest care under as nearly identical conditions as possible. They are due to causes over which the analyst has no control, and which, in general, are so intangible that they are incapable of analysis. The mathematical model that best satisfies such a distribution of random errors is called the Normal (or Gaussian) distribution. This is a bell-shaped curve that is symmetrical about the mean as shown in Fig. 3.1. An inspection of this error curve shows: that (a) small errors occur more frequently than large ones; and (b) positive and negative errors of the same numerical magnitude are equally likely to occur.

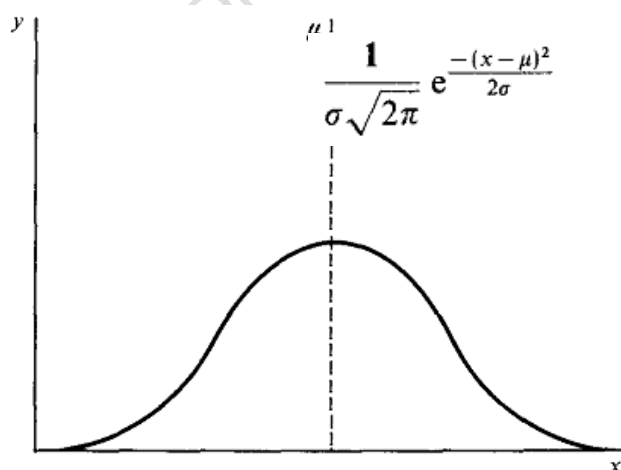


Figure 3.1. The Gaussian distribution curve

Accuracy

The accuracy of a determination may be defined as the concordance between it and the true or most probable value. It follows, therefore, that systematic errors cause a constant error (either too high or too low) and thus affect the accuracy of a result. For analytical methods there are two possible ways of determining the accuracy; the so-called absolute method and the comparative method.

Absolute method: A synthetic sample containing known amounts of the constituents in question is used. Known amounts of a constituent can be obtained by weighing out pure elements or compounds of known stoichiometric composition. These substances, primary standards, may be available commercially



or they may be prepared by the analyst and subjected to rigorous purification by recrystallization, etc. The substances must be of known purity. The test of the accuracy of the method under consideration is carried out by taking varying amounts of the constituent and proceeding according to specified instructions. The amount of the constituent must be varied, because the determinate errors in the procedure may be a function of the amount used. The difference between the mean of an adequate number of results and the amount of the constituent actually present, usually expressed as parts per thousand, is a measure of the accuracy of the method in the absence of foreign substances.

The constituent in question will usually have to be determined in the presence of other substances, and it will therefore be necessary to know the effect of these upon the determination. This will require testing the influence of a large number of elements, each in varying amounts - a major undertaking. The scope of such tests may be limited by considering the determination of the component in a specified range of concentration in a material whose composition is more or less fixed both with respect to the elements which may be present and their relative amounts. It is desirable, however, to study the effect of as many foreign elements as feasible. In practice, it is frequently found that separations will be required before a determination can be made in the presence of varying elements; the accuracy of the method is likely to be largely controlled by the separations involved.

Comparative method: Sometimes, as in the analysis of a mineral, it may be impossible to prepare solid synthetic samples of the desired composition. It is then necessary to resort to standard samples of the material in question (mineral, ore, alloy, etc.) in which the content of the constituent sought has been determined by one or more supposedly 'accurate' methods of analysis. This comparative method, involving secondary standards, is obviously not altogether satisfactory from the theoretical standpoint, but is nevertheless very useful in applied analysis.

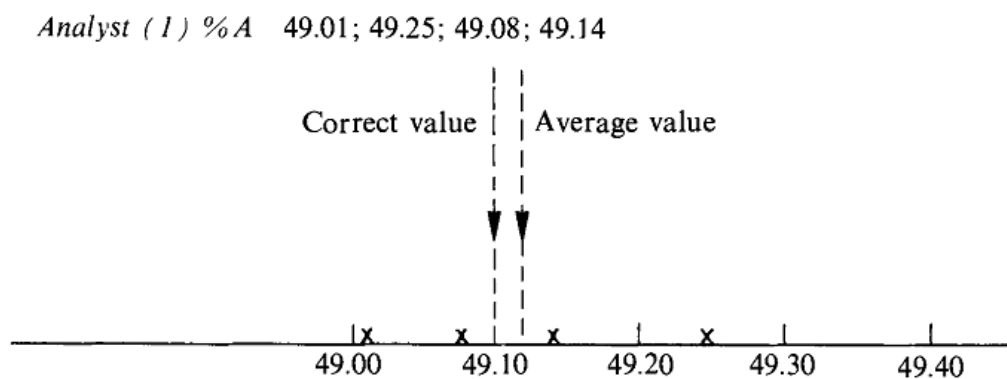
If several fundamentally different methods of analysis for a given constituent are available, e.g. gravimetric, titrimetric, spectrophotometric, or spectrographic, the agreement between at least two methods of essentially different character can usually be accepted as indicating the absence of an appreciable systematic error in either (a systematic error is one which can be evaluated experimentally or theoretically).

Precision

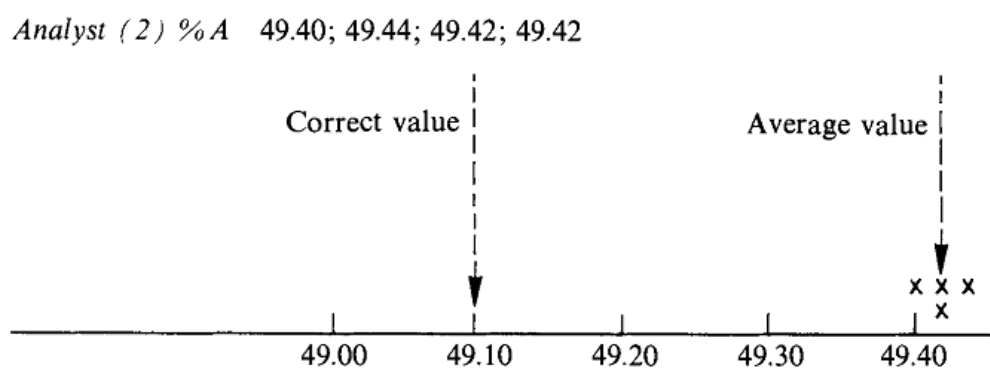
Precision is the degree of agreement between the results of repeated measurements. Precision may also be defined as the concordance of a series of measurements of the same quantity. Accuracy expresses the correctness of a measurement, and precision is the 'reproducibility' of a measurement (the latter definition will be modified later). Precision always accompanies accuracy, but a high degree of precision does not imply accuracy. This may be illustrated by the following example.

Example 3.1: A substance was known to contain 49.10 ± 0.02 percent of a constituent A.

The results obtained by two analysts using the same substance and the same analytical method were as follows.



The arithmetic mean is 49.12% and the results range from 49.01% to 49.25%.



The arithmetic mean is 49.42% and the results range from 49.40% to 49.44%.

Find accuracy and precision.

Answer:

We can summarise the results of the analyses as follows.

- (a) The values obtained by Analyst 1 are accurate (very close to the correct result), but the precision is inferior to the results given by Analyst 2. The values obtained by Analyst 2 are very precise but are not accurate.
- (b) The results of Analyst 1 face on both sides of the mean value and could be attributed to random errors. It is apparent that there is a constant (systematic) error present in the results of Analyst 2.

Precision was previously described as the reproducibility of a measurement. However, the modern analyst makes a distinction between the terms '**reproducible**' and '**repeatable**'. On further consideration of the above example:

- (c) If Analyst 2 had made the determinations on the same day in rapid succession, then this would be defined as '**repeatable**' analysis. However, if the determinations had been made on separate days when laboratory conditions may vary, this set of results would be defined as '**reproducible**'.

Thus, there is a distinction between a within-run precision (**repeatability**) and a between-run precision (**reproducibility**).

Minimization of Errors

Systematic errors can often be materially reduced by several methods, some of them are below:

1. *Calibration of apparatus and application of corrections.* All instruments (weights, flasks, burettes, pipettes, etc.) should be calibrated, and the appropriate corrections applied to the original



measurements. In some cases where an error cannot be eliminated, it is possible to apply a correction for the effect that it produces; thus an impurity in a weighed precipitate may be determined and its weight deducted.

2. *Running a blank determination.* This consists in carrying out a separate determination, the sample being omitted, under exactly the same experimental conditions as are employed in the actual analysis of the sample. The object is to find out the effect of the impurities introduced through the reagents and vessels, or to determine the excess of standard solution necessary to establish the end-point under the conditions met within the titration of the unknown sample. A large blank correction is undesirable, because the exact value then becomes uncertain and the precision of the analysis is reduced.
3. *Running a control determination.* This consists in carrying out a determination under as nearly as possible identical experimental conditions upon a quantity of a standard substance which contains the same weight of the constituent as is contained in the unknown sample. The weight of the constituent in the unknown can then be calculated from the relation:

$$\frac{\text{Result found for standard}}{\text{Result found for unknown}} = \frac{\text{Weight of constituent in standard}}{x}$$

where x is the weight of the constituent in the unknown.

In this connection, it must be pointed out that standard samples which have been analyzed by a number of skilled analysts are commercially available. These include certain primary standards (sodium oxalate, potassium hydrogenphthalate, arsenic (III) oxide, and benzoic acid) and ores, ceramic materials, irons, steels, steel-making alloys, and non-ferrous alloys.

Many of these are also available as BCS Certified Reference Materials (CRM) supplied by the Bureau of Analysed Samples Ltd, Newham Hall, Middlesborough, UK, who also supply EURONORM Certified Reference Materials (ERCM), the composition of which is specified on the basis of results obtained by a number of laboratories within the EEC. BCS Reference Materials are obtainable from the Community Bureau of Reference, Brussels, Belgium. In the USA similar reference materials are supplied by the National Bureau of Standards.

4. *Use of independent methods of analysis.* In some instances, the accuracy of a result may be established by carrying out the analysis in an entirely different manner. Thus iron may first be determined gravimetrically by precipitation as iron(III) hydroxide after removing the interfering elements, followed by ignition of the precipitate to iron(III) oxide. It may then be determined titrimetrically by reduction to the iron(II) state, and titration with a standard solution of an oxidizing agent, such as potassium dichromate or cerium(IV) sulfate. Another example that may be mentioned is the determination of the strength of a hydrochloric acid solution both by titration with a standard solution of a strong base and by precipitation and weighing as silver chloride. If the results obtained by the two radically different methods are concordant, it is highly probable that the values are correct within small limits of error.
5. *Running parallel determinations.* These serve as a check on the result of a single determination and indicate only the precision of the analysis. The values obtained for constituents which are present in not too small an amount should not vary among themselves by more than three parts per thousand. If larger variations are shown, the determinations must be repeated until satisfactory concordance is obtained. Duplicate, and at most triplicate, determinations should suffice. It must be emphasized that



good agreement between duplicate and triplicate determinations does not justify the conclusion that the result is correct; a constant error may be present. The agreement merely shows that the accidental errors, or variations of the determinate errors, are the same, or nearly the same, in the parallel determinations.

6. *Standard addition.* A known amount of the constituent being determined is added to the sample, which is then analyzed for the total amount of constituent present. The difference between the analytical results for samples with and without the added constituent gives the recovery of the amount of added constituent. If the recovery is satisfactory our confidence in the accuracy of the procedure is enhanced. The method is usually applied to physico-chemical procedures such as polarography and spectrophotometry.
7. *Internal standards.* This procedure is of particular value in spectroscopic and chromatographic determinations. It involves adding a fixed amount of a reference material (the internal standard) to a series of known concentrations of the material to be measured. The ratios of the physical value (absorption or peak size) of the internal standard and the series of known concentrations are plotted against the concentration values. This should give a straight line. Any unknown concentration can then be determined by adding the same quantity of internal standard and finding where the ratio obtained falls on the concentration scale.

Statistical Data Treatment

Variations are always present.

If there seems to be none, the resolution is not high enough.

Expression Variations Graphically:

There are several methods to represent a variability in values some of which are:

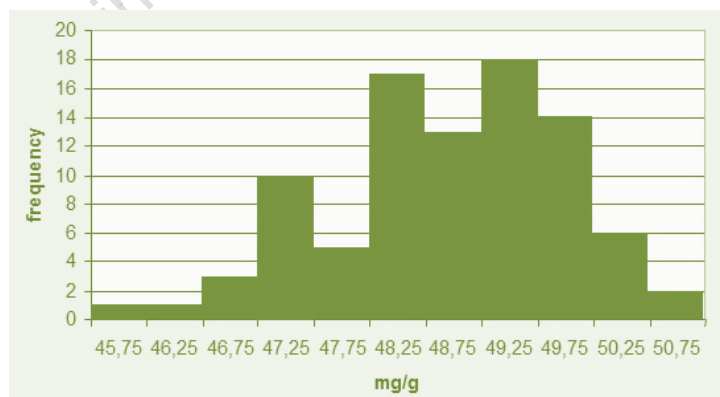
1- Histogram

Used for the description of the variability.

1-Divide range of possible measurements into a number of groups.

2-Count observations in each group.

3-Draw a boxplot of the frequencies as in example follow:



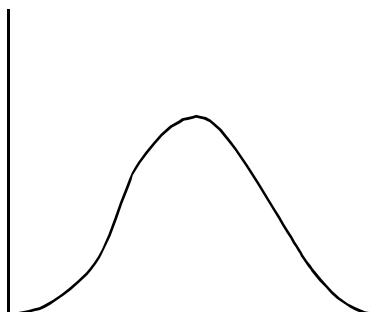
215	215.2	215.19
215	215.3	215.32
215	215.1	215.14
215	215.7	215.68
215	215.8	215.77
215	215.3	215.34
215	215.2	215.19
215	215.1	215.05
215	215.1	215.11
215	215.2	215.19
215	215.7	215.65
215	215.5	215.45
215	215.4	215.38
215	215.7	215.72
215	215.3	215.29
215	215.1	215.10

Table 3.2 Illustration of differences in data resolution



2- Distribution

If the number of values rises and the groups have a smaller range, the histogram changes into a distribution curve.

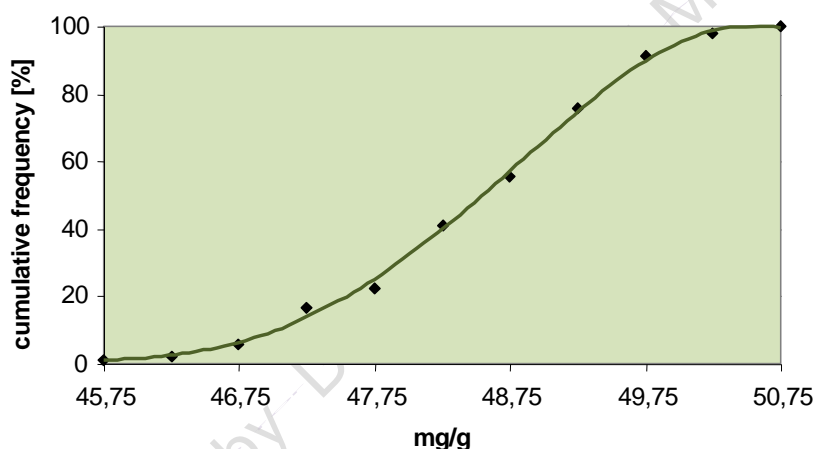


3- Cumulative Distribution

The cumulative distribution is obtained by summing up all frequencies.

It can be used to find the proportion of values that fall above or below a certain value.

For distributions (or histograms) with a maximum, the cumulative distribution curve shows the typical S-shape.



Population vs. Sample

It is important to know, whether all data (the population) or only a subset (a sample) is known.

Sample

Population

A selection of 1000 inhabitants of a town

All inhabitants of a town

Any number of measurements of aluminum in a soil

Not possible

Distribution Descriptives

The data distribution can be described with four characteristics:

1- Measures of **Location**: using arithmetic mean, median, mode, other means such as geometric mean, harmonic mean, robust mean...

2- Measures of **Dispersion**: using variance of a population, variance of a sample, standard deviation, standard deviation of the mean, relative standard deviation

3- **Skewness**

4- **Kurtosis**.



Systematic errors should be detected and eliminated but, random errors are always associated with measurements. Statistics deals with only random errors.

Mean, Median and Mode

Measures of central tendency, or averages, are used in a variety of contexts and form the basis of statistics.

Mean (Arithmetic Mean)

Also known as the average - Is the sum of the measured values (x_i) divided by the number of measurements (n).

Since Σ (Sigma Notation) is the symbol used to indicate that values are to be summed we obtain the following formula for the mean (\bar{x}).

$$\bar{x} = \frac{\sum_i x_i}{n} = \frac{1}{n}(x_1 + x_2 + x_3 + \dots + x_n)$$

- Deviation from mean is the difference between the values measured and the mean.

$$d_x = |x_i - \bar{x}|$$

Deviation from mean is useful to measure precision (*reproducibility*) of results.

Median

- The median (\bar{y}) is the “middle value” of a list. If the list has an odd number of entries, the median is the middle entry in the list after sorting the list into increasing order. If the list has an even number of entries, the median is equal to the sum of the two middle (after sorting) numbers divided by two.

- Deviation from median is the difference between the values measured and the median.

$$d_y = |y_i - \bar{y}|$$

Example 3.2: The analysis of chloride ion on samples A, B and C gives the following result

Sample	%Cl ⁻	Deviation from mean	Deviation from median
A	24.39	0.10	0.11
B	24.20	0.09	0.08
C	24.28	0.01	0.00
	Mean $\bar{x} = ?$	Average deviation of mean $(\delta) = \Sigma (\bar{d}_x)/n$	Average deviation of median $(\delta) = \Sigma (\bar{d}_y)/n$
	Median $\bar{y} = ?$	= ?	= ?

Calculate Average deviation from mean & Average deviation from median.

Answer:

$$\text{mean } (\bar{x}) = \frac{24.39 + 24.20 + 24.28}{3} = 24.29$$

& median = 24.28

Therefore, deviation from mean for sample A =

$$d_x = |x_i - \bar{x}| = 24.39 - 24.29 = 0.10\%$$

For sample B = 0.09%, sample C = 0.01%

deviation from median for sample A =

$$d_y = |y_i - \bar{y}| = 24.39 - 24.28 = 0.11\%$$

For sample B = 0.08%, sample C = 0.00%

Average deviation of mean $(\bar{d}_x) = \Sigma (d_x)/n = (0.10 + 0.09 + 0.01)/3 = \mathbf{0.07}$



Average deviation of median (\bar{d}_y) = $\Sigma (\bar{d}_y)/n = (0.11 + 0.08 + 0.00)/3 = 0.06$

Mode

- The mode is the most common (frequent) value. A list can have more than one mode.

For the previous example, there is no mode.

Range

- The difference between the highest and the lowest values.

For example(1), range = 24.39- 24.20 = 0.19 %.

Standard Deviation

A measure of the width of the distribution. It is a measure of **precision** of a sample or population of data,

A small standard deviation gives narrow distribution curve

$$s = \sqrt{\frac{\sum_{i=1}^{i=n} (x_i - \bar{x})^2}{n-1}}$$

where, x_i = a measured value; n = number of measurements; $n-1$ = the degrees of freedom.

Standard deviation has the same number of decimal places as the mean.

- For σ when we have more than 30 measurements use n (or N) in denominator.

- For s when we have less than 30 measurements, use $n-1$ (or $N-1$) in denominator (we have one less degree of freedom - don't know μ).

- At end, round s to 2 sig figs or less if there are not enough sig figs in data.

Note: NEVER round off figures before the end of the calculation.

Relative Standard Deviation (or Coefficient of Variation)

$$\text{Relative Standard Deviation (RSD)} = \frac{s}{\bar{x}} \times 100$$

- The sample mean and sample standard deviation (\bar{x} and s) apply to a finite set of measurements.

- For infinite set of data use is made of the true mean or population mean (designated μ) and the true standard deviation (designated σ).

Solved problem 3.1: Find the average, standard deviation, and coefficient of variation for 821, 783, 834, and 855.

Solution The average is

$$\bar{x} = \frac{\sum x_i}{n} = \frac{1}{4}(821+783+834+855) = 823.2$$

To avoid accumulating round-off errors, retain one more digit than was present in the original data. The standard deviation is

$$s = \sqrt{\frac{\sum_{i=1}^{i=n} (x_i - \bar{x})^2}{n-1}} = \sqrt{\frac{(821-823.2)^2 + (783-823.2)^2 + (834-823.2)^2 + (855-823.2)^2}{(4-1)}} = 30.3$$



The average and the standard deviation should both end at the same decimal place. For $\bar{x} = 823.2$, we will write $s = 30.3$. The coefficient of variation is the percent relative uncertainty:

$$\text{RSD} = \frac{s}{\bar{x}} \times 100 = \frac{30.3}{823.2} \times 100 = 3.7\%$$

Test Yourself If each of the four numbers 821, 783, 834, and 855 in the problem is divided by 2, how will the mean, standard deviation, and coefficient of variation be affected?

(Answer: \bar{x} and s will be divided by 2, but the coefficient of variation is unchanged).

Standard Deviation of the Mean

To measure the mean lifetime of a large number of light bulbs, we could select one at a time and measure its lifetime. Alternatively, we could select, say, four at a time, measure the life of each, and compute the average of the four. We repeat this process of measuring four at (a) time many times and compute a mean μ and a standard deviation that we label σ_4 because it is based on sets of four bulbs. The mean of many sets of four bulbs is the same as the population means. However, the standard deviation of the means of sets of four bulbs is smaller than the population standard deviation, σ . The relation is $\sigma_4 = \sigma / \sqrt{4}$. We call σ_4 the **standard deviation of the mean** of sets of four samples. In general, the standard deviation of the mean for sets of n samples (values) is

$$\sigma_n = \frac{\sigma}{\sqrt{n}}$$

The more times you measure a quantity, the more confident you can be that the average is close to the population mean. Uncertainty decreases in proportion to $\frac{1}{\sqrt{n}}$, where n is the number of measurements.

You can decrease uncertainty by a factor of 2 ($=\sqrt{4}$) by making 4 times as many measurements and by a factor of 10 ($=\sqrt{100}$) by making 100 times as many measurements.

Variance

- Is the square of the standard deviation. Variance = σ^2 .

Probability

- Range of measurements for ideal Gaussian distribution
- The percentage of measurements lying within the given range (one, two, or three standard deviations on either side of the mean).

Range	Gaussian Distribution (%)
$\mu \pm 1\sigma$	68.3
$\mu \pm 2\sigma$	95.5
$\mu \pm 3\sigma$	99.7

Some data might not be normally distributed:

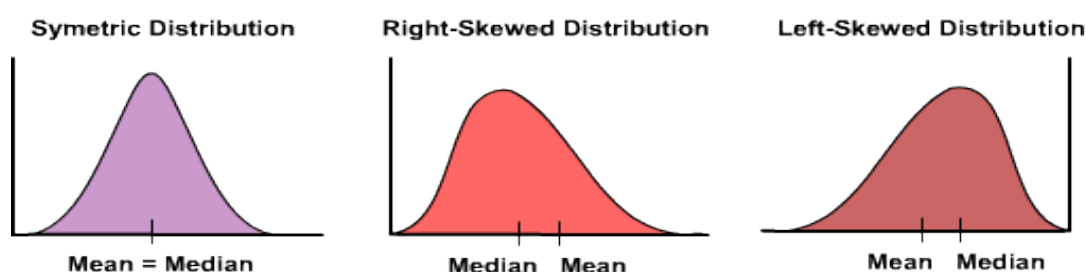


Figure 3.1 Distribution shapes



P values

p = probability value shows us whether the difference observed is just due to chance, or if it's statistically significant.

If $p > 0.05$, accept the null hypothesis (i.e. there IS NOT a statistically significant difference).

If $p < 0.05$, reject the null hypothesis (i.e. there IS a statistically significant difference).

Confidence Interval

- Range of values within which there is a specified probability of finding the true mean (μ).

- We are doing an analysis to find the true mean μ - it is unknown.
- What we measure is \bar{x} but it may not be the same as μ .
- Set a confidence limit eg 4.5 ± 0.3 g.
- The mean of the measurements was 4.5 g.
- The true mean is in the interval 4.2-4.8 with some specified degree of confidence.

- The t-test is used to express confidence intervals.

- Also used to compare results from different experiments.

The Student's t-Test was formulated by W. Gossett in the early 1900's. His employer (brewery) had regulations concerning trade secrets that prevented him from publishing his discovery, but in light of the importance of the t distribution, Gossett was allowed to publish under the pseudonym "Student".

The t-Test is typically used to compare the means of two populations.

$$t = \frac{(x_i - \mu)}{s}$$

- t depends on desired confidence limit.
- degrees of freedom (n-1).

Table 3.3. Values of t for various degrees of Probability

Degrees of Freedom	Confidence Level (CL) (%)				
	50%	80%	90%	95%	99.9%
1	1.000	3.081	6.314	12.706	636.578
2	0.816	1.892	2.920	4.303	31.598
3	0.765	1.641	2.353	3.182	12.924
4	0.741	1.534	2.132	2.776	8.610
5	0.727	1.483	2.015	2.571	6.869
6	0.718	1.442	1.943	2.447	5.959
7	0.711	1.420	1.895	2.365	5.408
8	0.706	1.401	1.860	2.306	5.041
∞	0.674	1.292	1.645	1.960	3.291

**Example 3.3:**

The carbohydrate content of a glycoprotein (a protein with sugars attached to it) is found to be 12.6, 11.9, 13.0, 12.7, and 12.5 wt% (g carbohydrate/100 g glycoprotein) in replicate analyses. Find the 50% and 90% confidence intervals for the carbohydrate content.

Answer:

First calculate $\bar{x} = (12.5_4)$ and $s = (0.40)$ for the five measurements. For the 50% confidence interval, look up t in Table 1 under 50 and across from four degrees of freedom (degrees of freedom = $n - 1$). The value of t is 0.741, so the 50% confidence interval is

$$50\% \text{ confidence interval} = \bar{x} \pm \frac{ts}{\sqrt{n}} = 12.5_4 \pm \frac{(0.741)(0.40)}{\sqrt{5}} = 12.5_4 \pm 0.1_3 \text{ wt\%}$$

The 90% confidence interval is

$$90\% \text{ confidence interval} = \bar{x} \pm \frac{ts}{\sqrt{n}} = 12.5_4 \pm \frac{(2.132)(0.40)}{\sqrt{5}} = 12.5_4 \pm 0.3_8 \text{ wt\%}$$

If we repeated sets of five measurements many times, half of 50% confidence intervals are expected to include the true mean, μ . Nine-tenths of the 90% confidence intervals are expected to include the true mean, μ .

Test Yourself Carbohydrate measured on one more sample was 12.3 wt%. Using six results, find the

$$90\% \text{ confidence interval. (Answer: } 12.5_0 \pm \frac{(2.015)(0.37)}{\sqrt{6}} = 12.5_0 \pm 0.3_1 \text{ wt\%)}$$

Calculating Confidence Intervals

From a limited number of measurements (n), we cannot find the true population mean, μ , or the true standard deviation, σ . What we determine are \bar{x} and s , the sample mean and the sample standard deviation.

The confidence interval is computed from the equation:

$$\mu = \bar{x} \pm \frac{ts}{\sqrt{n}}$$

where t is Student's t , taken from Table (3.3) for a desired level of confidence, such as 95%..

- That is, the range of confidence interval is $-ts/\sqrt{n}$ below the mean and $+ts/\sqrt{n}$ above the mean.

- For better precision reduce confidence interval by increasing n number of measurements.

Example 3.4:

Calculator obtained the following results for replicate determinations of calcium in limestone 14.35%, 14.41%, 14.40%, 14.32%, 14.37% each is x_i . Calculate the confidence interval.

Answer:

Average = 14.37 % , $s = 0.037\%$.

Using a 95 % confidence limit: degrees of freedom = $n - 1 = 5 - 1 = 4$

From t -table, $t = 2.776$ so

$$14.37\% \pm ts/n^{1/2}$$

$$14.37\% \pm 2.78 \times 0.037\% / 5^{1/2}$$

$$14.37 \pm 0.05 \%$$

Standard Deviation and Confidence Interval as Estimates of Experimental Uncertainty

If we were dividing a mass by a volume to find density, the uncertainty in density is derived from the uncertainties in mass and volume. Common estimates of uncertainty are the standard deviation and the confidence interval.

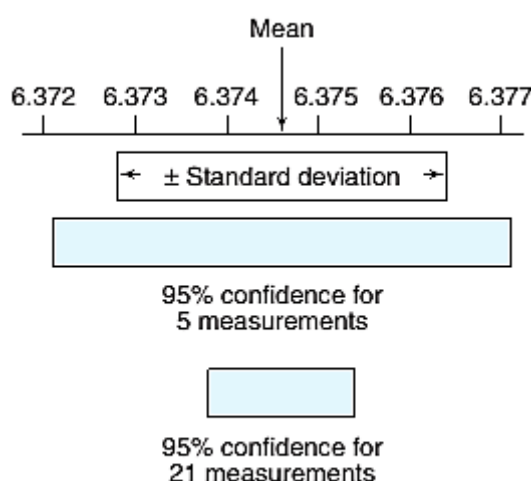


Suppose you measure the volume of a vessel five times and observe values of 6.375, 6.372, 6.374, 6.377, and 6.375 mL. The average is $\bar{x} = 6.374_6$ mL and the standard deviation is $s = 0.0018$ mL. We could report a volume of $6.374_6 \pm 0.001_8$ mL ($n = 5$), where n is the number of measurements.

You could choose a confidence interval (such as 95%) for the estimate of uncertainty.

Using Equation $\bar{x} \pm \frac{ts}{\sqrt{n}}$ with 4 degrees of freedom, you find that the 95% confidence interval is $\pm \frac{ts}{\sqrt{n}} = \pm \frac{(2.776)(0.001_8)}{\sqrt{5}} = \pm 0.002_5$. By this criterion, the uncertainty in volume is $\pm 0.002_5$ mL. *It is critical to specify what kind of uncertainty you are reporting*, such as the standard deviation for n measurements or the 95% confidence interval for n measurements.

We reduce uncertainty by making more measurements. If we make 21 measurements and have the same mean and standard deviation, the 95% confidence interval is reduced from $\pm 0.002_5$ to $\pm \frac{(2.086)(0.001_8)}{\sqrt{21}} = \pm 0.0008$ mL.



Note: Confidence limits and the t-test (and, later in this lecture, the Grubbs test) assume that data follow a Gaussian distribution.

Comparison of Means with Student's t

If you make two sets of measurements of the same quantity, the mean value from one set will generally not be equal to the mean value from the other set because of small, random variations in the measurements. We use a t-test to compare one mean value with another to decide whether there is a statistically significant difference between the two. That is, do the two means agree “within experimental error”? The null hypothesis in statistics states that the mean values from two sets of measurements are not different. Statistics gives us a probability that the observed difference between two means arises from random measurement error. We customarily reject the null hypothesis if there is less than a 5% chance that the observed difference arises from random variations. With this criterion, we have a 95% chance that our conclusion is correct. One time out of 20 when we conclude that two means are not different we will be wrong.

Here are three cases that are handled in slightly different manners:

Case 1 Comparing a Measured Result with a “Known” Value. We measure a quantity several times, obtaining an average value and standard deviation. We need to compare our answer with an accepted



answer. The average is not exactly the same as the accepted answer. Does our measured answer agree with the accepted answer “within experimental error”?

Case 2 Comparing Replicate Measurements. We measure a quantity multiple times by two different methods that give two different answers, each with its own standard deviation. Do the two results agree with each other “within experimental error”?

Case 3 Paired t-Test for Comparing Individual Differences. Sample A is measured once by method 1 and once by method 2; the two measurements do not give exactly the same result. Then a different sample, designated B, is measured once by method 1 and once by method 2; and, again, the results are not exactly equal. The procedure is repeated for n different samples. Do the two methods agree with each other “within experimental error”?

To test for comparison of means

- Calculate the pooled standard deviation (S_{pooled})
- Calculate t
- Compare the calculated t to the value of t from the table
- The two results are significantly different if the calculated t is greater than the tabulated t at 95% confidence level.

For two sets of data with

- n_1 and n_2 measurements
- averages of x_1 and x_2
- standard deviations of s_1 and s_2 .

$$s_p = \sqrt{\frac{s_1^2(n_1 - 1) + s_2^2(n_2 - 1) + \dots}{N - n_s}}$$

$n_s = \text{no of groups of samples}$
for two sets of data

$$s_p = \sqrt{\frac{\sum_{i=1}^{i=n_1} (x_i - \bar{x}_1)^2 + \sum_{i=1}^{i=n_2} (x_i - \bar{x}_2)^2}{n_1 + n_2 - 2}}$$

$$S_{\text{pooled}} = \sqrt{\frac{s_1^2(n_1 - 1) + s_2^2(n_2 - 1)}{n_1 + n_2 - 2}}$$

to find t - test

$$t = \frac{|\bar{x}_1 - \bar{x}_2|}{S_{\text{pooled}}} \sqrt{\frac{n_1 n_2}{n_1 + n_2}}$$

Degrees of freedom = $n_1 + n_2 - 2$

- We analyze several samples and want to know if they are the same or different.
- For each sample we take several measurements and obtain a mean.

$$\text{If } \bar{x}_1 - \bar{x}_2 < t \sqrt{\frac{s_1^2}{n_1} + \frac{s_2^2}{n_2}}$$

there is no significant difference



Comparing two means

$$\text{Compare } x_1 - x_2 \text{ to } \frac{ts_1}{\sqrt{n_1}} + \frac{ts_2}{\sqrt{n_2}}$$

If s is a pooled sd

$$t_{\text{calc}} = \frac{\bar{x}_1 - \bar{x}_2}{s} \sqrt{\frac{n_1 n_2}{n_1 + n_2}}$$

If $t_{\text{calc}} < t_{\text{table}}$ then the difference is not significant at the chosen CL

$$\mu = x \pm t \cdot \sqrt{\left(\frac{s_1}{\sqrt{n_1}}\right)^2 + \left(\frac{s_2}{\sqrt{n_2}}\right)^2}$$

If s is the pooled s

$$t = \frac{\bar{x}_1 - \bar{x}_2}{s} \sqrt{\frac{n_1 n_2}{n_1 + n_2}}$$

If $t_{\text{calc}} < t_{\text{table}}$ then the difference is not significant at the chosen confidence Level (CL)

Example 3.5:

Two barrels of juice were analyzed for their vit-C content to determine whether or not they were from different sources:

12.61% (6 analyses),

12.53% (4 analyses)

Pooled standard deviation = 0.07 %

Answer:

$$t = \frac{12.61\% - 12.53\%}{0.07\%} \sqrt{\frac{6 \cdot 4}{6 + 4}} = 1.77$$

Degrees of freedom = 6+4-2=8

From t-table at 95% CL for 8 deg of freedom = 2.306

$$t_{\text{calc}} < t_{\text{table}}$$

therefore, difference is not significant at the 95% CL – the two samples are the same at the 95% CL.

F-tests / Analysis of Variance (ANOVA)

T-tests - inferences about 2 sample means

But what if you have more than 2 conditions?

e.g. placebo, drug 20mg, drug 40mg, drug 60mg

Placebo vs. 20mg 20mg vs. 40mg

Placebo vs 40mg 20mg vs. 60mg

Placebo vs 60mg 40mg vs. 60mg

Chance of making a type 1 error increases as you do more t-tests

ANOVA controls this error by testing all means at once - it can compare k number of means. Drawback = loss of specificity



Different types of ANOVA depending upon experimental design (independent, repeated, multi-factorial)

Assumptions

- observations within each sample were independent
- samples must be normally distributed
- samples must have equal variances

$$t = \frac{\text{obtained difference between sample means}}{\text{difference expected by chance (error)}}$$

$$F = \frac{\text{variance (differences) between sample means}}{\text{variance (differences) expected by chance (error)}}$$

Difference between sample means is easy for 2 samples:

(e.g. $X_1=20$, $X_2=30$, difference = 10)

but if $X_3=35$ the concept of differences between sample means gets tricky.

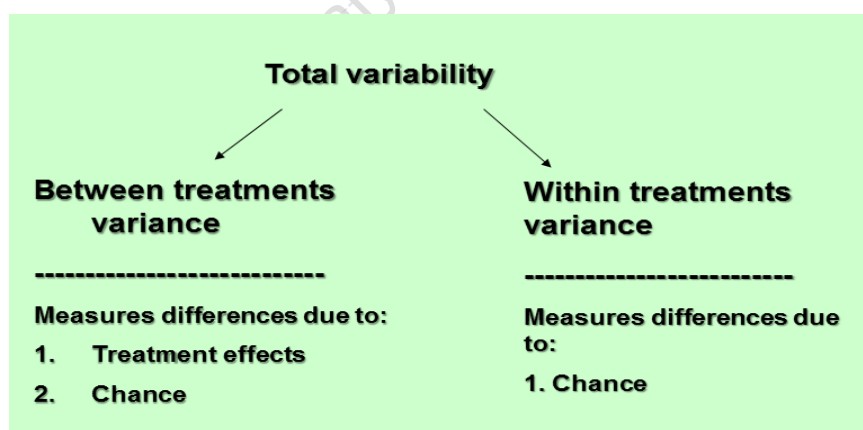
Solution is to use variance - related to SD

Standard deviation = $(\text{Variance})^{1/2}$

<i>E.g.</i>	<i>Set 1</i>	<i>Set 2</i>
	20	28
	30	30
	35	31
	$s^2=58.3$	$s^2=2.33$

These 2 variances provide a relatively accurate representation of the size of the differences

Simple ANOVA example



$$F = \frac{MS_{\text{between}}}{MS_{\text{within}}}$$

When treatment has no effect, differences between groups/treatments are entirely due to chance. The numerator and denominator will be similar. F -ratio should have a value around 1.00

When the treatment does have an effect then the between-treatment differences (numerator) should be larger than chance (denominator). F -ratio should be noticeably larger than 1.00.

Experimental Problem: A single tablet of antacid tablets for calcium is analyzed by a pair of students who perform the procedure in quadruplicate, i.e. two determinations per student. Complete the following



set of exercises based on data collected last time. Your answers should clearly show the calculations that you performed.

1) The following results were reported for two samples. In each case, determine the best value of the wt/wt% calcium and the uncertainty of the result at the 95% confidence level. Consider the deletion of outliers.

sample 12: 14.31, 15.36, 15.55, 15.85 wt/wt% Ca

sample 48: 15.13, 15.14, 10.83, 15.35 wt/wt% Ca

2) Two partners were not sure if their samples came from the same antacid tablet. Each student analyzed a sample in triplicate and they obtained the following results. Did they analyze the same tablet?

student I: 14.85, 14.95, 14.71 wt/wt% Ca

student II: 15.61, 15.74, 15.80 wt/wt% Ca

Detection of Gross Errors using Q Test (or Grubbs Test)

$Q_{\text{exp}} = \frac{\text{questionable value} - \text{nearest numerical value}}{\text{Range}}$

Range

$$Q_{\text{exp}} = \frac{|x_q - x_n|}{w}$$

where x_q = questionable result

x_n = nearest neighbour

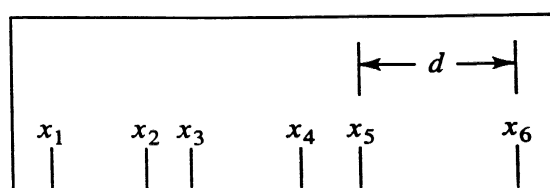
w = spread of entire set

-An outlier is a datum that is far from other points.

- Grubbs test is used to determine whether an outlier should be rejected or retained.

Look up Table of Q_{critical}

- If $Q_{\text{exp}} < Q_{\text{critical}}$, keep the point
- If more observations are taken it is easier to determine if a point is an outlier.



$$d = x_6 - x_5$$

$$w = x_6 - x_1$$

$$Q_{\text{exp}} = \frac{d}{w}$$

If $Q_{\text{exp}} > Q_{\text{crit}}$ reject x_6

**Table 3.4.** Q_{crit} (reject if $Q_{exp} > Q_{crit}$)

No. of observations	90%	95%	99%	confidence level
3	0.941	0.970	0.994	
4	0.765	0.829	0.926	
5	0.642	0.710	0.821	
6	0.560	0.625	0.740	
7	0.507	0.568	0.680	
8	0.468	0.526	0.634	
9	0.437	0.493	0.598	
10	0.412	0.466	0.568	

Rejection of outlier is recommended if $Q_{exp} > Q_{crit}$ for the desired confidence level.

Notes:

1. The higher the confidence level, the less likely is rejection to be recommended.
2. Rejection of outliers can have a marked effect on mean and standard deviation, esp. when there are only a few data points. *Always try to obtain more data.*
3. If outliers are to be retained, it is often better to report the *median* value rather than the *mean*.

Example (6):

The following values were obtained for the concentration of nitrite ions in a sample of river water: 0.403, 0.410, 0.401, 0.380 mg/L. Should the last reading be rejected?

Answer:

$$Q_{exp} = \frac{|0.380 - 0.401|}{(0.410 - 0.380)} = 0.7$$

But $Q_{crit} = 0.829$ (at 95% level) for 4 values

Therefore, $Q_{exp} < Q_{crit}$, and we cannot reject the suspect value.

Suppose 3 further measurements are taken, giving total values of:

0.403, 0.410, 0.401, 0.380, 0.400, 0.413, 0.411 mg/L. Should 0.380 still be retained?

$$Q_{exp} = \frac{|0.380 - 0.400|}{(0.413 - 0.380)} = 0.606$$

But $Q_{crit} = 0.568$ (at 95% level) for 7 values

Therefore, $Q_{exp} > Q_{crit}$, and rejection of 0.380 is recommended.

But note that 5 times in 100 it will be wrong to reject this suspect value!

Also note that if 0.380 is retained, $s = 0.011$ mg/L, but if it is rejected, $s = 0.0056$ mg/L, i.e. **precision appears to be twice as good, just by rejecting one value.**

Best Straight Line (Method of least squares)

The equation of a straight line

$$y = mx + b$$

m is the slope ($\Delta y / \Delta x$)

b is the y-intercept (where the line crosses the y-axis).

The method of least squares

- finds the best straight line.
- adjusts the line to minimize the vertical deviations.

Only vertical deviations are adjusted because



- experimental uncertainties in y values > in x values.
- calculations for minimizing vertical deviations are easier.

$$m = \frac{n \sum (x_i y_i) - \sum x_i \sum y_i}{D}$$

$$b = \frac{\sum (x_i^2) \sum y_i - \sum (x_i y_i) \sum x_i}{D}$$

$$D = n \sum (x_i^2) - (\sum x_i)^2$$

- n is the number of data points

Knowing m and b, the equation of the best straight line can be determined and the best straight line can be constructed.

x_i	y_i	$x_i y_i$	x_i^2
$\sum x_i =$	$\sum y_i =$	$\sum (x_i y_i) =$	$\sum x_i^2 =$

Statistics Exercises

Q1. Find the mode, median, and mean of the following:

- 3,12,11,7,5,5,6,4,10
- 16,19,10,24,19
- 8,2,8,5,5,8
- 28,39,42,29,39,40,36,46,41,30
- 133,215,250,108,206,159,206,178
- 76,94,76,82,78,86,90
- 52,61,49,52,49,52,41,58

Q2. A certain experiment yielded the following data values for lead: 10 ppm, 8 ppm, 7 ppm, 11 ppm, and 16 ppm. What are the mean and standard deviation for this experiment?

Q3. Q for Case 1: If an accepted value, such as a Certified Reference Material (CRM), is known.

Using the same data set utilized earlier in Q.2 for lead: 10 ppm, 8 ppm, 7 ppm, 11 ppm, and 16 ppm. Assume there is a Certified Reference Material (CRM) value of 9.43 ppm for lead in a sandy soil sample. Compare whether or not the data for the given experimental method is considered reliable and valid in contrast to the CRM value.

(t-table at the 95% confidence interval, at n-1, is 2.776).

Q4. Q for Case 2: When the accepted value is unknown

Given lead concentrations for two different method determinations using ICP-MS from Lab A and Lab B as follow:

Lab A Data/ppm of Pb	Lab B Data/ppm of Pb
17.1	17.2
16.2	17.1
14.6	17.0
22.8	19.0
18.7	18.3
$\bar{x}_1 = 17.9$	$\bar{x}_2 = 17.7$
$S_1 = 3.2$	$S_2 = 0.9$



At a 95% confidence interval, find whether both methods are valid procedures or not.

(Clue: use s_{pooled} & t-test to solve this question. The t-value from the table at a 95% confidence interval for 10 samples at degree of freedom n_1+n_2-2 is 2.306).

Q5. Considering, the original data set for lead: 10 ppm, 8 ppm, 7 ppm, 11 ppm and 16 ppm (Q. 2), examine if 16 ppm is accepted or a potential outlier value.

(Clue: to test the validity of this assumption, the Q-test will be utilized. For $n = 5$, $Q_{tab.} = 0.710$ at 95% CI).

Q6. Using data from Q4:

1) Is method/data set A more precise than method/data set B?

2) Is there a difference in the precision of the two methods?

(Clue: the F-test will be utilized. The critical value of F depends on the degrees of freedom $dof_A=n_A-1$ and $dof_B=n_B-1$ and can be taken from a F-table)

Table 3.5. Critical Values for F at A 95% Level

F statistics for P=0.05		degrees of freedom for numerator (A)									
		1	2	3	4	5	6	7	8	9	10
degrees of freedom for denominator (B)	1	647,79	799,50	864,16	899,58	921,85	937,11	948,22	956,66	963,29	968,63
	2	38,51	39,00	39,17	39,25	39,30	39,33	39,36	39,37	39,39	39,40
	3	17,44	16,04	15,44	15,10	14,89	14,74	14,62	14,54	14,47	14,42
	4	12,22	10,65	9,98	9,61	9,36	9,20	9,07	8,98	8,91	8,84
	5	10,01	8,43	7,76	7,39	7,15	6,98	6,85	6,76	6,68	6,62
	6	8,81	7,26	6,60	6,23	5,99	5,82	5,70	5,60	5,52	5,46
	7	8,07	6,54	5,89	5,52	5,29	5,12	5,00	4,90	4,82	4,76
	8	7,57	6,06	5,42	5,05	4,82	4,65	4,53	4,43	4,36	4,30
	9	7,21	5,72	5,08	4,72	4,48	4,32	4,20	4,10	4,03	3,96
	10	6,94	5,46	4,83	4,47	4,24	4,07	3,95	3,86	3,78	3,72

$n_A=5$

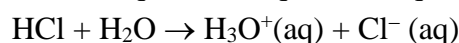
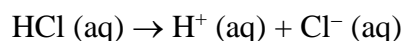


4. ACID-BASE EQUILIBRIA

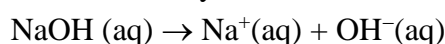
Theories of Acids and Bases: There are several definitions of acids and bases.

Arrhenius Definitions:

- **Arrhenius acid** is any substance that ionizes in water to produce **hydrogen ions (H⁺)** (hydronium ion, H₃O⁺, or proton).

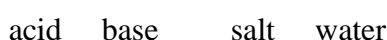
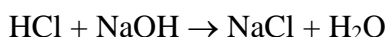


- **Arrhenius base** is any substance that ionizes in water to produce **hydroxide ions (OH⁻)**.



Definitions of Bronsted and Lowry:

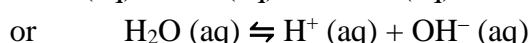
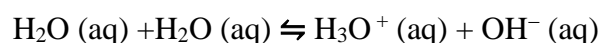
- **Bronsted and Lowry acid** is any substance that **donates a proton**, while a **base** is one which **accepts a proton**.



- Water is a unique solvent. One of its special properties is its ability to act either as an acid or as a base. Water functions as a **base** in reactions with acids such as HCl and CH₃COOH and it functions as an **acid** in reactions with bases such as NaOH and NH₃.

Ion Product of Water, K_w:

Water is a very weak electrolyte, but it does undergo ionization to a small extent:



The equilibrium expression for the autoionization reaction is:

$$K_{\text{eq}} = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]}$$

Because a very small fraction of water molecules are ionized, the concentration of water, [H₂O], remains virtually unchanged. Therefore:

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

The equilibrium constant **K_w** is called the ion-product constant of water.

In pure water at 25°C the value of **K_w** is found to be **1 x 10⁻¹⁴**:

$$[\text{H}^+].[\text{OH}^-] = 1 \times 10^{-14}$$

and the concentration of **H⁺** and **OH⁻** are **equal**.

$$[\text{H}^+] = [\text{OH}^-] = 1 \times 10^{-7} \text{ M} \quad (\text{in pure water})$$

- Whenever [H⁺] = [OH⁻], the aqueous solution is said to be **neutral**.
- In an **acid solution** there is an excess of hydrogen ions, so [H⁺] > [OH⁻].
- In a **basic solution** there is an excess of hydroxide ions, so [OH⁻] > [H⁺].

The pH Scale:

In chemistry, **pH** (potential of hydrogen) is a **numeric scale** used to specify the **acidity** or **basicity** of an **aqueous solution**. It is approximately the negative of the **base 10 logarithm** of the **molar concentration**, measured in units of moles per liter, of hydrogen ions. More precisely it is the negative of the base 10 logarithm of the **activity** of the hydrogen ion.

Mathematically,

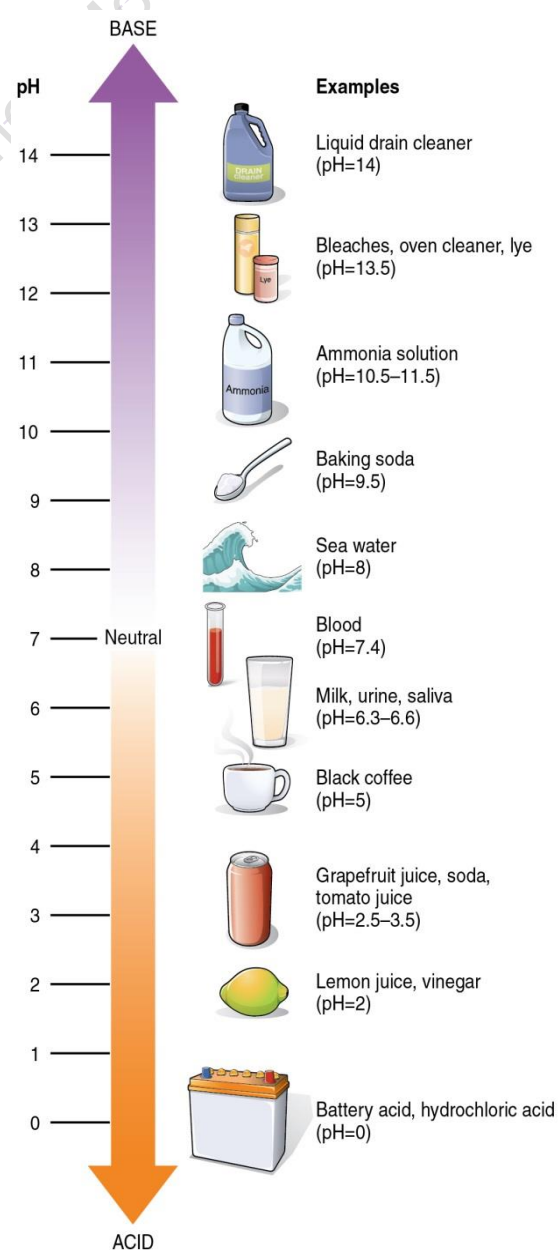


Figure 4.1: pH in dailylife



$$[\text{H}^+] = 1 \times 10^{-\text{pH}} \quad \text{or} \quad \text{pH} = -\log [\text{H}^+]$$

1. **Acidic solutions:** $[\text{H}^+] > 1 \times 10^{-7} \text{ M}$, $\text{pH} < 7$
2. **Basic solutions:** $[\text{H}^+] < 1 \times 10^{-7} \text{ M}$, $\text{pH} > 7$
3. **Neutral solutions:** $[\text{H}^+] = 1 \times 10^{-7} \text{ M}$, $\text{pH} = 7$

Monoprotic Acid-Base Equilibria

Acids and Bases are essential to virtually *every* application of chemistry

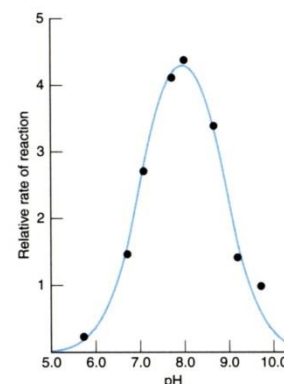
- Analytical procedures such as chromatography and electrophoresis.
- Protein purification, chemical reactions, environmental issues (e.g., Acid rain).

Knowledge of Acid-Base Equilibrium is Necessary to Understand:

- Buffer preparation and pH control.
- Acid-Base Titrations.
- Complexation, etc.

Illustration:

- Protein function and stability depend on pH, temperature and other conditions.
- Blood and milk have high protein concentrations.
- A common problem in mechanical heart valves is clot formation.
- Protein precipitation from milk provides a cheap and easy mimic of blood clotting for testing new heart valves → avoids expensive and long animal studies.



Protein activity is pH dependent



Milk precipitation on heart valve

Strength of Acids and Bases:

Acids and bases are classified into strong and weak ones according to the extent of their dissociation.

Strong Acids and Bases

- Strong acids/bases (Table 4-1) are strong electrolytes which are assumed to ionize completely in water (Completely dissociates).
- $[\text{H}_3\text{O}^+]$ or $[\text{OH}^-]$ equals the concentration of strong acid or base.

pH values at other concentrations of a strong acid or base are below:

$[\text{OH}^-] \text{ (M)}$	$[\text{H}^+] \text{ (M)}$	pH	Acid	K_a
1×10^{-1}	1×10^{-13}	13.0	HCl	$10^{3.9}$
1×10^{-2}	1×10^{-12}	12.0	HBr	$10^{5.8}$
1×10^{-3}	1×10^{-11}	11	HI	$10^{10.4}$
1×10^{-4}	1×10^{-10}	10	HNO_3	$10^{1.4}$
1×10^{-5}	1×10^{-9}	9		

Table 4-1 Common strong acids and bases

Formula	Name
ACIDS	
HCl	Hydrochloric acid (hydrogen chloride)
HBr	Hydrogen bromide
HI	Hydrogen iodide
H_2SO_4^a	Sulfuric acid
HNO_3	Nitric acid
HClO_4	Perchloric acid
BASES	
LiOH	Lithium hydroxide
NaOH	Sodium hydroxide
KOH	Potassium hydroxide
RbOH	Rubidium hydroxide
CsOH	Cesium hydroxide
R_4NOH^b	Quaternary ammonium hydroxide

Example (4-1):

What is the pH of a 0.1M solution of HCl?

Solution:

$$[\text{H}^+] = [\text{HCl}] = 0.1 \text{ M}$$

$$\text{pH} = -\log[\text{H}^+] = -\log(0.1 \text{ M}) = 1.00$$

Example (4-2):

What is the pH of a 0.1M solution of KOH?

**Solution:**

$$[\text{OH}^-] = [\text{KOH}] = 0.1 \text{ M}$$

$$K_w = [\text{H}^+][\text{OH}^-] = 1 \times 10^{-14} \Rightarrow [\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1 \times 10^{-14}}{0.10} = 1.0 \times 10^{-13} \text{ M}$$

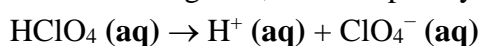
$$\text{pH} = -\log[\text{H}^+] = -\log(1.0 \times 10^{-13} \text{ M}) = 13.00$$

Example (4-3):

What is the **pOH** of a **0.040 M** HClO_4 solution?

Solution:

Because HClO_4 is strong acid, it is completely ionized, giving H^+ and ClO_4^- .



$$\therefore [\text{H}^+] = [\text{HClO}_4] = 0.040 \text{ M}$$

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

$$\text{pH} = -\log (0.040)$$

$$\text{pH} = 1.4$$

From equation:

$$\text{pH} + \text{pOH} = 14$$

$$\text{pOH} = 14 - \text{pH}$$

$$\text{pOH} = 14 - 1.4$$

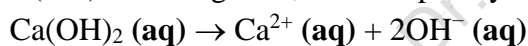
$$\therefore \text{pOH} = 12.6$$

Example (4-4):

What is the **pH** value of a 0.011 M of $\text{Ca}(\text{OH})_2$ solution?

Solution:

Because $\text{Ca}(\text{OH})_2$ is strong base, it is completely ionized, giving 2OH^- and Ca^{2+} .



$$\therefore [\text{OH}^-] = 2 \times [\text{Ca}(\text{OH})_2]$$

$$= 2 \times 0.011 = 0.022 \text{ M}$$

We can calculate the pH of the solution in two equivalent ways.

First, we could use the following equation:

$$[\text{H}^+][\text{OH}^-] = 1 \times 10^{-14}$$

To calculate $[\text{H}^+]$ and then use $\text{pH} = -\log [\text{H}^+]$

$$[\text{H}^+] = \frac{1 \times 10^{-14}}{[\text{OH}^-]}$$

$$[\text{H}^+] = \frac{1 \times 10^{-14}}{0.022 \text{ M}}$$

$$\therefore [\text{H}^+] = 4.6 \times 10^{-13} \text{ M}$$

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

$$\text{pH} = -\log (4.6 \times 10^{-13})$$

$$\text{pH} = 12.34$$

Alternatively, we could use $[\text{OH}^-]$ directly to calculate **pOH** and then use

pH + pOH = 14, to calculate the **pH**.

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

$$= -\log (0.022)$$

$$\therefore \text{pOH} = 1.66$$

$$\text{pH} + \text{pOH} = 14$$

$$\text{pH} = 14 - \text{pOH}$$

$$\text{pH} = 14 - 1.66$$

$$\therefore \text{pH} = 12.34$$



Relationship between pH and pOH:

$$\text{pH} + \text{pOH}^- = -\log K_w = 14.00 \text{ at } 25^\circ\text{C}$$

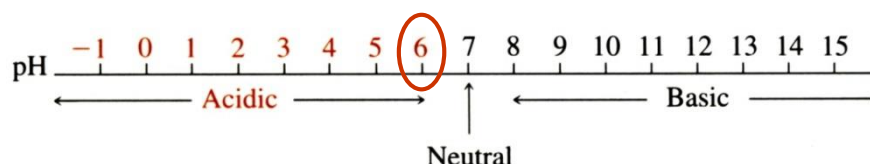
Dilemma: What is the pH of 1.0×10^{-8} M KOH?

Ans:

$$[\text{OH}^-] = [\text{KOH}] = 1.0 \times 10^{-8} \text{ M}$$

$$[\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1 \times 10^{-14}}{1.0 \times 10^{-8}} = 1.0 \times 10^{-6} \text{ M}$$

$$\text{pH} = -\log[\text{H}^+] = -\log(1.0 \times 10^{-6} \text{ M}) = 6.00$$



How can a base produce an acidic solution?!!

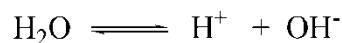
Wrong Assumption!!

So, $[\text{OH}^-] \neq [\text{KOH}] \neq 1.0 \times 10^{-8} \text{ M}$

For large concentration of acid or base,

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

For small concentration, must account for water dissociation

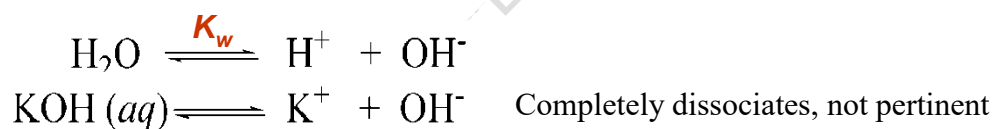


In pure water $[\text{OH}^-] = 1.0 \times 10^{-7} \text{ M}$, which is greater than $[\text{KOH}] = 1 \times 10^{-8} \text{ M}$

You must use systematic treatment of equilibrium

Systematic Treatment of Equilibrium

Step 1: Pertinent Reactions:



Step 2: Charge Balance (CB):

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

Step 3: Mass Balance (MB):

$$[\text{K}^+] = [1.0 \times 10^{-8}] \quad \text{All } \text{K}^+ \text{ comes from KOH}$$

Step 4: Equilibrium constant expression (one for each reaction):

Three equations (**Step 5**):

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

$$[\text{K}^+] = [1.0 \times 10^{-8}]$$

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

and three unknowns (**Step 5**):

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

Step 6: Solve (*Seeking pH or $[\text{H}^+]$*):

Set $[\text{H}^+] = x$, and substitute mass balance equation into charge balance equation:



From mass balance

$$[K^+] = [1.0 \times 10^{-8}]$$

$$[OH^-] = [K^+] + [H^+] = 1.0 \times 10^{-8} + x$$

Substitute OH^- equation into equilibrium equation:

$$[OH^-] = 1.0 \times 10^{-8} + x \quad K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$$

$$(x)(1.0 \times 10^{-8} + x) = 1.0 \times 10^{-14}$$

$$x^2 + (1.0 \times 10^{-8})x - 1.0 \times 10^{-14} = 0$$

Solve the quadratic equation*:

*In algebra, a quadratic equation (from the Latin *quadratus* for "square") is any equation having the form $a x^2 + b x + c = 0$

where x represents an unknown, and a , b , and c represent known numbers such that a is not equal to 0. If $a = 0$, then the equation is linear, not quadratic. The numbers a , b , and c are the coefficients of the equation, and may be distinguished by calling them, respectively, the quadratic coefficient, the linear coefficient and the constant or free term. With the above parameterization, the quadratic formula is:

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

Use quadratic equation:

$$x = \frac{-1.0 \times 10^{-8} \pm \sqrt{(1.0 \times 10^{-8})^2 - 4(1)(-1.0 \times 10^{-14})}}{2(1)}$$

$$x = 9.6 \times 10^{-8} M \text{ or } -1.1 \times 10^{-7} M$$

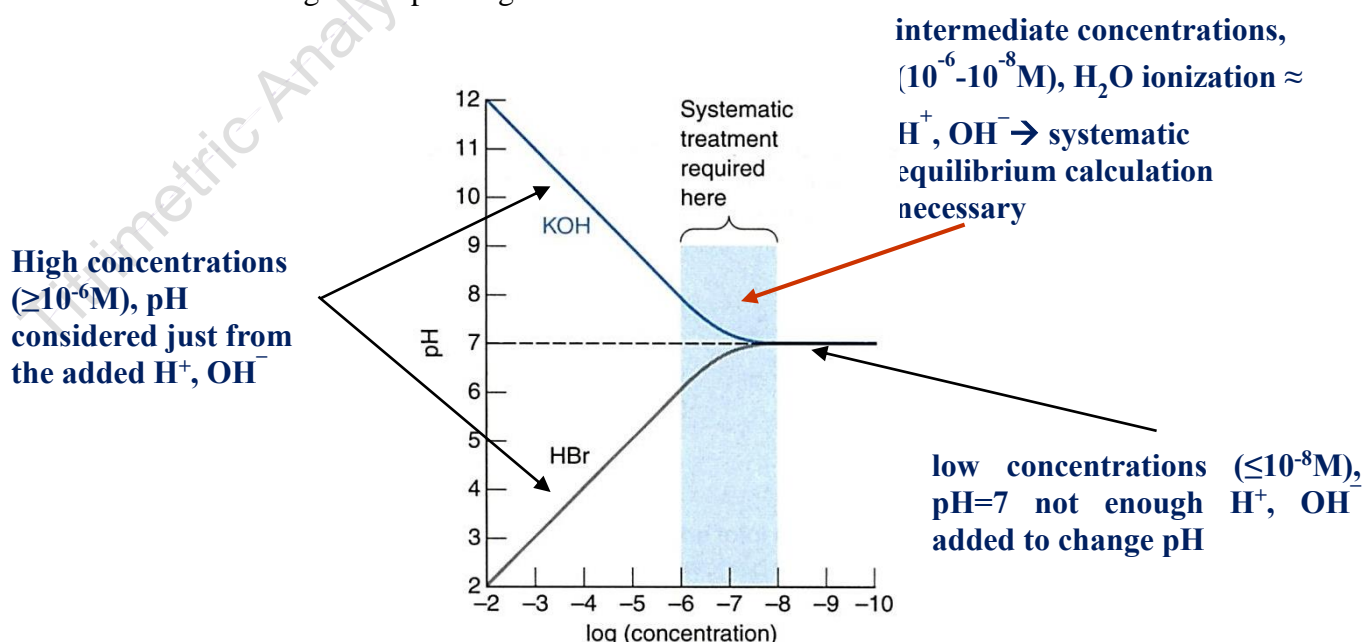
The negative number is physically meaningless
So

$$[H^+] = 9.6 \times 10^{-8} M$$

$$pH = -\log[H^+] = -\log(9.6 \times 10^{-8}) = 7.02$$

pH slightly basic, consistent with low [KOH]

To conclude: Three Regions depending on acid/base concentrations



Water almost never produces $10^{-7} M H^+$ and OH^-

$pH=7$ only true for pure water



Any acid or base suppresses water ionization

- Follows Le Châtelier's principal

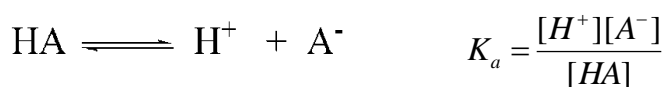
e.g. $[HBr] = [1.0 \times 10^{-4}] \Rightarrow pH = 4 \Rightarrow [OH^-] = 1 \times 10^{-10}$

In 10^{-4} M HBr solution, water dissociation produces only 10^{-10} M OH^- and H^+

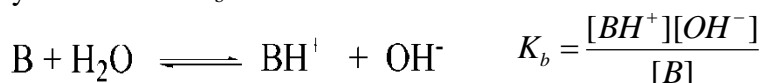
Weak Acids and Bases

Weak acids are weak electrolytes which are assumed to ionize partially in water. Weak acid/base do not completely dissociate.

Dissociation K_a for the acid HA:



Base Hydrolysis Constant K_b :



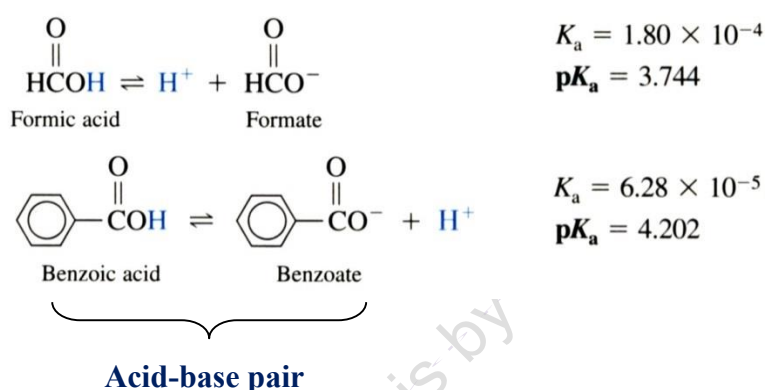
pK is negative logarithm of equilibrium constant

$$pK_a = -\log(K_a) \quad pK_b = -\log(K_b)$$

- As K_a or K_b increase \rightarrow pK_a or pK_b decrease

- Smaller $pK_a \rightarrow$ stronger acid

Conjugate acid-base pair – related by the gain or loss of a proton



Formic acid ($pK_a = 3.744$) stronger acid than benzoic acid ($pK_a = 4.202$).

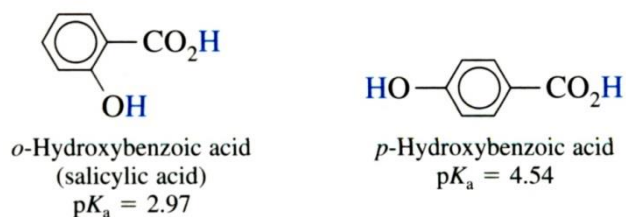
-Conjugate base of a weak acid is a weak base

-Conjugate acid of a weak base is a weak acid

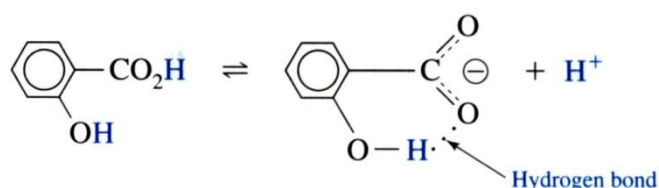
-Conjugate base of a strong acid is a very weak base or salt.

Any Effect that Increases the Stability of the Product Drives the Reaction Forward.

e.g. Formation of internal hydrogen bond for an acid/base.



Para isomer can't form internal hydrogen bond. Ortho isomer is stronger acid because product forms internal hydrogen bond.



General Systematic Treatment of Equilibrium



Unlike concentrated strong acid, in weak acid we need to account for water ionization

Q: Find pH for a solution of a general weak acid HA.

Solution:

Step 1: Pertinent reactions:



Step 2: Charge Balance:

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

Step 3: Mass Balance:

$$F = [\text{HA}] + [\text{A}^-]$$

where, F – formal concentration of acid.

Step 4: Equilibrium constant expression (one for each reaction):

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \quad K_w = [\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14}$$

Find pH for a solution of a general weak acid HA.

Step 5: Count equations and unknowns:

Four Equations:

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

$$F = [\text{HA}] + [\text{A}^-]$$

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

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

Four Unknowns:

$$[\text{A}^-], [\text{HA}], [\text{H}^+], [\text{OH}^-]$$

Step 6: Solve (Not easy to solve → cubic equation results!):

- Again, need to make assumptions to simplify equations.
- The goal is to determine $[\text{H}^+]$, so we can measure pH.

Make Some Initial Assumptions:

For a typical weak acid, $[\text{H}^+]$ from HA will be much greater than $[\text{H}^+]$ from H_2O .

If dissociation of HA is much greater than H_2O , $[\text{H}^+] \gg [\text{OH}^-]$.

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

Set $[\text{H}^+] = x$:

$$[\text{H}^+] = x \Rightarrow [\text{A}^-] = x$$

substitute

$$[\text{HA}] = F - [\text{A}^-] = F - x$$

Substitute into Equilibrium Equation:

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

$$[\text{HA}] = F - x$$

Rearrange:

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{(x)(x)}{F - x}$$

$$x^2 + (K_a)x - (F)(K_a) = 0$$



Using quadratic equation to solve this problem:

$$x = \frac{-K_a \pm \sqrt{K_a^2 + 4(1)(F)(K_a)}}{2(1)} = [x^-]$$

Step 7: Verify Assumption:

Was the approximation $[H^+] \approx [A^-]$ justified ($[H^+] \gg [OH^-]$)?

Setting $F = 0.050 \text{ M}$ and $K_a = 1.07 \times 10^{-3}$ for *o*-hydroxybenzoic acid:

$$x = \frac{-K_a \pm \sqrt{K_a^2 + 4(1)(F)(K_a)}}{2(1)} = \frac{-1.07 \times 10^{-3} \pm \sqrt{(1.07 \times 10^{-3})^2 + 4(1)(0.0500)(1.07 \times 10^{-3})}}{2(1)}$$

$$x = 6.8 \times 10^{-3} \text{ M} = [H^+] = [A^-]$$

$$pH = -\log x = 2.17$$

Determine $[OH^-]$ from water dissociation:

$$[OH^-] = \frac{K_w}{[H^+]} = \frac{1 \times 10^{-14}}{6.8 \times 10^{-3}} = 1.5 \times 10^{-12}$$

$[H^+] \gg [OH^-]$
 $6.8 \times 10^{-3} \text{ M} \gg 1.5 \times 10^{-12} \text{ M}$
assumption is justified!

Fraction of Dissociation

Fraction of acid HA in the form $A^-(a)$:

$$\alpha = \frac{[A^-]}{[A^-] + [HA]} = \frac{x}{x + (F - x)} = \frac{x}{F}$$

Example (5-5):

What is the percent fraction dissociation for $F = 0.050 \text{ M}$ and $K_a = 1.07 \times 10^{-3}$ for *o*-hydroxybenzoic acid?

Solution:

$$\alpha = \frac{x}{F} = \frac{6.8 \times 10^{-3} \text{ M}}{0.0500 \text{ M}} = 0.14 = 14\%$$

Percent dissociation increases with dilution.

Weak Base Equilibria

Treatment of Weak Base is Very Similar to Weak Acid

Assume all OH^- comes from base and not dissociation of water.

Step 1: Pertinent reactions:

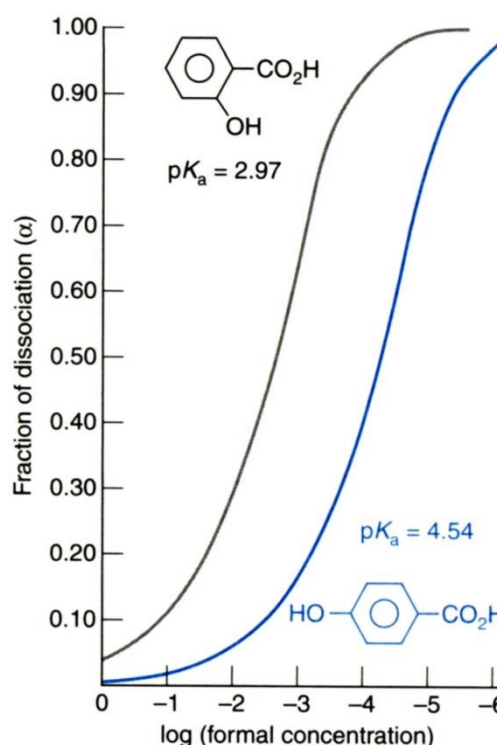


Step 2: Charge Balance:

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

Step 3: Mass Balance:

$$F = [B] + [BH^+] \Rightarrow [B] = F - [BH^+]$$





F – formal concentration of base.

Step 4: Equilibrium constant expression (one for each reaction):

$$K_b = \frac{[BH^+][OH^-]}{[B]} \quad K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$$

Assume all OH^- comes from base and not dissociation of water

Step 6: Solve (Assume $[BH^+] \gg [H^+] \rightarrow [BH^+] \approx [OH^-]$):

Set $[OH^-]=x$ and substitute into Equilibrium Equation:

$$[BH^+] = [OH^-] = x \quad [B] = F - x$$

$$K_b = \frac{[BH^+][OH^-]}{[B]} = \frac{(x)(x)}{F-x} = \frac{x^2}{F-x}$$

Rearrange:

$$x^2 + (K_b)x - (F)(K_b) = 0$$

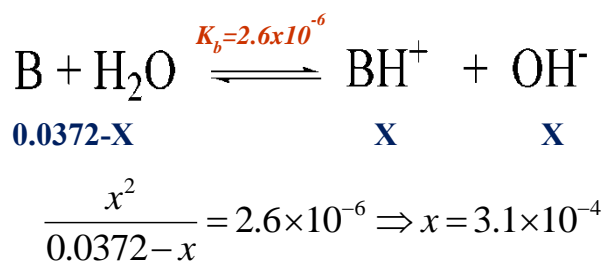
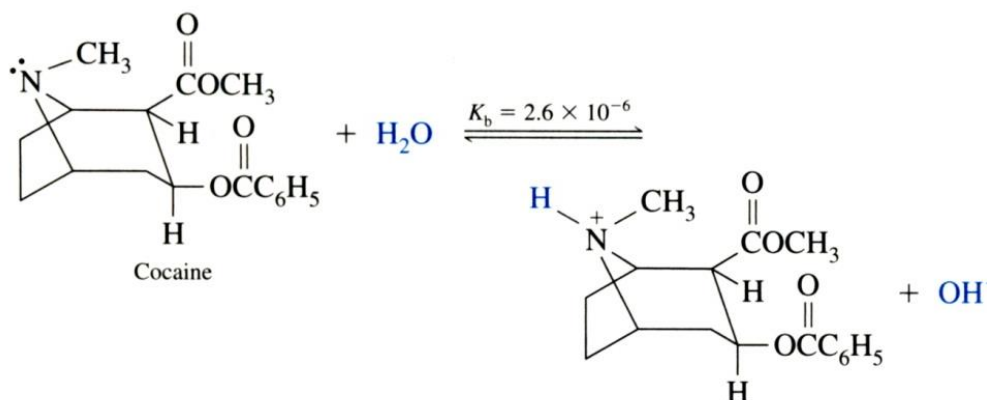
Solve a quadratic equation:

$$x = \frac{-K_b \pm \sqrt{K_b^2 + 4(1)(F)(K_b)}}{2(1)} = [OH^-]$$

Example (4-6):

What is the pH of cocaine dissolved in water? $F = 0.0372 \text{ M}$ and $K_b = 2.6 \times 10^{-6}$ for cocaine?

Solution:



Because $x = [OH^-]$, we need to solve for $[H^+]$

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{3.1 \times 10^{-4}} = 3.2 \times 10^{-11}$$

$$pH = -\log[H^+] = -\log(3.2 \times 10^{-11}) = 10.49$$

pH change or titration indicator may help identify/quantify drug.
(positive field test for cocaine).



Fraction of Association:

Fraction of Base B in BH^+ form (α):

$$\alpha = \frac{[BH^+]}{[BH^+] + [B]} = \frac{x}{x + (F - x)} = \frac{x}{F}$$

Example (4-7):

What is the percent fraction dissociation of cocaine reacted with water? $F = 0.0372 \text{ M}$ and $K_b = 2.6 \times 10^{-6}$ for cocaine?

Solution:

$$\alpha = \frac{x}{F} = \frac{3.1 \times 10^{-4} \text{ M}}{0.0372 \text{ M}} = 0.0083 = 0.83\%$$

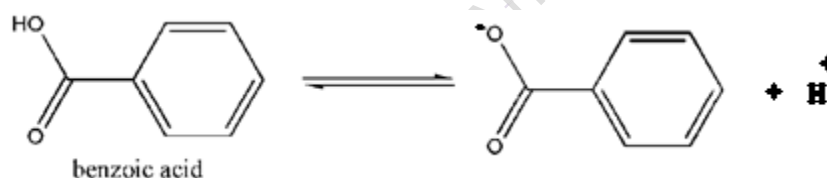
Fraction of Association

Fraction of Base B in BH^+ form (α):

$$\alpha = \frac{[BH^+]}{[BH^+] + [B]} = \frac{x}{x + (F - x)} = \frac{x}{F}$$

Problem:

A 0.0450 M solution of benzoic acid has a pH of 2.78. Calculate pK_a for this acid. What is the percent fraction dissociation?



Buffers

A buffered solution resists changes in pH when acids or bases are added.

Buffer: is a mixture of a weak acid (or a weak base) and its conjugate base (or conjugate acid).

For an organism to survive, it must control the pH of each subcellular compartment.

Enzyme-catalyzed reactions are pH dependent.

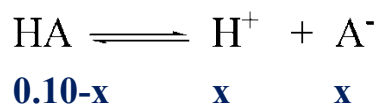
Mixing a Weak Acid and Its Conjugated Base

Very little reaction occurs.

Very little change in concentrations.

Example (4-8):

Consider a 0.10 M of acid with pK_a of 4.00.



Find α .

Solution:

$$\frac{x^2}{F - x} = K_a \Rightarrow x = 3.1 \times 10^{-3}$$



$$\alpha = \frac{x}{F} = \frac{3.1 \times 10^{-3} M}{0.10 M} = 0.031 = 3.1\%$$

Example (5-9):

Consider adding 0.10 M of conjugate base with pK_b of 10.00



Find α .

Solution:

$$\frac{x^2}{F-x} = K_b \Rightarrow x = 3.2 \times 10^{-6}$$

$$\alpha = \frac{x}{F} = \frac{3.2 \times 10^{-6} M}{0.10 M} = 3.2 \times 10^{-5}$$

HA dissociates very little and A^- reacts very little with water

Henderson-Hasselbalch Equation

Rearranged form of K_a equilibrium equation:

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

Take log of both sides:

$$\log K_a = \log \frac{[H^+][A^-]}{[HA]} = \log[H^+] + \log \frac{[A^-]}{[HA]}$$

rearrange:

$$\underbrace{-\log[H^+]}_{\text{pH}} = \underbrace{-\log K_a}_{\text{pKa}} + \log \frac{[A^-]}{[HA]}$$

$$pH = pK_a + \log \left(\frac{[A^-]}{[HA]} \right)$$

Henderson-Hasselbalch equation determines pH of a buffered solution and we need to know ratio of conjugate [acid] and [base].

$$pH = pK_a + \log \left(\frac{[A^-]}{[HA]} \right)$$

$[A^-]/[HA]$	pH
100:1	$pK_a + 2$
10:1	$pK_a + 1$
1:1	pK_a
1:10	$pK_a - 1$
1:100	$pK_a - 2$

If $[A^-] = [HA]$ then, $pH = pK_a$

All equilibria must be satisfied simultaneously in any solution at equilibrium

Only one concentration of H^+ in a solution

Similar equation for weak base and conjugate acid

$$pH = pK_a + \log \left(\frac{[B]}{[BH^+]} \right) \leftarrow pK_a \text{ is for this acid}$$



A strong acid and a weak base react “completely” to give the conjugate acid:

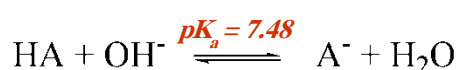


Also, a strong base and a weak acid react “completely” to give the conjugate base:



Problem:

Calculate how many milliliters of 0.626 M KOH should be added to 5.00 g of 4-Morpholinobutane-1-sulfonic acid (MOBS; $\text{C}_8\text{H}_{17}\text{NO}_4\text{S}$; F.wt. 223.29) to give a pH of 7.40?



What is the pH if an additional 5 mL of the KOH solution is added?

Why Does a Buffer Resist Change in pH?

Strong acid or base is consumed by B or BH^+ .

Maximum capacity to resist pH change occurs at $\text{pH} = \text{p}K_a$.

Buffer Capacity (b): measure of a solution's resistance to pH change.

$$\beta = \frac{dC_b}{d\text{pH}} = -\frac{dC_a}{d\text{pH}}$$

where C_a and C_b are the number of moles of strong acid and strong base per liter needed to produce a unit change in pH.

Choosing a Buffer

Choose a buffer with $\text{p}K_a$ as close as possible to the desired pH

Useful buffer range is $\text{p}K_a \pm 1 \text{ pH units}$

Buffer pH depends on temperature and ionic strength \rightarrow activity coefficients.

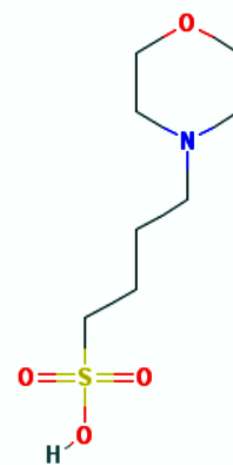
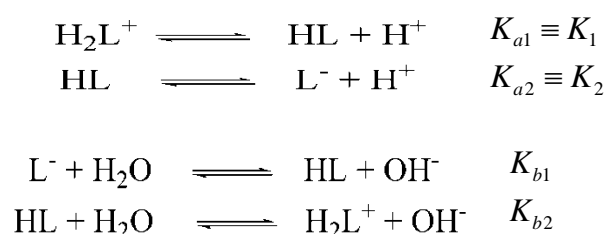
A wide number of buffers are available that cover an essential complete range of pHs.

Choose a buffer with a $\text{p}K_a$ as close as possible to the desired pH.

Diprotic/Polyprotic Acid-Base Equilibria

In polyprotic (or poly basic) systems, acids or bases can donate or accept more than one proton. Proteins are a common example of a polyprotic system.

Diprotic Acids and Bases





Relationship between K_a and K_b

$$K_{a1} \times K_{b2} \equiv K_w$$

$$K_{a2} \times K_{b1} \equiv K_w$$

If $K_1 \gg K_2$

Assume H_2L^+ behaves as a monoprotic acid

Even if K_1 is just 10x larger than K_2

Error in pH is only 4% or 0.01 pH units. So, assumption $K_a = K_{a1}$ is safe.

For base $K_{b1} \gg K_{b2}$

Assume L^- behaves as a monoprotic base $K_b = K_{b1}$

Titrimetric Analysis by Dr. Adel Ahmed Mohammed Saeed



5. NEUTRALIZATION TITRATIONS

Titrimetric method (Titration): Analytical procedures in which the amount of analyte is determined from the amount of a standard reagent required to react with the analyte completely.

Like any titration, neutralization titrations depend on a chemical reaction between the analyte and a standard reagent. The point of chemical equivalence is indicated by a chemical indicator or an instrumental measurement. An acid/base **indicator** is a weak organic acid or a weak organic base whose undissociated form differs in color from its conjugate form.

Standard Solutions

The standard solutions employed in neutralization titrations are strong acids or strong bases because these substances react more completely with an analyte than their weaker counterparts do and thus yield sharper end points. Standard solutions of acids are prepared by diluting concentrated hydrochloric, perchloric, or sulfuric acid.

Standard solutions of bases are ordinarily prepared from solid sodium or potassium and occasionally barium hydroxides. The concentrations of these bases must be established by standardization.

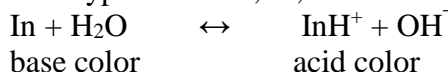
Acid/Base Indicators

Many substances display colors that depend on the pH of the solutions in which they are dissolved. An acid/base indicator is a weak organic acid or a weak organic base whose undissociated form differs in color from its conjugate form. e.g., the behavior of an acid-type indicator, HIn , is described by the equilibrium



acid color base color

The equilibrium for a base-type indicator, In , is



base color acid color

The equilibrium-constant expression for the dissociation of an acid-type indicator takes the form

$$K_a = \frac{[H_3O^+][In^-]}{[HIn]}$$

Rearranging leads to

$$[H_3O^+] = K_a \frac{[HIn]}{[In^-]}$$

The hydronium ion concentration determines the ratio of the acid to the conjugate base form of the indicator and thus determines the color developed by the solution.

The color imparted to a solution by a typical indicator appears to the average observer to change rapidly only within the limited concentration ratio of approximately 10 to 0.1

$$\frac{[HIn]}{[In^-]} \geq \frac{10}{1}$$

and its base color when

$$\frac{[HIn]}{[In^-]} \leq \frac{1}{10}$$

The color appears to be intermediate for ratios between these two values. These ratios vary considerably from indicator to indicator.

For the full acid color,

$$[H_3O^+] = 10K_a$$

and similarly for the full base color,

$$[H_3O^+] = 0.1K_a$$

To obtain the indicator pH range, we take the negative logarithms of the two expressions:

$$pH \text{ (acid color)} = -\log(10K_a) = pK_a + 1$$

$$pH \text{ (basic color)} = -\log(0.1K_a) = pK_a - 1$$

$$\text{indicator pH range} = pK_a \pm 1$$



TABLE 6-1

Some Important Acid/Base Indicators

Common Name	Transition Range, pH	pK _a *	Color Change†	Indicator Type‡
Thymol blue	1.2–2.8	1.65§	R–Y	1
	8.0–9.6	8.96§	Y–B	
Methyl yellow	2.9–4.0		R–Y	2
Methyl orange	3.1–4.4	3.46§	R–O	2
Bromocresol green	3.8–5.4	4.66§	Y–B	1
Methyl red	4.2–6.3	5.00§	R–Y	2
Bromocresol purple	5.2–6.8	6.12§	Y–P	1
Bromothymol blue	6.2–7.6	7.10§	Y–B	1
Phenol red	6.8–8.4	7.81§	Y–R	1
Cresol purple	7.6–9.2		Y–P	1
Phenolphthalein	8.3–10.0		C–R	1
Thymolphthalein	9.3–10.5		C–B	1
Alizarin yellow GG	10–12		C–Y	2

*At ionic strength of 0.1.

†B = blue; C = colorless; O = orange; P = purple; R = red; Y = yellow.

‡(1) Acid type: $\text{HIn} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{In}^-$; (2) Base type: $\text{In} + \text{H}_2\text{O} \rightleftharpoons \text{InH}^+ + \text{OH}^-$.

§For the reaction $\text{InH}^+ + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{In}$.

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Calculating pH in Titrations of Strong Acids & Strong Bases

The hydronium ions in an aqueous solution of a strong acid have two sources: (1) the reaction of the acid with water and (2) the dissociation of water itself. In all but the most dilute solutions, however, the contribution from the strong acid far exceeds that from the solvent. Thus, for a solution of HCl with a concentration greater than about 10^{-6} M, we can write

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

where $[\text{OH}^-]$ represents the contribution of hydronium ions from the dissociation of water. An analogous relationship applies for a solution of a strong base, such as sodium hydroxide. That is,

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

Titration of Strong Acids & Strong Bases

We will be interested here, in calculating hypothetical titration curves of pH versus volume of titrant. Three types of calculation must be done to construct the hypothetical titration curve for titrating a solution of a strong acid with a strong base. Each calculation corresponds to a distinct stage in the titration:

1. Preequivalence
2. Equivalence
3. Postequivalence

In the **preequivalence** stage, we compute the concentration of the acid from its starting concentration and the amount of base that has been added.

At the **equivalence** point, the hydronium and hydroxide ions are present in equal concentrations, and the hydronium ion concentration is derived directly from the ion-product constant for water.

In the **post-equivalence** stage, the analytical concentration of the excess base is computed, and the hydroxide ion concentration is assumed to be equal to or a multiple of the analytical concentration.

Equivalence point

Quantity of added titrant is the exact amount necessary for stoichiometric reaction with the analyte.

-Ideal theoretical result.



Endpoint

What we actually measure.

-Marked by a sudden change in the physical property of the solution.

-Change in color, pH, voltage, current, absorbance of light, presence/absence ppt.

Endpoint occurs from the addition of a slight *excess* of the titrant. It does not equal an equivalence point.

After the equivalence point occurs, excess titrant turns solution color (Endpoint).

Titration Error

It is a difference between the endpoint and the equivalence point.

This error can be corrected by a blank titration as follow:

- Repeat procedure without analyte.
- Determine the amount of titrant needed to observe change.
- Subtract blank volume from titration.

Primary Standard

-Accuracy of titration requires knowing precisely the quantity of titrant added. Using a substance with 99.9% pure or better leads to measure concentration accurately.

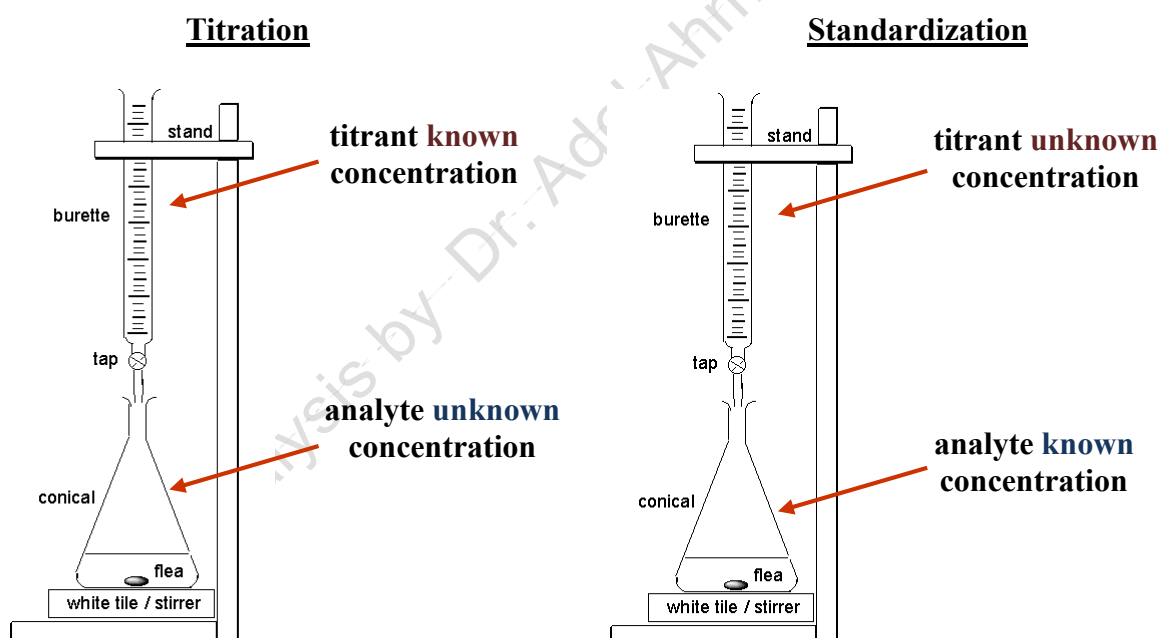
Standardization is required when a non-primary titrant is used.

-Prepare titrant with approximately the desired concentration

-Use it to titrate a primary standard.

-Determine the concentration of the titrant.

-Reverse of the normal titration process!!!



Calculating pH of Strong Acids-Strong Bases Titrations

The hydronium ions in an aqueous solution of a strong acid have two sources: (1) the reaction of the acid with water and (2) the dissociation of water itself.

Before the equivalence point, we calculate the pH from the molar concentration of unreacted acid.

At the equivalence point, the solution is neutral and $\text{pH}=7.00$.

Beyond the equivalence point, we first calculate pOH and then pH. Remember that $\text{pH} = \text{p}K_w - \text{pOH} = 14.00 - \text{pOH}$.

Example 5-1:

Do the calculations needed to generate the hypothetical titration curve for the titration of 50.00 mL of 0.0500 M HCl with 0.1000 M NaOH?



Solution:

(1) Initial Point

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log 0.0500 = 1.30$$

(2) After Addition of 10.00 mL of Reagent

$$\begin{aligned} c_{\text{HCl}} &= \frac{\text{no. mmol HCl remaining after addition of NaOH}}{\text{total volume soln}} \\ &= \frac{\text{original no. mmol HCl} - \text{no. mmol NaOH added}}{\text{total volume soln}} \\ &= \frac{(50.00 \text{ mL} \times 0.0500 \text{ M}) - (10.00 \text{ mL} \times 0.1000 \text{ M})}{50.00 \text{ mL} + 10.00 \text{ mL}} \\ &= \frac{(2.500 \text{ mmol} - 1.000 \text{ mmol})}{60.00 \text{ mL}} = 2.500 \times 10^{-2} \text{ M} \end{aligned}$$

$$[\text{H}_3\text{O}^+] = 2.500 \times 10^{-2}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (2.500 \times 10^{-2}) = 1.602$$

(3) Equivalence Point

We can check the volume of titrant that make neutralization using neutralization law:

$$\begin{aligned} M_a \times V_a &= M_b \times V_b \\ 0.0500\text{M} \times 50 \text{ mL (HCl)} &= 0.1000\text{M} \times ? \text{ (NaOH)} \\ ? &= 25 \text{ mL} \end{aligned}$$

This means, the equivalence point is at 25 mL of 0.1000M NaOH added to 50 mL of 0.0500 M HCl. At this point, the formed solution is neutral;

$$\begin{aligned} [\text{H}_3\text{O}^+] &= \sqrt{K_w} = \sqrt{1.00 \times 10^{-14}} = 1.00 \times 10^{-7} \\ \text{pH} &= -\log (1.00 \times 10^{-7}) = 7.00 \end{aligned}$$

(4) After Addition of 25.10 mL of Reagent

$$\begin{aligned} c_{\text{NaOH}} &= \frac{\text{no. mmol NaOH added} - \text{original no. mmol HCl}}{\text{total volume soln}} \\ c_{\text{NaOH}} &= \frac{25.10 \times 0.100 - 50.00 \times 0.0500}{75.10} = 1.33 \times 10^{-4} \text{ M} \end{aligned}$$

$$[\text{OH}^-] = c_{\text{NaOH}} = 1.33 \times 10^{-4} \text{ M}$$

$$\text{pOH} = -\log (1.33 \times 10^{-4}) = 3.88$$

and

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



TABLE 5-2

Changes in pH During the Titration of a Strong Acid With a Strong Base

Volume of NaOH, mL	pH	
	50.00 mL of 0.0500 M HCl with 0.100 M NaOH	50.00 mL of 0.000500 M HCl with 0.00100 M NaOH
0.00	1.30	3.30
10.00	1.60	3.60
20.00	2.15	4.15
24.00	2.87	4.87
24.90	3.87	5.87
25.00	7.00	7.00
25.10	10.12	8.12
26.00	11.12	9.12
30.00	11.80	9.80

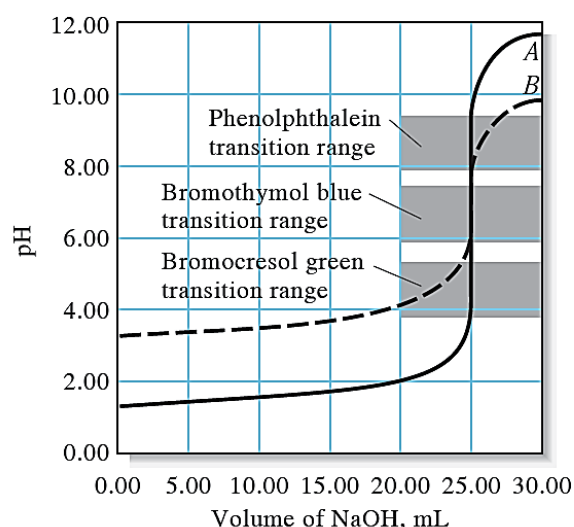


Figure 5-1 Titration curves for HCl with NaOH. Curve A: 50.00 mL of 0.0500 M HCl with 0.1000 M NaOH. Curve B: 50.00 mL of 0.000500 M HCl with 0.001000 M NaOH.

What about Titrating a Strong Base with a Strong Acid!!

Problem (1): Do the calculations needed to generate the hypothetical titration curve for the titration of 50.00 mL of 0.0500 M NaOH with 0.1000 M HCl.

Solution:

With care, follow the same steps mentioned in example 5-1.

(1) Initial Point

$$\text{pOH} = -\log [\text{OH}^-] = -\log 0.0500 = 1.30$$

$$\text{pH} = 14 - 1.30 = 12.70$$

(2) After Addition of 10.00 mL of Reagent

We will find the remaining C_{NaOH} similar to example 5-1.

(3) Equivalence point (same as example 5-1).

(4) After Addition of 25.10 mL of Reagent

We will find excess C_{HCl} similar to example 5-1.

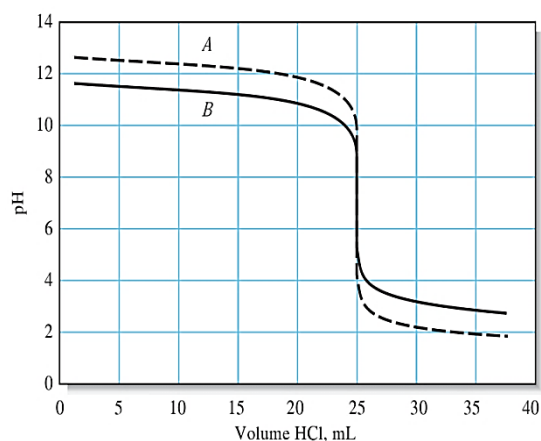


Figure 5-2 Titration curves for NaOH with HCl. Curve A: 50.00 mL of 0.0500 M NaOH with 0.1000 M HCl. Curve B: 50.00 mL of 0.00500 M NaOH with 0.0100 M HCl.



Calculating pH of Weak Acid/Strong Base Titrations

Four Regions to Titration Curve

(1) **Initial Point** (Before any added base). Just weak acid (HA) is in water; so, pH is determined by pK_a .



(2) **After Addition of strong base and before equivalence point.** Buffer solution formed and pH determined by Henderson Hasselbach equation.

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right)$$

(3) **At the equivalence point,** all HA is converted into A^- . Weak base with pH determined by K_b .



(4) **Beyond the equivalence point,** an excess strong base is added to A^- solution. pH is determined by excess titrant (strong base) and calculation is similar to titration of a strong acid with a strong base.

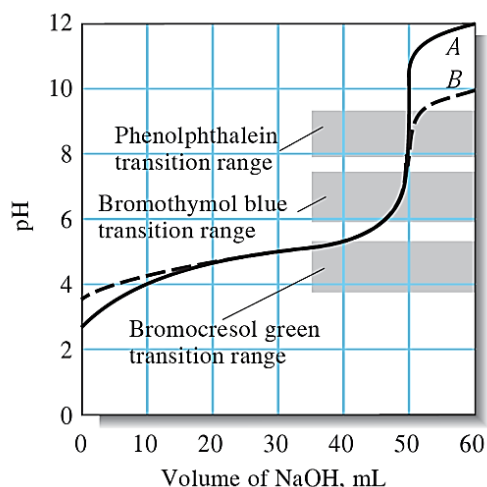


Figure 5-4 Curve for the titration of acetic acid with sodium hydroxide. Curve A: 0.1000 M acid with 0.1000 M base. Curve B: 0.001000 M acid with 0.001000 M base.

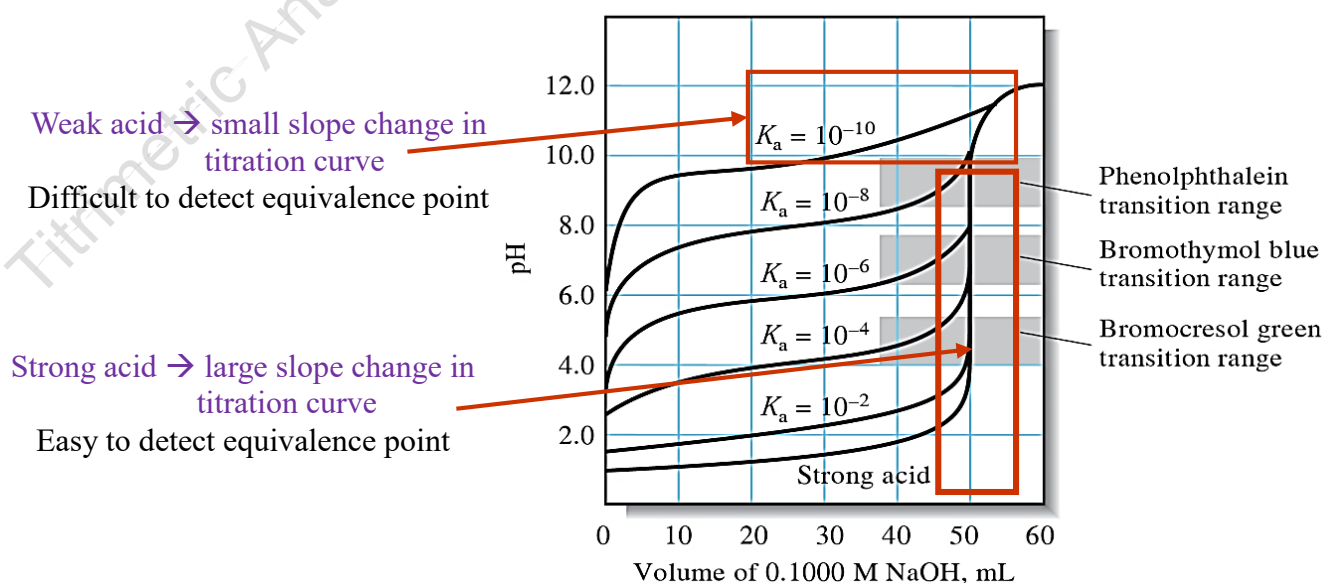
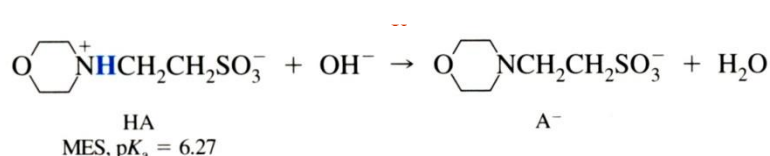


Figure 5-5 The effect of acid strength (dissociation constant, K_a) on titration curves. Each curve represents the titration of 50.00 mL of 0.1000 M acid with 0.1000 M base.

**Example 5-2:**

Titration of 50.00 mL of 0.02000 M MES with 0.1000 M NaOH. (MES is a weak acid with $pK_a = 6.27$)

**Solution:**

Reaction goes to completion with addition of strong base.

$$K_{eq} = \frac{1}{K_b} = \frac{1}{(K_w / K_a)} = \frac{1}{(1 \times 10^{-14} / 10^{-6.27})} = 5.4 \times 10^7$$

Volume Needed to Reach the Equivalence Point

Titration of 50.00 mL of 0.02000 M MES with 0.1000 M NaOH

Strong plus weak react completely.

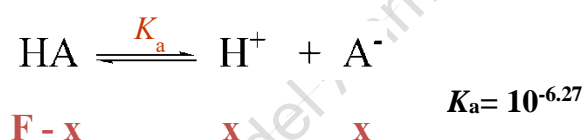
$$\underbrace{(V_e \text{ (mL)})(0.1000 \text{ M})}_{\text{mmol of base}} = \underbrace{(50.00 \text{ mL})(0.02000 \text{ M})}_{\text{mmol of HA}} \Rightarrow V_e = 10.00 \text{ mL}$$

Region 1: Initial Point (Before any added base).

Titration of 50.00 mL of 0.02000 M MES with 0.1000 M NaOH

Simply a weak-acid problem

Calculate $[H^+]$:



$$\frac{x^2}{F - x} = \frac{x^2}{0.02000 - x} = K_a \Rightarrow x = [H^+] = 1.03 \times 10^{-4}$$

Calculate pH:

$$pH = -\log[H^+] = -\log(1.03 \times 10^{-4} \text{ M}) = 3.99$$

Region 2: Before the Equivalence Point

Adding OH^- creates a mixture of HA and $\text{A}^- \rightarrow$ Buffer

Calculate pH from $[A^-]/[HA]$ using Henderson-Hasselbach equation

Calculate $[A^-]/[HA]$:

When adding 3.00 mL of 0.1000 M NaOH:

mmol of A^- formed comes from 3.00 mL of 0.1000 M NaOH so

$$n = 3.00 \text{ mL} \times 0.1000 \text{ M} = 0.300 \text{ mmol.}$$

$$V_{\text{total}} = 50.00 \text{ mL} + 3.00 \text{ mL} = 53.00 \text{ mL}$$

$$\& [A^-] = 0.300 \text{ mmol} / 53 \text{ mL}$$

The remaining amount of weak acid (MES or HA) unreacted can be calculated as follows:

$$\text{mmol of HA remained} = (50.00 \text{ mL} \times 0.02000 \text{ M}) - (3.00 \text{ mL} \times 0.1000 \text{ M}) = 1 \text{ mmol} - 0.3 \text{ mmol} = 0.700 \text{ mmol.}$$

$$[HA] \text{ remained} = 0.700 \text{ mmol} / 53.00 \text{ mL then,}$$

Calculate pH:

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right) = 6.27 + \log\left(\frac{0.3/53}{0.7/53}\right) = 5.90$$

**Region 2: Before the Equivalence Point**

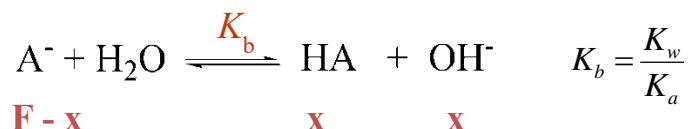
$pH = pK_a$ when the volume of titrant equals $1/2V_e$ (that's at 5.00 mL).

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right) = pK_a + \log\left(\frac{1/2}{1/2}\right) = pK_a$$

Region 3: At the Equivalence Point

Exactly enough NaOH to consume HA

The solution only contains $A^- \rightarrow$ weak base (salt).



$$\frac{x^2}{F-x} = K_b = \frac{K_w}{K_a}$$

Calculate the Formal concentration of $[A^-]$:

A^- is no longer 0.02000 M, diluted by the addition of NaOH.

$$F' = (0.02000 M) \left(\frac{50.00}{50.00 + 10.00} \right) = 0.0167 M$$

Initial volume of HA
 Initial concentration of HA Dilution factor Total volume

Calculate $[OH^-]$:

$$\frac{x^2}{F-x} = K_b = \frac{K_w}{K_a} = \frac{1 \times 10^{-14}}{10^{-6.27}} = 1.86 \times 10^{-8}$$

$$\frac{x^2}{0.0167-x} = 1.86 \times 10^{-8} \Rightarrow x = [OH^-] = 1.76 \times 10^{-5} M$$

Calculate pH:

$$pH = -\log[H^+] = -\log\left(\frac{K_w}{x}\right) = -\log\left(\frac{1 \times 10^{-14}}{0.0167}\right) = 9.25$$

pH at equivalence point is **not**
7.00

pH will always be *above* 7.00 for titration of a weak acid because acid is converted into conjugate base at the equivalence point.

Region 4: After the Equivalence Point

-Adding NaOH to a solution of A^-

-NaOH is a much stronger base than A^-

-pH is determined by the excess of OH^-

Calculate the volume of excess OH^- :

Suppose, the amount of added NaOH is 10.10 mL with equivalence point is 10 mL

So, excess volume of OH^- is:

$$V_{added} - V_{equivalence} = 10.10 - 10.00 = 0.10 mL$$

and excess $[OH^-]$:



$$[\text{OH}^-] = \underbrace{(0.1000 \text{ M})}_{\text{Initial concentration of OH}^-} \underbrace{\left(\frac{0.10}{50.00 + 10.10} \right)}_{\text{Dilution factor}} = 1.66 \times 10^{-4} \text{ M}$$

Volume of excess OH⁻
Total volume

Calculate pH:

$$\text{pH} = -\log[H^+] = -\log\left[\frac{K_w}{[\text{OH}^-]}\right] = -\log\left(\frac{1.00 \times 10^{-14}}{1.66 \times 10^{-4}}\right) = 10.22$$

Titration Curve

Two Important Features of the Titration Curve.

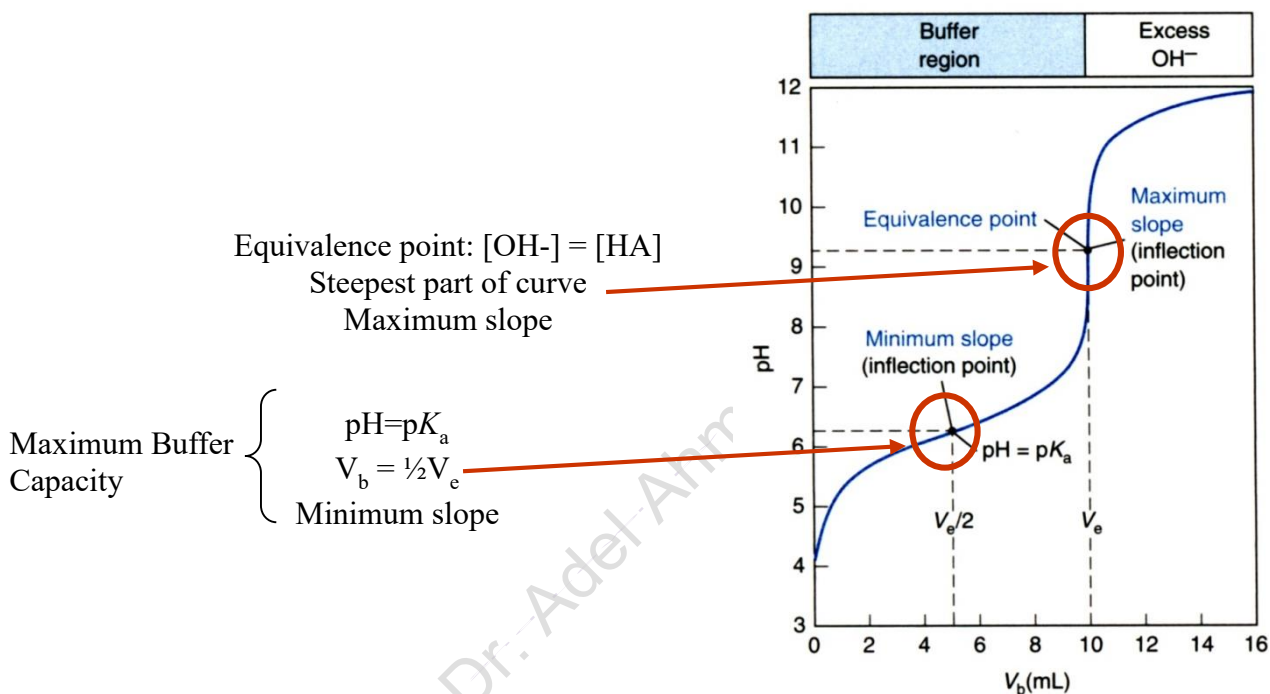


Figure 5-6 Titration curve of a weak acid with a strong base.

What about Calculating pH of Weak Base/Strong Acid Titrations!!

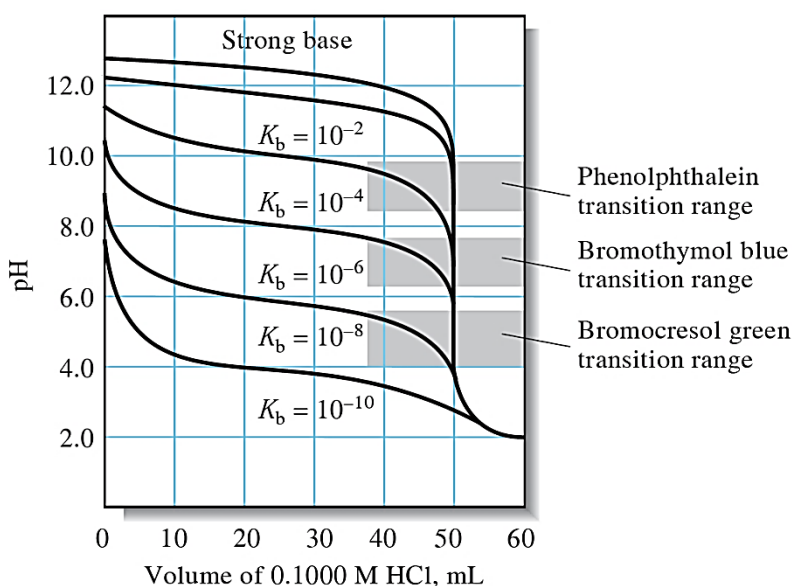


Figure 5-7 The effect of base strength (K_b) on titration curves. Each curve represents the titration of 50.00 mL of 0.1000 M base with 0.1000 M HCl.



What Are the Unique Properties of Buffer Solutions?

1. The Effect of Dilution

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 (**Figure 5-8**).

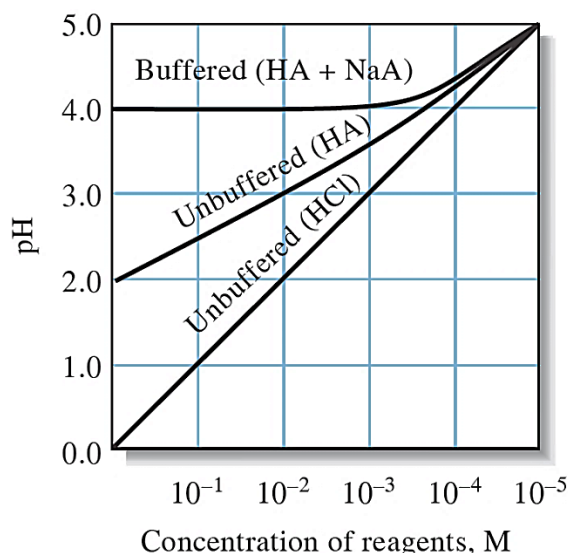


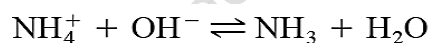
Figure 5-8 The effect of dilution of the pH of buffered and unbuffered solutions. The dissociation constant for HA is 1.00×10^{-4} . Initial solute concentrations are 1.00 M.

2. The Effect of Added Acids/Bases:

Example 5-3:

Calculate the pH change that takes place when a 100-mL portion of (a) 0.0500M NaOH and (b) 0.0500 M HCl is added to 400 mL of the buffer solution 0.200 M NH_3 /0.300 M NH_4Cl .

(a) Addition of NaOH converts part of the NH_4^+ in the buffer to NH_3 :



Solution:

The analytical concentrations of NH_3 and NH_4Cl then become

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

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

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

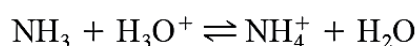
$$[\text{H}_3\text{O}^+] = 5.70 \times 10^{-10} \times \frac{0.230}{0.170} = 7.71 \times 10^{-10}$$

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

and the change in pH is

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

(b) Addition of HCl converts part of the NH_3 to NH_4^+ ; thus,





Solution:

$$c_{\text{NH}_3} = \frac{400 \times 0.200 - 100 \times 0.0500}{500} = \frac{75.0}{500} = 0.150 \text{ M}$$

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

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

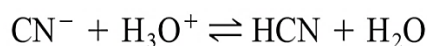
$$\text{pH} = -\log(9.50 \times 10^{-10}) = 9.02$$

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

Calculating pH of Basic Salt/Strong Acid Titrations

Example 5-4:

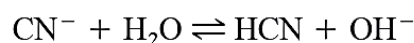
A 50.00-mL aliquot of 0.0500 M NaCN is titrated with 0.1000 M HCl. The reaction is



Calculate the pH after the addition of (a) 0.00, (b) 10.00, (c) 25.00, and (d) 26.00 mL of acid.

Solution:

(a) 0.00 mL of reagent:



$$K_b = \frac{[\text{OH}^-][\text{HCN}]}{[\text{CN}^-]} = \frac{K_w}{K_a} = \frac{1.00 \times 10^{-14}}{6.2 \times 10^{-10}} = 1.61 \times 10^{-5}$$

$$[\text{OH}^-] = [\text{HCN}]$$

$$[\text{CN}^-] = c_{\text{NaCN}} - [\text{OH}^-] \approx c_{\text{NaCN}} = 0.050 \text{ M}$$

$$[\text{OH}^-] = \sqrt{K_b c_{\text{NaCN}}} = \sqrt{1.61 \times 10^{-5} \times 0.0500} = 8.97 \times 10^{-4}$$

$$\text{pH} = 14.00 - [-\log(8.97 \times 10^{-4})] = 10.95$$

(b) 10.00 mL of reagent:

$$c_{\text{NaCN}} = \frac{50.00 \times 0.0500 - 10.00 \times 0.1000}{60.00} = \frac{1.500}{60.00} \text{ M}$$

$$c_{\text{HCN}} = \frac{10.00 \times 0.1000}{60.00} = \frac{1.000}{60.00} \text{ M}$$



$$[\text{H}_3\text{O}^+] = \frac{6.2 \times 10^{-10} \times (1.000/60.00)}{1.500/60.00} = 4.13 \times 10^{-10}$$

$$\text{pH} = -\log 4.13 \times 10^{-10} = 9.38$$

(c) 25.00 mL of reagent:

$$c_{\text{HCN}} = \frac{25.00 \times 0.1000}{75.00} = 0.03333 \text{ M}$$

$$[\text{H}_3\text{O}^+] = \sqrt{K_a c_{\text{HCN}}} = \sqrt{6.2 \times 10^{-10} \times 0.03333} = 4.45 \times 10^{-6} \text{ M}$$

$$\text{pH} = -\log 4.45 \times 10^{-6} = 5.34$$

(d) 26.00 mL of reagent:

$$[\text{H}_3\text{O}^+] = c_{\text{HCl}} = \frac{26.00 \times 0.1000 - 50.00 \times 0.0500}{76.00} = 1.32 \times 10^{-3} \text{ M}$$

$$\text{pH} = -\log 1.32 \times 10^{-3} = 2.88$$

What about Calculating pH of Acidic Salt /Strong Base Titrations!

Problem (2): A 50.00-mL aliquot of 0.0500 M NH_4Cl is titrated with 0.1000 M NaOH. The reaction is



Calculate the pH after the addition of (a) 0.00, (b) 10.00, (c) 25.00, and (d) 26.00 mL of base.

Back Titration

Add excess of one standard reagent (known concentration and volume of acid or base).

-Completely react all the analyte.

-Add enough acid (or base) so all base (or acid) is converted to product.

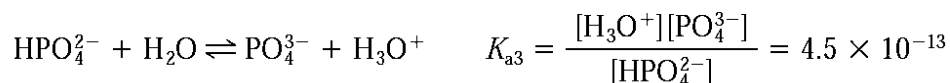
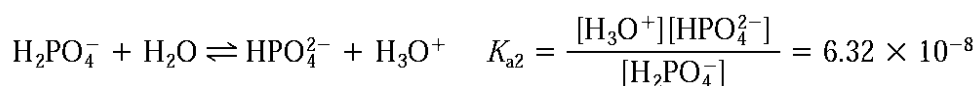
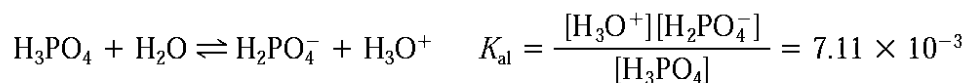
Titrate excess standard reagent to determine how much is left.

-Titrate using another standard (base or acid) to determine the amount of excess acid or base that did not react with the analyte.

-Differences are related to the amount of analyte.

-Useful if better/easier to detect endpoint.

Polyfunctional Acids



With this acid, as with other polyprotic acids, $K_{a1} > K_{a2} > K_{a3}$.



Titration Curve for Polyfunctional Acids

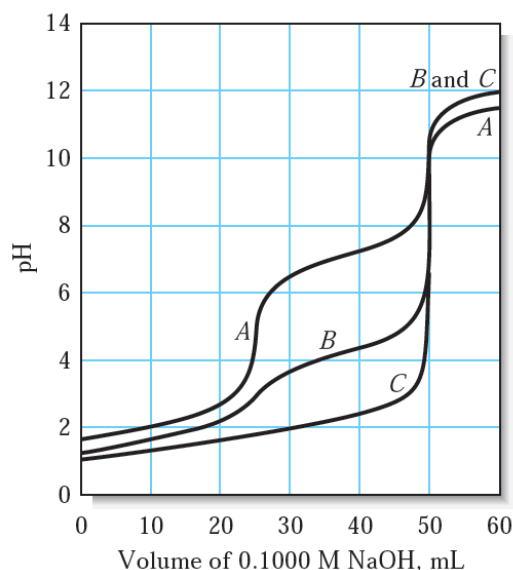
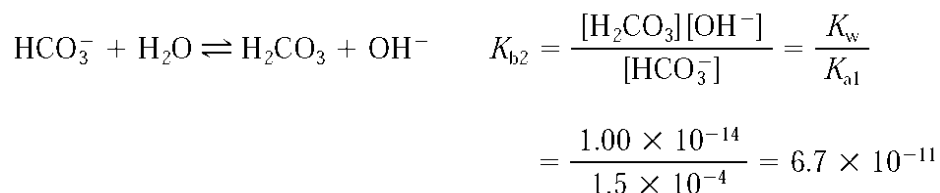
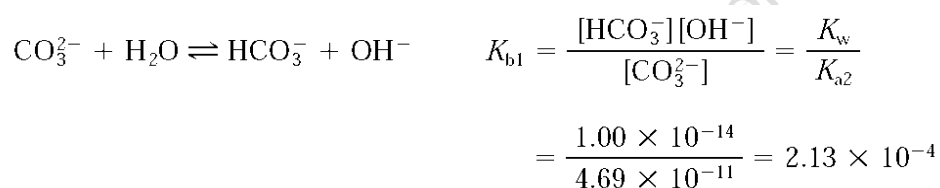
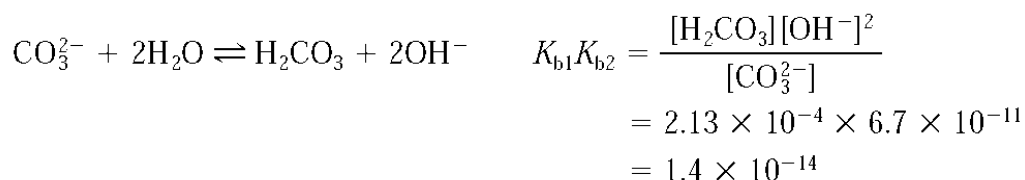


Figure 5-9 Curves for the titration of polyprotic acids. A 0.1000 M NaOH solution is used to titrate 25.00 mL of 0.1000 M H_3PO_4 (curve A), 0.1000 M oxalic acid (curve B), and 0.1000 M H_2SO_4 (curve C).

Describing Polyfunctional Bases

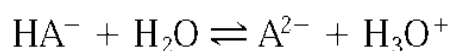


The overall basic dissociation reaction of sodium carbonate is described by the equations.

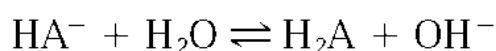


The overall basic dissociation reaction of sodium carbonate is described by the equations. Solving the several simultaneous equations that are involved can be difficult and time-consuming. Fortunately, simplifying assumptions can be invoked when the successive equilibrium constants for the acid (or base) differ by a factor of about 10^3 (or more).

The solution could be acidic because of



or basic because of



Whether a solution of NaHA is acidic or basic depends on the relative magnitude of the equilibrium constants for these processes:



$$K_{a2} = \frac{[\text{H}_3\text{O}^+][\text{A}^{2-}]}{[\text{HA}^-]} \quad \text{or} \quad K_{b2} = \frac{K_w}{K_{a1}} = \frac{[\text{H}_2\text{A}][\text{OH}^-]}{[\text{HA}^-]}$$

As we can see in the last equation, solution of it yields an approximate value of $[\text{H}_3\text{O}^+]$ that is given by the equation

$$[\text{H}_3\text{O}^+] = \sqrt{\frac{K_{a2}c_{\text{NaHA}} + K_w}{1 + c_{\text{NaHA}}/K_{a1}}}$$

Frequently, the ratio c_{NaHA}/K_{a1} is much larger than unity in the denominator of the previous Equation and $K_{a2}c_{\text{NaHA}}$ is considerably greater than K_w in the numerator. So, we reduce the previous Equation to get:

$$[\text{H}_3\text{O}^+] \cong \sqrt{K_{a1}K_{a2}} \quad (\S)$$

Example 5-5:

Calculate the hydronium ion concentration of a 0.100 M NaHCO_3 solution.

Solution:

We first examine the assumptions leading to Equation §. The dissociation constants for H_2CO_3 are $K_{a1} = 1.5 \times 10^{-4}$ and $K_{a2} = 4.69 \times 10^{-11}$. Clearly, c_{NaHA}/K_{a1} in the denominator is much larger than unity; in addition, $K_{a2}c_{\text{NaHA}}$ has a value of 4.69×10^{-12} , which is substantially greater than K_w . Thus,

$$[\text{H}_3\text{O}^+] = \sqrt{1.5 \times 10^{-4} \times 4.69 \times 10^{-11}} = 8.4 \times 10^{-8} \text{ M}$$

Titration Curve for Polyfunctional Bases

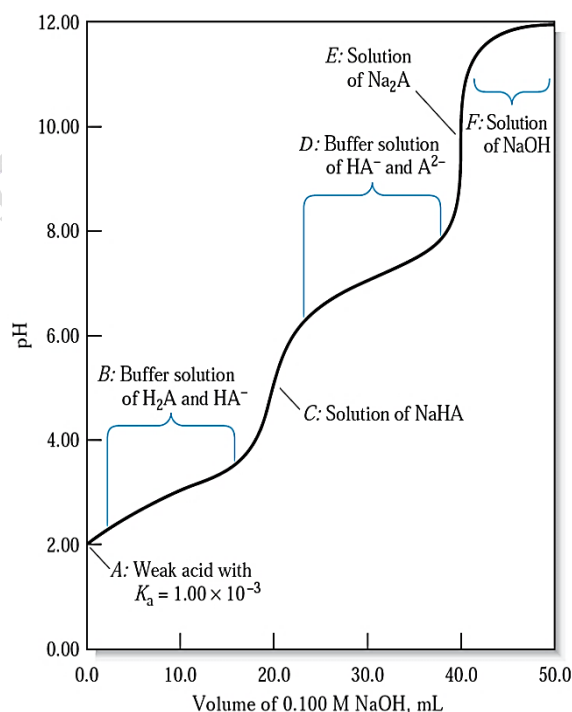


Figure 5-10 Titration of 20.00 mL of 0.1000 M H_2A with 0.1000 M NaOH . For H_2A , $K_{a1} = 1.00 \times 10^{-3}$ and $K_{a2} = 1.00 \times 10^{-7}$. The method of pH calculation is shown for several points and regions on the titration curve.

Problem: Calculate a pH & draw a titration curve of 50.00 mL 0.100 M Na_2CO_3 with 0.1000M HCl at: 0.00 mL, 10.00mL, 25.000mL, 40.00mL, 50.00mL, 75.00mL, 100.00mL, and 102.0mL.



6. OXIDATION/REDUCTION (REDOX) EQUILIBRIA

Characterizing Oxidation/Reduction Reactions

In oxidation/reduction (or redox) reactions, the key chemical event is the net movement of electrons from one reactant to the other. This movement of electrons occurs from the reactant (or atom in the reactant) with less attraction for electrons to the reactant (or atom) with more attraction for electrons.

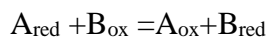
Such movement of electron charge occurs in the formation of both ionic and covalent compounds.

Oxidations are the loss of electrons, and reduction is the gain of electrons. The oxidizing agent is the species doing the oxidizing. Similarly, the reducing agent is the species doing the reducing.

Each atom in a molecule (or ionic compound) is assigned an oxidation number (O.N.), or oxidation state, the charge the atom would have if electrons were not shared but were transferred completely.

Comparing Oxidation/Reduction Reactions to Acid/Base Reactions

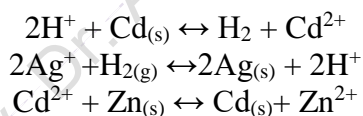
Oxidation/reduction reactions can be viewed in a way that is analogous to the Brønsted-Lowry concept of acid/base reactions. In both, one or more charged particles are transferred from a donor to an acceptor—the particles being electrons in oxidation/reduction and protons in neutralization. When an acid donates a proton, it becomes a conjugate base that is capable of accepting a proton. By analogy, when a reducing agent donates an electron, it becomes an oxidizing agent that can then accept an electron. This product could be called a conjugate oxidant, but that terminology is seldom, if ever, used. With this idea in mind, we can write a generalized equation for a redox reaction as



In this equation, B_{ox} , the oxidized form of species B, accepts electrons from A_{red} to form the new reductant, B_{red} . At the same time, reductant A_{red} having given up electrons, becomes an oxidizing agent, A_{ox} . If we know from chemical evidence that the equilibrium in Equation above lies to the right, we can state that B_{ox} is a better electron acceptor (stronger oxidant) than A_{ox} . Likewise, A_{red} is a more effective electron donor (better reductant) than B_{red} .

Example 6-1:

The following reactions are spontaneous and thus proceed to the right, as written:



What can we deduce regarding the strengths of H^+ , Ag^+ , Cd^{2+} , and Zn^{2+} as electron acceptors (or oxidizing agents)?

Solution

The second reaction establishes that Ag^+ is a more effective electron acceptor than H^+ ; the first reaction demonstrates that H^+ is more effective than Cd^{2+} . Finally, the third equation shows that Cd^{2+} is more effective than Zn^{2+} . Thus, the order of oxidizing strength is $\text{Ag}^+ > \text{H}^+ > \text{Cd}^{2+} > \text{Zn}^{2+}$.

Rules for Assigning an Oxidation Number (O.N.)

General Rules

1. For an atom in its elemental form (Na, O_2 , Cl_2 , etc.): O.N. = 0
2. For a monatomic ion: O.N. = ion charge
3. The sum of O.N. values for the atoms in a molecule or formula unit of a compound equals zero. The sum of O.N. values for the atoms in a polyatomic ion equals the ion's charge.

Rules for Specific Atoms or Periodic Table Groups

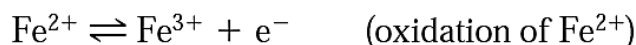
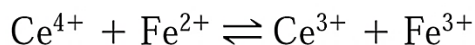
1. For Group 1A(1): O.N. = +1 in all compounds
2. For Group 2A(2): O.N. = +2 in all compounds
3. For hydrogen: O.N. = +1 in combination with nonmetals, O.N. = -1 in combination with metals and boron.
4. For fluorine: O.N. = -1 in all compounds
5. For oxygen: O.N. = -1 in peroxides, O.N. = -2 in all other compounds (except with F).
6. For Group 7A(17): O.N. = -1 in combination with metals, nonmetals (except O), and other halogens lower in the group.



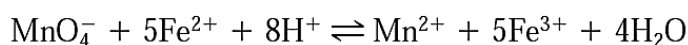
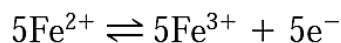
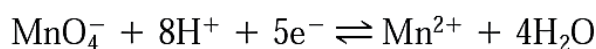
Balancing Redox Equations:

See General Chemistry (I).

An oxidation/reduction reaction.



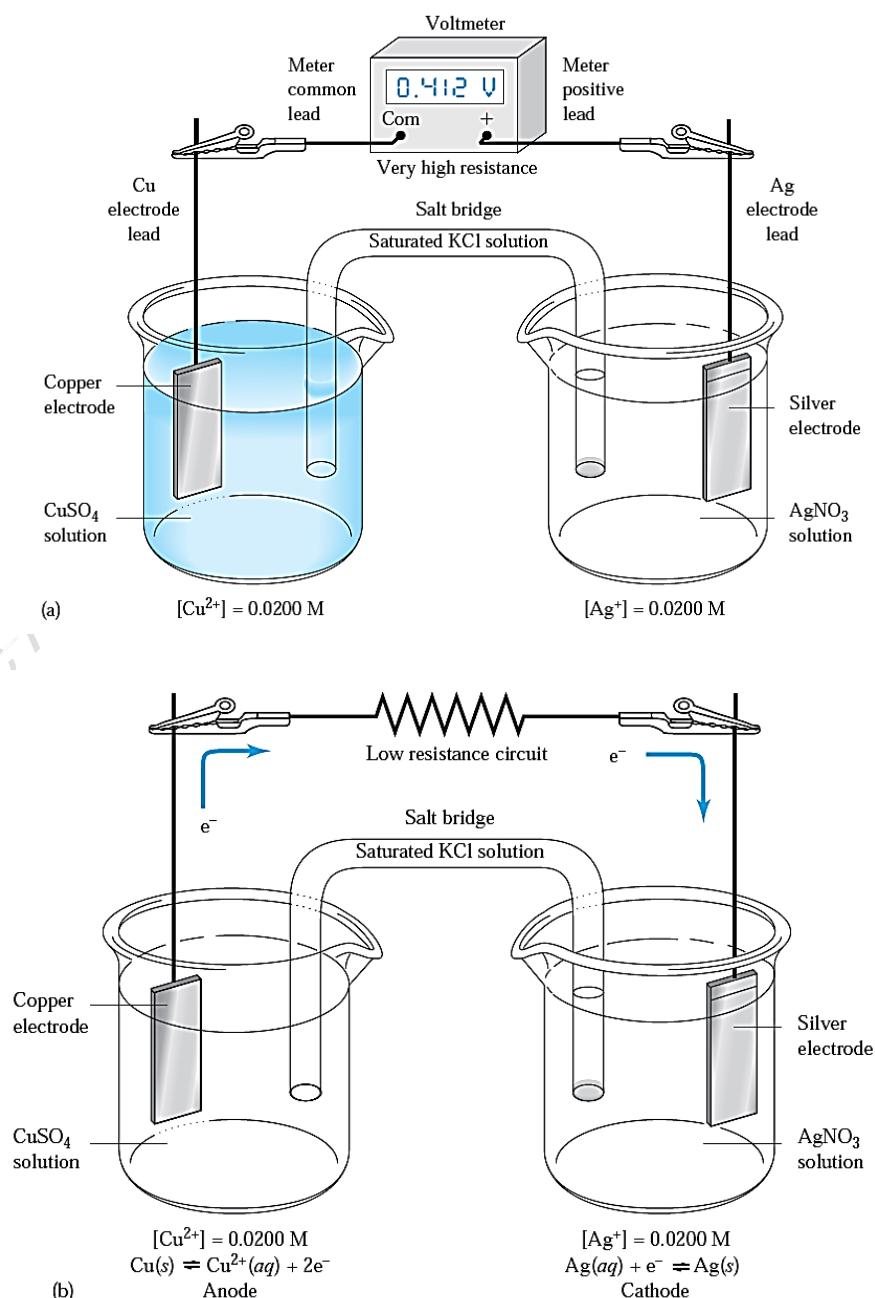
For the oxidation of Fe^{2+} by MnO_4^- the half-reactions are



Oxidation/Reduction Reactions in Electrochemical Cells

- in an *electrochemical cell* in which the oxidizing agent and the reducing agent are physically separated from one another. Figure 6-1 shows such an arrangement. Note that a *salt bridge* isolates the reactants but maintains electrical contact between the two halves of the cell.

- *cell potential*, is a measure of the tendency of the cell reaction to proceed toward equilibrium.



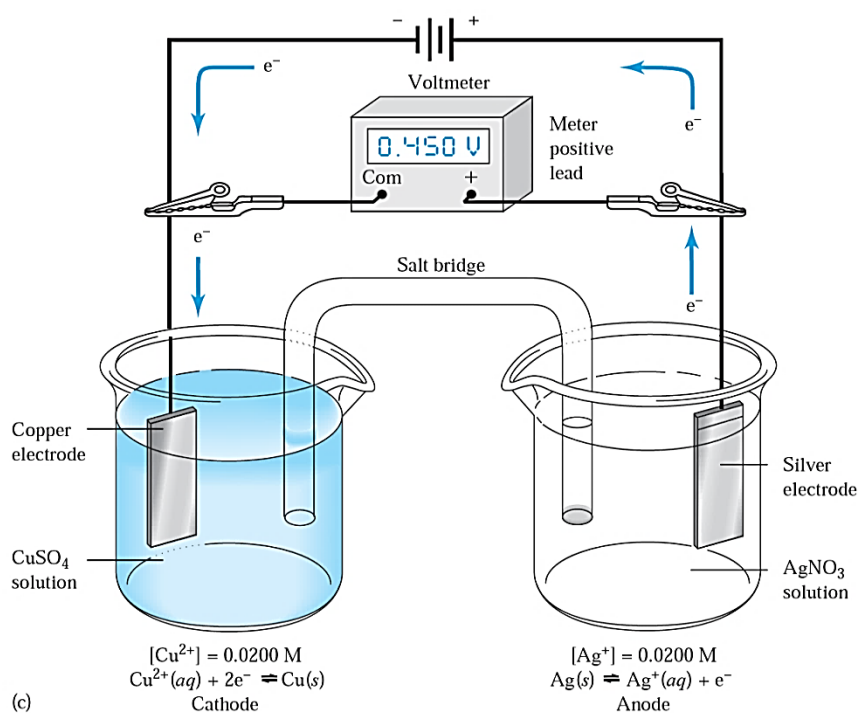


Figure 6-1. (a) A galvanic cell at an open circuit, (b) a galvanic cell doing work, and (c) an electrolytic cell

Describing Currents in Electrochemical Cells

In a galvanic cell, the movement of ions/electrons charges leads to generate a current as in scheme below

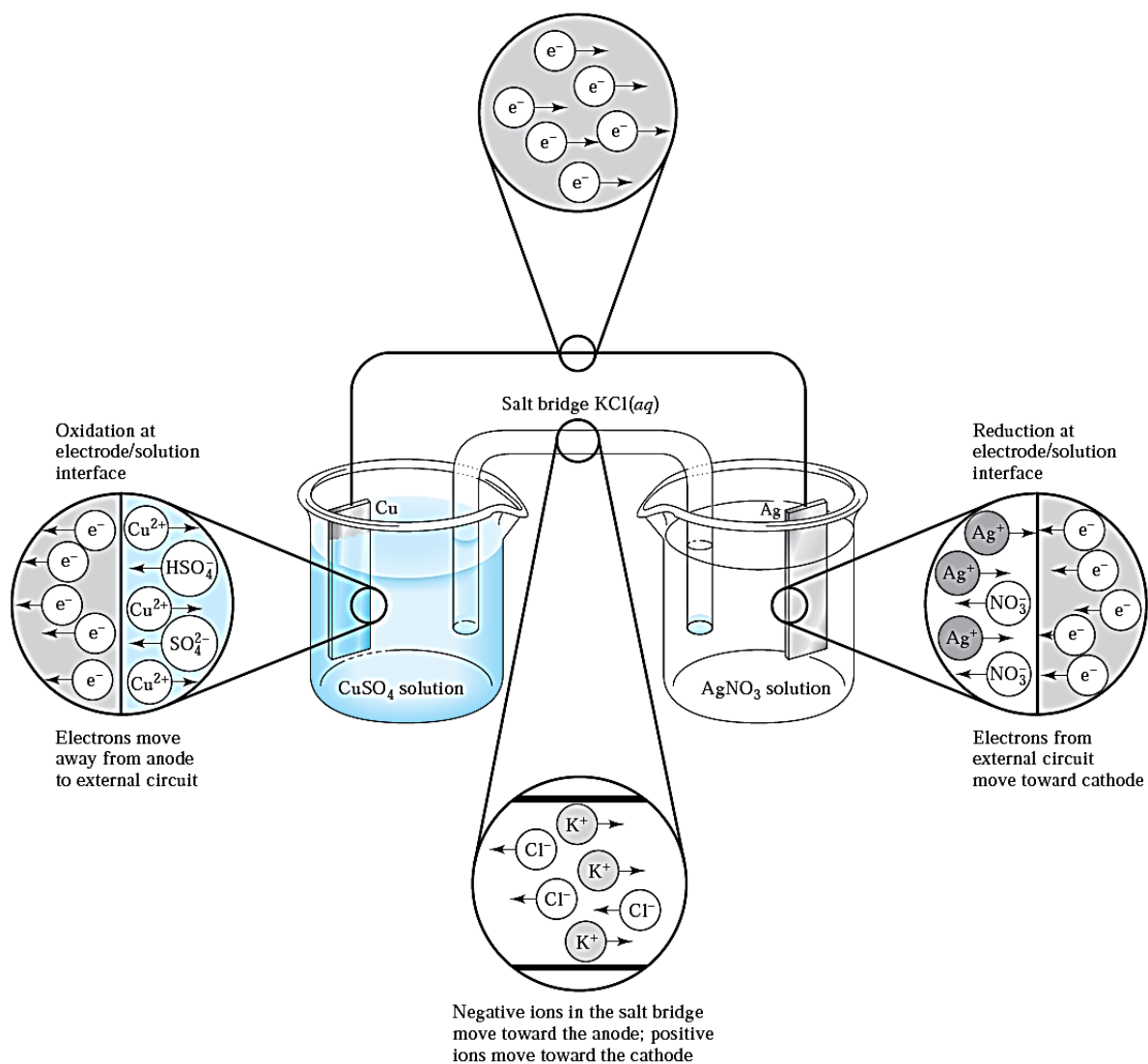


Figure 6-2. Movement of charge in a galvanic cell



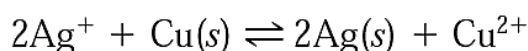
Cathodes and Anodes

A metal electrode type is a metal in contact with a solution containing the cation of the same metal for measuring the metal cation. An example is a silver metal electrode dipping in a solution of silver nitrate. The *cathode* in an electrochemical cell is the electrode at which a reduction reaction occurs. The *anode* is the electrode at which an oxidation takes place.

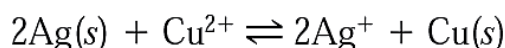
Two Types of Electrochemical Cells

1- Galvanic, or voltaic, cells store electrical energy.

Galvanic cells operate spontaneously,

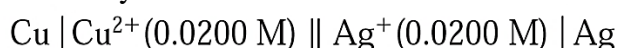


2- An *electrolytic cell* requires an external source of electrical energy for operation.



Representing Cells Schematically

The cell in Figure 6-1a is described by

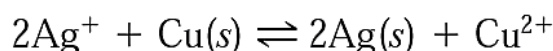


An alternative way of writing the cell shown in Figure 7-1a is



Electrode Potentials

The potential difference that develops between the electrodes of the cell in Figure 6-1a is a measure of the tendency for the reaction



The cell potential E_{cell} is related to the free energy of the reaction ΔG by

$$\Delta G = -nFE_{\text{cell}}$$

where n is the number of electrons transferred in the reaction

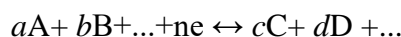
- The *standard cell potential*.

$$\Delta G^0 = -nFE_{\text{cell}}^0 = -RT \ln K_{\text{eq}}$$

where R is the gas constant, and T is the absolute temperature.

Effect of Concentration on Electrode Potentials: The Nernst Equation

Consider the reversible half-reaction



where the capital letters represent formulas for the participating species (atoms, molecules, or ions), e^- represents the electrons, and the lower case italic letters indicate the number of moles of each species appearing in the half-reaction as it has been written. The electrode potential for this process is given by the Nernst equation:

$$E = E^0 - \frac{RT}{nF} \ln \frac{[\text{C}]^c [\text{D}]^d \dots}{[\text{A}]^a [\text{B}]^b \dots}$$

where

E^0 = the standard electrode potential, which is characteristic for each half-reaction

R = the ideal gas constant, $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

T = the absolute temperature, K

n = number of moles of electrons that appears in the half-reaction for the electrode process as written

F = the faraday = $96,485 \text{ C (coulombs) per mole of electrons}$

\ln = natural logarithm = $2.303 \log$.

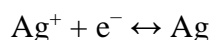


Although we cannot determine the absolute potentials of electrodes, we can readily determine relative electrode potentials.

For all electrode systems, an electrode half-reaction can be written from which the potential of the electrode is described. The electrode system can be represented by M/Mn^+ , in which the line represents an electrode–solution interface. For the silver electrode, we have



and the half-reaction is



The potential of the electrode is:

$$E = E_{Ag^+,Ag}^0 - \frac{2.303RT}{nF} \log \frac{1}{a_{Ag^+}}$$

where a_{Ag^+} represents the activity of the silver ion. The value of n here is 1. For simplification, we use concentration instead of activity in a diluted solution.

$$a_{Ag^+} = f[Ag^+]$$

f = activity coefficient ≈ 1 in a diluted solution.

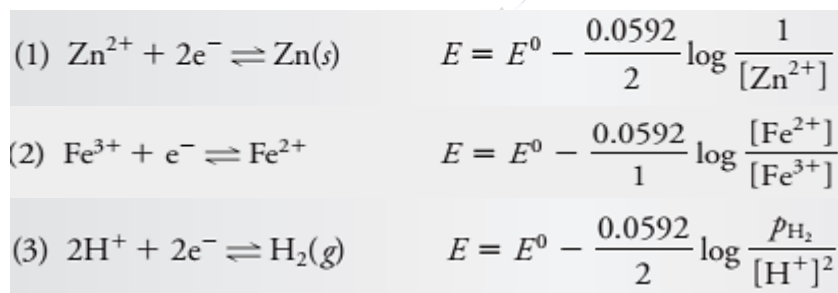
If we substitute numerical values for the constants, convert to base 10 logarithms, and specify 25°C for the temperature, we get

$$E = E^0 - \frac{0.0592}{n} \log \frac{[C]^c[D]^d \dots}{[A]^a[B]^b \dots}$$

Strictly speaking, the letters in brackets represent activities, but we will usually follow the practice of substituting molar concentrations for activities in most calculations.

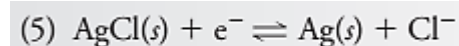
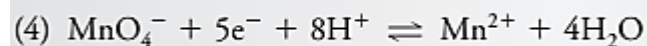
Thus, if some participating species A is a solute, [A] is the concentration of A in moles per liter. If A is a gas, [A] in the previous Equation is replaced by p_A , the partial pressure of A in atmospheres. If A is a pure liquid, a pure solid, or a solvent, its activity is unity, and no term for A is included in the equation.

Typical half-cell reactions and their corresponding Nernst expressions follow:



Problem:

Give the corresponding Nernst expressions for the half-cell reactions below:



The Standard Electrode Potential, E^0

When we look carefully at previous Equations, we see that the constant E^0 is the electrode potential whenever the concentration quotient (actually, the activity quotient) has a value of 1. This constant is by definition the standard electrode potential for the half-reaction. Note that the quotient is always equal to 1 when the activities of the reactants and products of a half-reaction are unity.

The standard electrode potential is an important physical constant that provides quantitative information regarding the driving force for a half-cell reaction. The important characteristics of these constants in accord with the IUPAC recommendations are the following:



1. The standard electrode potential is a relative quantity in the sense that it is the potential of an electrochemical cell in which the reference electrode (left-hand electrode) is the standard hydrogen electrode (SHE) (sometimes called normal hydrogen electrode-NHE), whose potential has been assigned a value of 0.000 V.
2. The standard electrode potential for a half-reaction refers exclusively to a reduction reaction, that is, it is a relative reduction potential.
3. The standard electrode potential measures the relative force tending to drive the half-reaction from a state in which the reactants and products are at unit activity to a state in which the reactants and products are at their equilibrium activities relative to the standard hydrogen electrode.
4. The standard electrode potential is independent of the number of moles of reactant and product shown in the balanced half-reaction. Thus, the standard electrode potential for the half-reaction

$$\text{Fe}^{3+} + e \leftrightarrow \text{Fe}^{2+} \quad E^0 = +0.771 \text{ V}$$
 does not change if we choose to write the reaction as

$$5\text{Fe}^{3+} + 5e \leftrightarrow 5\text{Fe}^{2+} \quad E^0 = +0.771 \text{ V}$$
5. A positive electrode potential indicates that the half-reaction is spontaneous with respect to the standard hydrogen electrode half-reaction. In other words, the oxidant in the half-reaction is a stronger oxidant than is hydrogen ion.
A negative sign indicates just the opposite.
6. The standard electrode potential for a half-reaction is temperature-dependent.

Standard electrode potential data are available for an enormous number of half-reactions. Many have been determined directly from electrochemical measurements. Others have been computed from equilibrium studies of oxidation/reduction systems and from thermochemical data associated with such reactions.

Table 6-1 contains some standard electrode potential data for selected half-reactions.

Standard Electrode Potentials*	
Reaction	E^0 at 25°C, V
$\text{Cl}_2(\text{g}) + 2e^- \rightleftharpoons 2\text{Cl}^-$	+1.359
$\text{O}_2(\text{g}) + 4\text{H}^+ + 4e^- \rightleftharpoons 2\text{H}_2\text{O}$	+1.229
$\text{Br}_2(\text{aq}) + 2e^- \rightleftharpoons 2\text{Br}^-$	+1.087
$\text{Br}_2(\text{l}) + 2e^- \rightleftharpoons 2\text{Br}^-$	+1.065
$\text{Ag}^+ + e^- \rightleftharpoons \text{Ag}(\text{s})$	+0.799
$\text{Fe}^{3+} + e^- \rightleftharpoons \text{Fe}^{2+}$	+0.771
$\text{I}_3^- + 2e^- \rightleftharpoons 3\text{I}^-$	+0.536
$\text{Cu}^{2+} + 2e^- \rightleftharpoons \text{Cu}(\text{s})$	+0.337
$\text{UO}_2^{2+} + 4\text{H}^+ + 2e^- \rightleftharpoons \text{U}^{4+} + 2\text{H}_2\text{O}$	+0.334
$\text{Hg}_2\text{Cl}_2(\text{s}) + 2e^- \rightleftharpoons 2\text{Hg}(\text{l}) + 2\text{Cl}^-$	+0.268
$\text{AgCl}(\text{s}) + e^- \rightleftharpoons \text{Ag}(\text{s}) + \text{Cl}^-$	+0.222
$\text{Ag}(\text{S}_2\text{O}_3)_2^{3-} + e^- \rightleftharpoons \text{Ag}(\text{s}) + 2\text{S}_2\text{O}_3^{2-}$	+0.017
$2\text{H}^+ + 2e^- \rightleftharpoons \text{H}_2(\text{g})$	0.000
$\text{AgI}(\text{s}) + e^- \rightleftharpoons \text{Ag}(\text{s}) + \text{I}^-$	-0.151
$\text{PbSO}_4 + 2e^- \rightleftharpoons \text{Pb}(\text{s}) + \text{SO}_4^{2-}$	-0.350
$\text{Cd}^{2+} + 2e^- \rightleftharpoons \text{Cd}(\text{s})$	-0.403
$\text{Zn}^{2+} + 2e^- \rightleftharpoons \text{Zn}(\text{s})$	-0.763

Compilations of electrode-potential data, such as that shown in Table 6-1, provide chemists with qualitative insights into the extent and direction of electron transfer reactions. For example, the standard potential for silver(I) (+0.799 V) is more positive than that for copper(II) (+0.337 V). We therefore conclude that a piece of copper immersed in a silver(I) solution will cause the reduction of that ion and the oxidation of the copper. On the other hand, we would expect no reaction if we place a piece of silver in a copper(II) solution.

Cell Potentials: Output of a Voltaic Cell

The purpose of a voltaic cell is to convert the free energy change of a spontaneous reaction into the kinetic energy of electrons moving through an external circuit (electrical energy). This electrical energy is proportional to the difference in electrical potential between the two electrodes, which is called the cell potential (E_{cell}), also the **voltage** of the cell or the **electromotive force (emf)**.

Electrons flow spontaneously from the negative to the positive electrode, that is, toward the electrode with the more positive electrical potential. Thus, when the cell operates spontaneously, there is a positive cell potential:

$$E_{\text{cell}} > 0 \text{ for a spontaneous process}$$



The more positive E_{cell} is, the more work the cell can do, and the farther the reaction proceeds to the right as written. A negative cell potential, on the other hand, is associated with a nonspontaneous cell reaction. If $E_{\text{cell}} = 0$, the reaction has reached equilibrium and the cell can do no more work.

How are the units of cell potential related to those of energy available to do work? As you've seen, work is done when charge moves between electrode compartments that differ in electrical potential. The SI unit of electrical potential is the **volt (V)**, and the SI unit of electrical charge is the **coulomb (C)**. By definition, for two electrodes that differ by 1 volt of electrical potential, 1 joule of energy is released (that is, 1 joule of work can be done) for each coulomb of charge that moves between the electrodes. Thus,

$$1 \text{ V} = 1 \text{ J/C}$$

Table 6-2 lists the voltages of some commercial and natural voltaic cells. Next, we'll see how to measure cell potential.

Table 6-2 Voltages of Some Voltaic Cells

Voltaic Cell	Voltage (V)
Lithium-ion laptop battery	3.7
Lead-acid car battery (6 cells = 12 V)	2.1
Common alkaline flashlight battery	1.5
Calculator battery (mercury)	1.3
Electric eel (~5000 cells in 6-ft eel = 750 V)	0.15
Nerve of giant squid (across cell membrane)	0.070

Standard Cell Potentials

The measured potential of a voltaic cell is affected by changes in concentration as the reaction proceeds and by energy losses due to the heating of the cell and the external circuit. Therefore, in order to compare the output of different cells, we obtain a standard cell potential (E°_{cell}), the potential measured at a specified temperature (usually $25^{\circ}\text{C} = 298 \text{ K}$) with no current flowing and all components in their standard states: 1 atm for gases, 1 M for solutions, the pure solid for electrodes.

When the zinc-copper cell begins operating under standard state conditions, that is, when $[\text{Zn}^{2+}] = [\text{Cu}^{2+}] = 1 \text{ M}$, the cell produces 1.10 V at 298 K (Figure 6-3).

Because electrons flow spontaneously toward the copper electrode (cathode), it must have a more positive E° half-cell than the zinc electrode (anode). Therefore, to obtain a positive E°_{cell} , we subtract E°_{zinc} from $E^{\circ}_{\text{copper}}$:

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{copper}} - E^{\circ}_{\text{zinc}}$$

We can generalize this result for any voltaic cell: the standard cell potential is the difference between the standard electrode potential of the cathode (reduction) half-cell and the standard electrode potential of the anode (oxidation) half-cell:

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode (reduction)}} - E^{\circ}_{\text{anode (oxidation)}}$$

For a spontaneous reaction at standard conditions, $E^{\circ}_{\text{cell}} > 0$.



Figure 6-3 Measurement of a standard cell potential. The zinc-copper cell, operating at 298 K under standard-state conditions, produces a voltage of **1.10 V**.



Cell Potential Sign Convention

In a cell measurement using the NHE as the second half-cell, the voltage is

$$E_{\text{measd.}} = E_{\text{cell}} = E_{\text{ind vs. NHE}} = E_{\text{ind}} - E_{\text{NHE}}$$

where E_{ind} is the potential of the indicator electrode (the one that responds to the test solution, Ag^+ ions in this case). Since E_{NHE} is zero,

$$E_{\text{cell}} = E_{\text{ind}}$$

corresponds to writing the cells as

reference electrode|salt bridge|analyte solution|indicator electrode

$$E_{\text{ref}} | \text{solution} | E_{\text{ind}}$$

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} = E_{\text{ind}} - E_{\text{ref}} = E_{\text{ind}} - \text{constant}$$

where E_{ref} is the potential of the reference electrode, whose potential is constant. Note that E_{cell} (or E_{ind}) may be positive or negative, depending on the concentration of the silver ion or the relative potentials of the two electrodes. This is in contrast to the convention for a voltaic cell, in which a cell was always set up to give a positive voltage and thereby indicate what the spontaneous cell reaction would be.

What Are Half-Cell Potentials?

-the half-reaction at the right-hand electrode (E_{right}), the other associated with the half-reaction at the left-hand electrode (E_{left}).

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} = E_{\text{cathode}} (\text{reduction}) - E_{\text{anode}} (\text{oxidation})$$

We can use standard cell potentials to find the equilibrium constant (K_{eq}) as follow:

$$\ln K_{\text{eq}} = -\frac{\Delta G^0}{RT} = \frac{nFE_{\text{cell}}^0}{RT}$$

and

$$\log K_{\text{eq}} = \frac{nE_{\text{cell}}^0}{0.0592} = \frac{n(E_{\text{right}}^0 - E_{\text{left}}^0)}{0.0592}$$

Problem

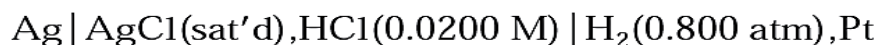
- Draw a diagram, (2) show balanced equations, and (3) write the notation, (4) Nernst equation and (5) K_{eq} for a voltaic cell that consists of one half-cell with a Cr bar in a $\text{Cr}(\text{NO}_3)_3$ solution, another half-cell with an Ag bar in an AgNO_3 solution, and a KNO_3 salt bridge. Measurement indicates that the Cr electrode is negative relative to the Ag electrode.

Clue: ($\text{Ag}^+ + \text{e}^- \leftrightarrow \text{Ag}_{(\text{s})} = +0.799 \text{ V}$ in 1 M HNO_3 & $\text{Cr}^{+3} + 3\text{e}^- \leftrightarrow \text{Cr}_{(\text{s})} = -0.744 \text{ V}$ in 1 M HNO_3).

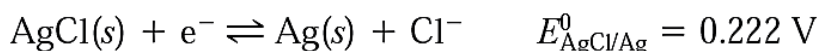


7. OXIDATION/REDUCTION (REDOX) TITRATIONS

Example 7-1: Calculate the cell potential for



Note that this cell does not require two compartments (nor a salt bridge) because molecular H_2 has little tendency to react directly with the low concentration of Ag in the electrolyte solution.



Solution:

$$E_{\text{right}} = 0.000 - \frac{0.0592}{2} \log \frac{P_{\text{H}_2}}{[\text{H}^+]^2} = \frac{0.0592}{2} \log \frac{0.800}{(0.0200)^3}$$

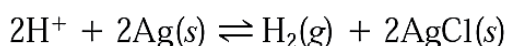
$$= -0.0977 \text{ V}$$

$$E_{\text{left}} = 0.222 - 0.0592 \log [\text{Cl}^-] = 0.222 - 0.0592 \log 0.0200$$

$$= 0.3226 \text{ V}$$

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} = -0.0977 - 0.3226 = -0.420 \text{ V}$$

The negative sign indicates that the cell reaction as considered,



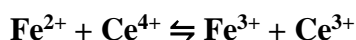
is nonspontaneous.

Redox Titration Curves

Oxidation/reduction chemistry can be used to determine the unknown concentrations of many analytes of interest via titration. As with acid-base titration, the objective is to identify the quantity of a standard solution needed to reach the equivalence point. In acid-base titrations, we think of titration curves in terms of **pH or pOH versus the concentration of standard**. In redox titrations we think of titration curves in terms of **cell potential versus the concentration of the standard**.

The equivalence point in a redox titration can be identified with a redox indicator or via an electrical measurement, such as the potential of the solution. With the Nernst equation, we can predict the shape of a redox titration curve...

We will use the following reaction to illustrate:



Note: the reagent is $\text{Ce}(\text{NO}_3)_4 \cdot 2\text{NH}_4\text{NO}_3$, a primary standard often used in redox titrations. Acidic solutions are used to avoid hydrolysis involving Ce(IV) to yield $\text{Ce}(\text{OH})_x^{4-x}$ species (which have different reduction potentials).



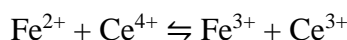
Why different E° for different acids and/or with different acids concentrations?

Ce^{4+} is actually present in solutions associated with the various anions, e.g. $\text{Ce}(\text{ClO}_4)^{3+}$, $\text{Ce}(\text{NO}_3)_2^{2+}$, $\text{Ce}(\text{SO}_4)^{2+}$, etc. Reduction potential depends upon solvation structure. Furthermore, these anions associate with Ce^{4+} more than Ce^{3+} . Differential degrees of the association are therefore anion and anion concentration dependent.

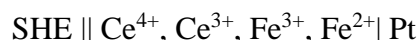




Reduction potentials for iron(III) vary with acid and acid concentration for the same reasons cerium (IV) does.



How might we write the **shorthand notation** for a hypothetical cell relevant to this reaction?



Note that we could actually make this cell by using a standard hydrogen electrode to serve as a reference and a platinum electrode to measure the solution potential relative to the SHE. In fact, this is one way to follow the progress of the titration (potentiometry). However, we do not need to use any electrodes to perform a redox titration provided we have an alternate means for identifying the equivalence point, such as a redox indicator.

Nernst equations for the reduction potentials:

For iron, the electrode potential will be

$$E_{\text{Fe}^{3+}/\text{Fe}^{2+}} = E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^{\circ} - \frac{0.0592}{n} \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]}, n = 1$$

$$E_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 0.68 - \frac{0.0592}{1} \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} \text{ in } 1\text{M } \text{H}_2\text{SO}_4$$

For cerium, the electrode potential will be

$$E_{\text{Ce}^{4+}/\text{Ce}^{3+}} = E_{\text{Ce}^{4+}/\text{Ce}^{3+}}^{\circ} - \frac{0.0592}{n} \log \frac{[\text{Ce}^{3+}]}{[\text{Ce}^{4+}]}, n = 1$$

$$E_{\text{Ce}^{4+}/\text{Ce}^{3+}} = 1.44 - \frac{0.0592}{1} \log \frac{[\text{Ce}^{3+}]}{[\text{Ce}^{4+}]} \text{ in } 1\text{M } \text{H}_2\text{SO}_4$$

Which electrode potential reflects the potential of the solution (i.e., the system)?

Both are equal to E_{system} if an equilibrium is established:

$$E_{\text{Fe}^{3+}/\text{Fe}^{2+}} = E_{\text{Ce}^{4+}/\text{Ce}^{3+}} = E_{\text{system}} = E_{\text{In}}$$

(Note that if a redox indicator is present, E_{In} will also assume the potential of the system. If it is present at a very low concentration, it will have a minimal effect on the value of E_{system}).

E_{system} can be determined by calculating either $E_{\text{Fe}^{3+}/\text{Fe}^{2+}}$ or $E_{\text{Ce}^{4+}/\text{Ce}^{3+}}$. It is more convenient to use one or the other, depending upon conditions.

Points in the redox titration:

- (1) Initial Point (Before titration).
- (2) Prior to the equivalence point.
- (3) At the equivalence point.
- (4) After the equivalence point.

Example 7-2:

Do the calculations needed to generate the hypothetical titration curve (Figure 7-1) for the titration of 50.00 mL solution of 0.100 M Fe^{2+} with 0.100 M Ce^{4+} in 1 M H_2SO_4 .

Solution:

(1) Before titration: no Ce^{4+} added, very little Fe^{3+} present and its concentration is likely to be unknown:

$$E_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 0.68 - \frac{0.0592}{1} \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]}$$

$$E_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 0.68 - \frac{0.0592}{1} \log \frac{0.100 \text{ M}}{??}, \text{insufficient info}$$

If we know $[\text{Fe}^{3+}]$, say it's 10^{-8}M , we can determine E_{system} :



$$E_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 0.68 - \frac{0.0592}{1} \log \frac{0.100 \text{ M}}{10^{-8} \text{ M}} = 0.27 \text{ V}$$

(2) Prior to the equivalence point: When Ce^{4+} is added, it is essentially completely consumed by reaction with Fe^{2+} and its' concentration is not accurately known. Therefore, it is more convenient to calculate E_{system} via the $\text{Fe}^{2+}/\text{Fe}^{3+}$ couple:

1% reaction – addition of 0.5 mL, 0.100 M Ce^{4+} solution

$$[\text{Fe}^{2+}] = (5 \times 10^{-3} \text{ mole} - 5 \times 10^{-5} \text{ mole}) / 50.5 \text{ mL} = 9.8 \times 10^{-2} \text{ M}$$

$$[\text{Fe}^{3+}] = 5 \times 10^{-5} \text{ mole} / 50.5 \text{ mL} = 9.9 \times 10^{-4} \text{ M}$$

$$E_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 0.68 - \frac{0.0592}{1} \log \frac{9.8 \times 10^{-2} \text{ M}}{9.9 \times 10^{-4} \text{ M}} = 0.56 \text{ V}$$

10% reaction – addition of 5.0 mL, 0.100 M Ce^{4+} :

$$[\text{Fe}^{2+}] = (4.5 \times 10^{-3} \text{ mole}) / 55.0 \text{ mL} = 8.2 \times 10^{-2} \text{ M}$$

$$[\text{Fe}^{3+}] = (5 \times 10^{-4} \text{ mole}) / 55.0 \text{ mL} = 9.1 \times 10^{-3} \text{ M}$$

$$E_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 0.68 - \frac{0.0592}{1} \log \frac{8.2 \times 10^{-2} \text{ M}}{9.1 \times 10^{-3} \text{ M}} = 0.62 \text{ V}$$

50% reaction – addition of 25.0 mL of 0.100 M Ce^{4+} :

$$[\text{Fe}^{2+}] = (2.5 \times 10^{-3} \text{ mole}) / 75.0 \text{ mL} = 3.3 \times 10^{-3} \text{ M}$$

$$[\text{Fe}^{3+}] = (2.5 \times 10^{-3} \text{ mole}) / 75.0 \text{ mL} = 3.3 \times 10^{-3} \text{ M}$$

$$E_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 0.68 - \frac{0.0592}{1} \log \frac{3.3 \times 10^{-3} \text{ M}}{3.3 \times 10^{-3} \text{ M}} = 0.68 \text{ V}$$

90% reaction – addition of 45.0 mL of 0.100 M Ce^{4+} :

$$[\text{Fe}^{2+}] = (5 \times 10^{-4} \text{ mole}) / 95.0 \text{ mL} = 5.26 \times 10^{-3} \text{ M}$$

$$[\text{Fe}^{3+}] = (4.5 \times 10^{-3} \text{ mole}) / 95.0 \text{ mL} = 4.7 \times 10^{-2} \text{ M}$$

$$E_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 0.68 - \frac{0.0592}{1} \log \frac{5.26 \times 10^{-3} \text{ M}}{4.7 \times 10^{-2} \text{ M}} = 0.74 \text{ V}$$

at 99%, 0.798 V

at 99.9%, 0.857 V

(3) At the equivalence point:

At the equivalence point, $[\text{Ce}^{3+}] = [\text{Fe}^{3+}]$ and $[\text{Ce}^{4+}] = [\text{Fe}^{2+}]$

$$E_{\text{system}} = E_{\text{Fe}} = E_{\text{Ce}}$$

Add the two Nernst equations (after multiplying by n):

$$\begin{aligned} nE_{\text{Ce}^{4+}/\text{Ce}^{3+}} &= nE_{\text{Ce}^{4+}/\text{Ce}^{3+}}^{\circ} - 0.0592 \log \frac{[\text{Ce}^{3+}]}{[\text{Ce}^{4+}]} \\ nE_{\text{Fe}^{3+}/\text{Fe}^{2+}} &= nE_{\text{Fe}^{3+}/\text{Fe}^{2+}}^{\circ} - 0.0592 \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} \end{aligned}$$

$$(n_{\text{Ce}^{4+}/\text{Ce}^{3+}} + n_{\text{Fe}^{3+}/\text{Fe}^{2+}})E_{\text{system}} = nE_{\text{Ce}^{4+}/\text{Ce}^{3+}}^{\circ} + nE_{\text{Fe}^{3+}/\text{Fe}^{2+}}^{\circ} - 0.0592 \log \frac{[\text{Ce}^{3+}][\text{Fe}^{2+}]}{[\text{Ce}^{4+}][\text{Fe}^{3+}]}$$

at the equivalence point,

$$[\text{Fe}^{3+}] = [\text{Ce}^{3+}]$$

$$[\text{Fe}^{2+}] = [\text{Ce}^{4+}]$$

$$\log \frac{[\text{Ce}^{3+}][\text{Fe}^{2+}]}{[\text{Ce}^{4+}][\text{Fe}^{3+}]} = \log 1 = 0$$

Hence,



$$E_{system} = \frac{nE^{\circ}_{Ce^{4+}/Ce^{3+}} + nE^{\circ}_{Fe^{3+}/Fe^{2+}}}{(n_{Ce^{4+}/Ce^{3+}} + n_{Fe^{3+}/Fe^{2+}})} = \frac{1 \times 1.44 + 1 \times 0.68}{1 + 1} = 1.06 V$$

(4) After the equivalence point: Beyond the equivalence point, Fe^{2+} has been essentially completely converted to Fe^{3+} . Additional Ce^{4+} has no Fe^{2+} with which to react, hence it is straightforward to calculate E_{system} from the concentrations of Ce^{3+} and Ce^{4+} . It is much more difficult to attempt to do so with the Fe^{2+}/Fe^{3+} couple because of the very low and unknown concentration of Fe^{2+} :

1% beyond equivalence point:

5×10^{-3} mole Ce^{3+} , 5×10^{-5} mole Ce^{4+}

$$E_{Ce^{4+}/Ce^{3+}} = 1.44 - \frac{0.0592}{n} \log \frac{[Ce^{3+}]}{[Ce^{4+}]}$$

$$E_{Ce^{4+}/Ce^{3+}} = 1.44 - \frac{0.0592}{1} \log \frac{5 \times 10^{-3} M}{5 \times 10^{-5} M}$$

$$E_{Ce^{4+}/Ce^{3+}} = 1.44 - \frac{0.0592}{1} \log \frac{100}{1} = 1.322 V$$

10% beyond equivalence point:

$$E_{Ce^{4+}/Ce^{3+}} = 1.44 - \frac{0.0592}{1} \log \frac{10}{1} = 1.381 V$$

100% beyond equivalence point:

$$E_{Ce^{4+}/Ce^{3+}} = 1.44 - \frac{0.0592}{1} \log \frac{1}{1} = 1.44 V$$

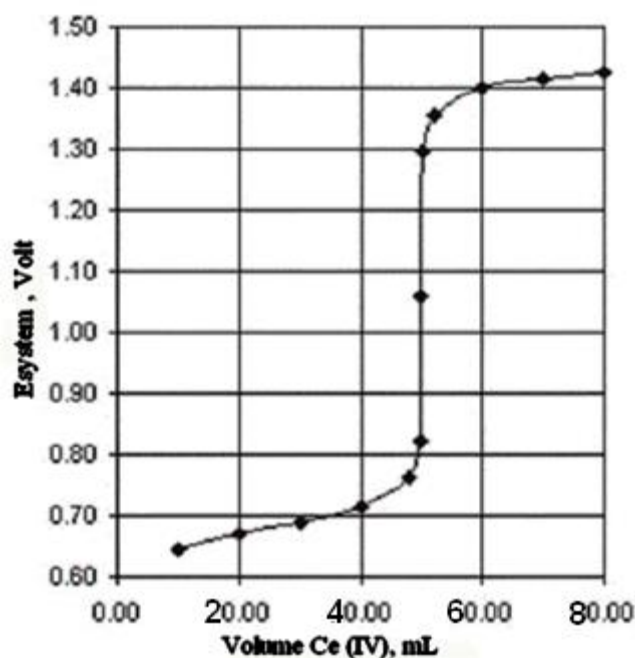
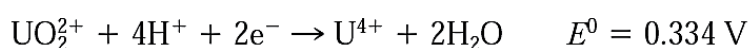
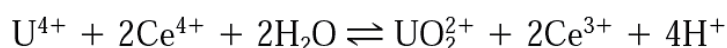


Figure 7-1. Titration curves for 50.00 mL solution of 0.100 M Fe^{2+} with 0.100 M Ce^{4+} .

Example 7-3:

Obtain an expression for the equivalence-point potential in the titration of 50 mL of 0.02500 M U^{4+} with 0.1000 M Ce^{4+} . Assume that both solutions are 1.0 M in H_2SO_4 .

Solution:





$$E_{\text{eq}} = E_{\text{UO}_2^{2+}/\text{U}^{4+}}^0 - \frac{0.0592}{2} \log \frac{[\text{U}^{4+}]}{[\text{UO}_2^{2+}][\text{H}^+]^4}$$

$$E_{\text{eq}} = E_{\text{Ce}^{4+}/\text{Ce}^{3+}}^{0'} - \frac{0.0592}{1} \log \frac{[\text{Ce}^{3+}]}{[\text{Ce}^{4+}]}$$

To combine the log terms, we must multiply the first equation by 2 to give

$$2E_{\text{eq}} = 2E_{\text{UO}_2^{2+}/\text{U}^{4+}}^0 - 0.0592 \log \frac{[\text{U}^{4+}]}{[\text{UO}_2^{2+}][\text{H}^+]^4}$$

At equivalence

$$[\text{U}^{4+}] = \frac{[\text{Ce}^{4+}]}{2}$$

$$[\text{UO}_2^{2+}] = \frac{[\text{Ce}^{3+}]}{2}$$

$$\begin{aligned} E_{\text{eq}} &= \frac{2E_{\text{UO}_2^{2+}/\text{U}^{4+}}^0 + E_{\text{Ce}^{4+}/\text{Ce}^{3+}}^{0'}}{3} - \frac{0.0592}{3} \log \frac{2[\text{Ce}^{4+}][\text{Ce}^{3+}]}{2[\text{Ce}^{3+}][\text{Ce}^{4+}][\text{H}^+]^4} \\ &= \frac{2E_{\text{UO}_2^{2+}/\text{U}^{4+}}^0 + E_{\text{Ce}^{4+}/\text{Ce}^{3+}}^{0'}}{3} - \frac{0.0592}{3} \log \frac{1}{[\text{H}^+]^4} \end{aligned}$$

The equivalence-point potential for this titration is pH-dependent.

Let us first consider the titration of 50.00 mL of 0.0500 M Fe^{2+} with 0.1000 M Ce^{4+} in a medium that is 1.0 M in H_2SO_4 at all times.

We can solve this titration as the previous example (example 7-2 except $[\text{Fe}^{2+}] = 0.0500$ M not 0.100 M). Finding titration for those two reactions can be represented as below (Figure 7-2):

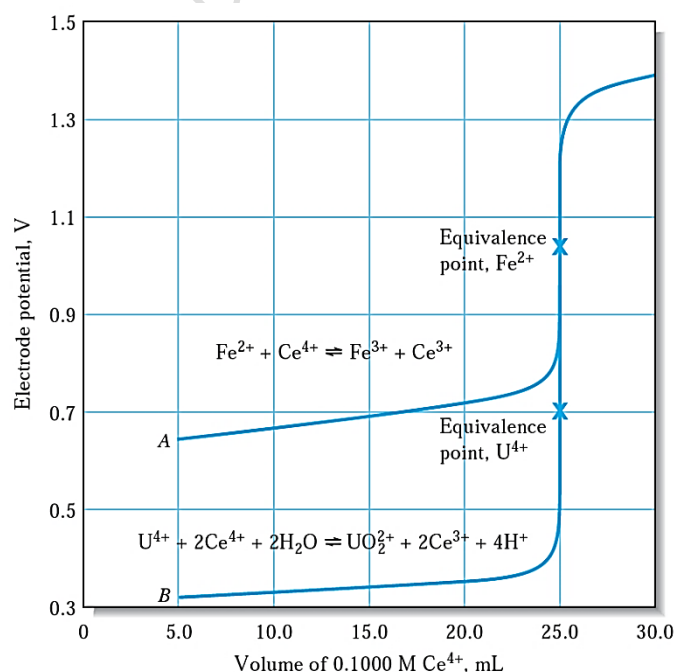


Figure 7-2 Titration curves for 0.1000 M Ce^{4+} titration. A: Titration of 50.00 mL of 0.05000 M Fe^{2+} . B: Titration of 50.00 mL of 0.02500 M U^{4+} .

Effect of Variables on Redox Titration Curves

1- Reactant Concentration

Titration curves for oxidation/reduction reactions are usually independent of analyte and reagent concentrations.

2- Completeness of the Reaction



The change in the equivalence-point region of an oxidation/reduction titration becomes larger as the reaction becomes more complete.

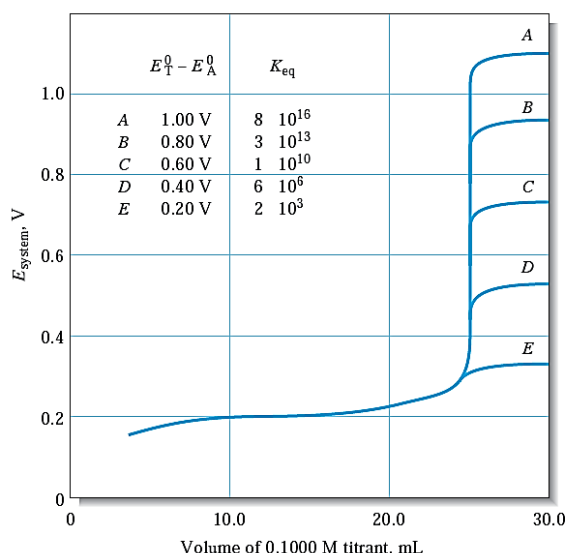
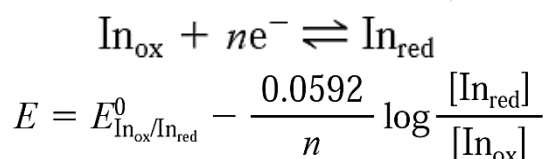


Figure 7-3. Effect of titrant electrode potential on reaction completeness. The standard electrode potential for the analyte is 0.200 V; starting with curve A, standard electrode potentials for the titrant are 1.20, 1.00, 0.80, 0.60, and 0.40, respectively. Both analyte and titrant undergo a one-electron change.

General Redox Indicators

General oxidation/reduction indicators are substances that change color upon being oxidized or reduced.



A color change is seen when

$$\frac{[\text{In}_{\text{red}}]}{[\text{In}_{\text{ox}}]} \approx \frac{1}{10}$$

changes to

$$\frac{[\text{In}_{\text{red}}]}{[\text{In}_{\text{ox}}]} \approx 10$$

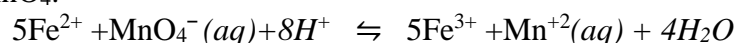
The potential change required to produce the full-color change of a typical general indicator

$$E = E_{\text{In}}^0 \pm \frac{0.0592}{n}$$

If the titrant is highly colored, this color may be used to detect endpoint (self indicator).

0.02 M potassium permanganate is deep purple. A dilute solution is pink. The product of its reduced form (Mn^{2+}) is colorless.

The unknown sample of iron contains, iron in Fe^{2+} oxidation state. So we are basically doing a redox titration of Fe^{2+} vs. KMnO_4 .



At equivalence point:

$$\text{Moles of } \text{Fe}^{2+} = 5 \times [\text{moles of } \text{MnO}_4^-]$$

a typical general indicator exhibits a detectable color change when a titrant causes the system potential to shift from $E_{\text{In}}^0 + 0.0592/n$ to $E_{\text{In}}^0 - 0.0592/n$ or about $(0.118/n)$ V.

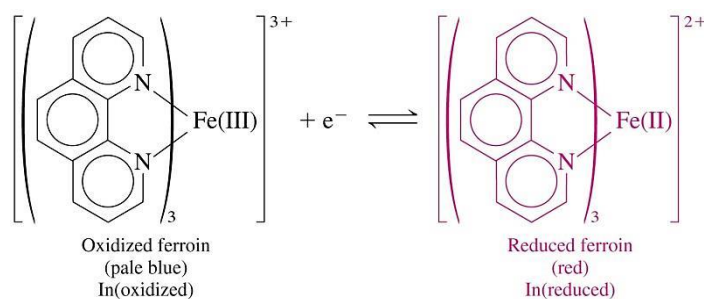
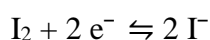


Figure 7-4. Ferrion indicator change color according to redox reaction

Titrimetric Involving Iodine

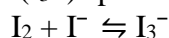
One of the most common redox titrations involves either using iodine (I_2) as a mild oxidizing agent or iodide (I^-) as a mild reducing agent.

Iodine as an oxidizing agent:



When iodine is used as the titrant the method is known as **iodimetry**.

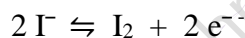
I_2 is not very soluble in water (only about 1.3×10^{-3} mol/L). Its solubility is increased in the presence of excess iodide by the formation of the triiodide (I_3^-) species,



So it is really the triiodide species, though it will commonly be referred to as iodine that is involved in the chemical reactions.

Due to the difficulty in maintaining the concentration of I_2 , (limited solubility in water, appreciable vapor pressure of the I_2 .) iodometric methods are more commonly used. The amount of I_2 produced by the action of the oxidizing analyte on excess iodide is usually titrated with standardized sodium thiosulfate, $Na_2S_2O_3$.

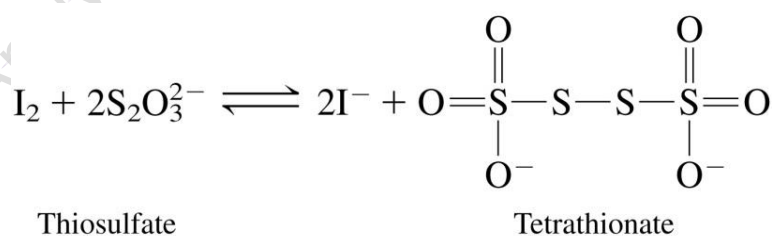
Iodide as a reducing agent:



When iodine is produced by the addition of an oxidizing analyte to an excess of iodide, the method is as **iodometry**.

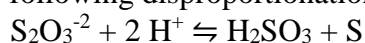
Thiosulfate ($S_2O_3^{2-}$) is commonly used in titration reactions involving iodine, both for iodimetric and iodometric methods. The iodimetric methods generally involve an excess of standard I_2 (as I_3^-) followed by back titration with standard thiosulfate.

In the iodometric methods, an excess of iodide is added to the sample of an oxidizing analyte and a stoichiometric amount of iodine (I_2 or I_3^-) is produced. This iodine is titrated with a standard solution of thiosulfate. This reaction is shown next.



The reaction with iodine needs to occur in a solution whose $pH < 9$ to prevent side reactions which produce iodates (IO_3^-). Generally acetic acid is added to the analyte mixture before titration to assure the proper pH . In some cases, appropriate pH buffers may also be added.

The titrant solution of thiosulfate cannot be prepared directly. It is made to an approximate concentration and then standardized with a primary standard oxidizing agent by iodometry. The thiosulfate solution is unstable if the $pH < 5$, undergoing the following disproportionation reaction.



This disproportionation reaction is prevented by using freshly boiled deionized water as the solvent and adding a small amount of $NaOH$. Although the thiosulfate needs to be stored in a basic solution, as mentioned earlier, its reaction as a reductant titrant needs to occur in an acid solution.

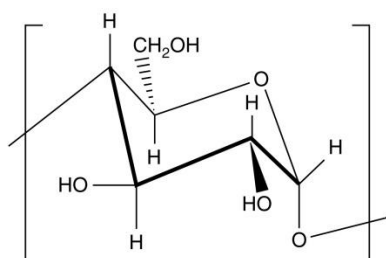


Iodine Methods

The indicator for both iodimetric and iodometric titrations is a starch solution; in the presence of iodine, it shows a blue or purple color. The starch indicator should not be added when I_2 is in large excess because the desorption of I_2 from the starch molecule is not reversible.

Starch/Iodine Solutions

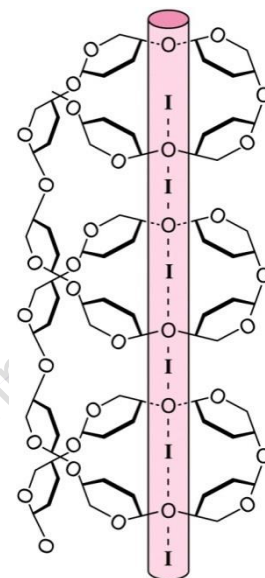
A starch solution containing a little triiodide or iodide ion can also function as a true redox indicator. The best-known specific indicator is starch, which forms a dark blue complex with triiodide ion as discussed above. This complex signals the endpoint in titrations in which iodine is either produced or consumed.



The repeating *amylose* unit in the starch molecule. Starch is amylose.

a polymer of

The starch-iodine complex where the sugar chain forms a helix about I_6 units.



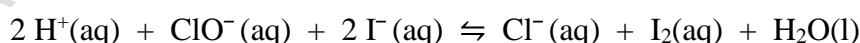
Iodimetric titrations: Titrations with standard iodine (actually I_3^-)

Many commercial products, such as bleaches and hair coloring agents, contain oxidizing agents. The most common oxidizing agent in bleaches is sodium hypochlorite, $NaClO$ (sometimes written $NaOCl$). Commercial bleaches are made by bubbling chlorine gas into a sodium hydroxide solution. Some of the chlorine is oxidized to the hypochlorite ion, ClO^- , and some is reduced to the chloride ion, Cl^- . The solution remains strongly basic. The chemical equation for the process is:

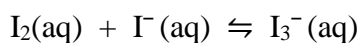


The amount of hypochlorite ion present in a solution of bleach can be determined by an oxidation-reduction titration. One of the best methods is the iodine-thiosulfate titration procedure. The iodide ion, I^- , is easily oxidized by almost any oxidizing agent. In acid solution, hypochlorite ions oxidize iodide ions to form iodine, I_2 . The iodine that forms is then titrated with a standard solution of sodium thiosulfate. The analysis takes place in a series of steps:

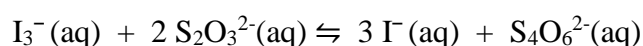
- Acidified iodide ion is added to hypochlorite ion solution and the iodide is oxidized to iodine.



- Iodine is only slightly soluble in water, but it dissolves very well in an aqueous solution of iodide ions, in which it forms a complex ion called the triiodide ion. Triiodide is a combination of a neutral I_2 molecule with an I^- ion. The triiodide ion is yellow in dilute solution and dark red-brown when concentrated.



- The triiodide is titrated with a standard solution of thiosulfate ions, which reduces the iodine back to iodide ions.



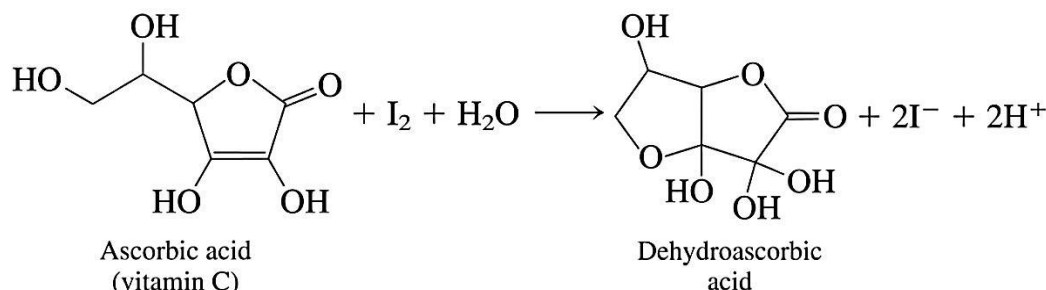
During this last reaction, the red-brown color of the triiodide ion fades to yellow and then to the clear color of the iodide ion. It is possible to use the disappearance of the color of the triiodide ion as the method of determining the endpoint, but this is not a very sensitive procedure. The addition of starch to a solution that contains iodine or triiodide ion forms a reversible blue complex. The disappearance of this blue-colored complex is a much more sensitive method of determining the endpoint. However, if the starch is added to a solution which contains a great deal of iodine, the complex which forms may not be reversible.



Therefore, the starch is not added until shortly before the endpoint is reached. The quantity of thiosulfate used in step 3 is directly related to the amount of hypochlorite initially present

Species analyzed	Oxidation reaction
SO_2	$\text{SO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{SO}_3$ $\text{H}_2\text{SO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{SO}_2^{4-} + 4\text{H}^+ + 2\text{e}^-$
H_2S	$\text{H}_2\text{S} \rightleftharpoons \text{S}(\text{s}) + 2\text{H}^+ + 2\text{e}^-$
$\text{Zn}^{2+}, \text{Cd}^{2+},$ $\text{Hg}^{2+}, \text{Pb}^{2+}$	$\text{M}^{2+} + \text{H}_2\text{S} \rightarrow \text{MS}(\text{s}) + 2\text{H}^+$ $\text{MS}(\text{s}) \rightleftharpoons \text{M}^{2+} + \text{S} + 2\text{e}^-$

Ascorbic acid (or vitamin C)



Potentiometric End Points

Endpoints for many oxidation/reduction titrations are readily observed by making the solution of the analyte part of the cell:



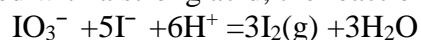
Auxiliary Oxidizing and Reducing Reagents

The analyte in an oxidation /reduction titration must be in a single oxidation state at the outset. When an iron-containing sample is dissolved usually contains a mixture of iron(II) and iron(III) ions. We must first treat the sample solution with an auxiliary reducing agent to convert all the iron to iron(II). To be useful as a preoxidant or a prereductant, a reagent must react quantitatively with the analyte. In addition, any reagent excess must be readily removable because the excess reagent usually interferes by reacting with the standard solution.

A number of metals are good reducing agents and have been used for the prerduction of analytes. Included among these are zinc, aluminum, cadmium, lead, nickel, copper, and silver.

Standardizing Thiosulfate Solutions

Potassium iodate is an excellent primary standard for thiosulfate solutions. In this application, weighed amounts of primary-standard-grade reagent are dissolved in water containing an excess of potassium iodide. When this mixture is acidified with a strong acid, the reaction



occurs instantaneously. The liberated iodine is then titrated with the thiosulfate solution. The stoichiometry of the reactions is



Example 7-4:

A solution of sodium thiosulfate was standardized by dissolving 0.1210 g KIO_3 (214.00 g/mol) in water, adding a large excess of KI, and acidifying with HCl.

The liberated iodine required 41.64 mL of the thiosulfate solution to decolorize the blue starch/iodine complex. Calculate the molar concentration of the $\text{Na}_2\text{S}_2\text{O}_3$.



Solution:

$$\begin{aligned}\text{amount Na}_2\text{S}_2\text{O}_3 &= 0.1210 \text{ g KIO}_3 \times \frac{1 \text{ mmol KIO}_3}{0.21400 \text{ g KIO}_3} \times \frac{6 \text{ mmol Na}_2\text{S}_2\text{O}_3}{\text{mmol KIO}_3} \\ &= 3.3925 \text{ mmol Na}_2\text{S}_2\text{O}_3 \\ c_{\text{Na}_2\text{S}_2\text{O}_3} &= \frac{3.3925 \text{ mmol Na}_2\text{S}_2\text{O}_3}{41.64 \text{ mL Na}_2\text{S}_2\text{O}_3} = 0.08147 \text{ M}\end{aligned}$$

Problem: Calculate the potential at 298 K as a function of titrant volume in the titration of 100 mL of 0.100M Fe^{2+} in 0.500M H_2SO_4 with: (1) 0.00, (2) 10.0, (3) 50.0, (4) 100, and (5) 200 mL of 0.0200M MnO_4^- . What is K_{eq} for this reaction?



8. PRECIPITATION EQUILIBRIA (SOLUBILITY) & TITRATIONS

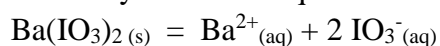
Precipitation Equilibria

Solubility equilibrium is a type of dynamic equilibrium. It exists when a chemical compound in the solid state is in chemical equilibrium with a solution of that compound. The solid may dissolve unchanged, with dissociation, or with a chemical reaction with another constituent of the solvent, such as acid or alkali. Each type of equilibrium is characterized by a temperature-dependent equilibrium constant. Solubility equilibria are important in pharmaceutical, environmental, and many other scenarios.

Solubility is defined as moles/L, g/L, or mg/L of the dissolving species in solution.

Precipitation (Insoluble Salts)

- Many metal ions form compounds that are insoluble in water.
- We call them insoluble or slightly soluble salts or precipitates.
- Common precipitates are carbonates, hydroxides, sulfates, and sulfides.
- An insoluble salt in contact with water maintains an equilibrium with the ions. In simple cases where there are no common ions or competing equilibria, the ion concentrations depend only on the equilibrium constant for the particular precipitate. When we talk about solubility equilibria we always write the equilibrium with the solid on the left. For example:



- The equilibrium constant expression for an insoluble salt is written following the same rules as for any other equilibrium.
- The equilibrium constant is called the solubility product, K_{sp} . The K_{sp} expression for the above equilibrium is:

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

Example 8-1: How is the solubility of lead chloride, PbCl_2 , related to the solution concentrations of Pb^{2+} and Cl^{-} ?

Solution:

Each formula unit of PbCl_2 that dissolves produces one lead ion, Pb^{2+} , and two chloride ions, Cl^{-} .

The molar solubility of PbCl_2 is equivalent to the concentration of Pb^{2+} , $S_{\text{PbCl}_2} = [\text{Pb}^{2+}]$.

Since two Cl^{-} s are produced per PbCl_2 formula unit that dissolves, the molar solubility of PbCl_2 equals one-half the solution concentration of Cl^{-} ,

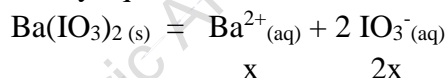
$$S_{\text{PbCl}_2} = 0.5[\text{Cl}^{-}].$$

$$S_{\text{PbCl}_2} = [\text{Pb}^{2+}] = 0.5[\text{Cl}^{-}].$$

Example 8-2: What is the solubility of barium iodate, $\text{Ba}(\text{IO}_3)_2$, in pure water at 25 °C?

Solution:

The solubility equilibrium is:



$$K_{\text{sp}} = [\text{Ba}^{2+}][\text{IO}_3^{-}]^2 = 1.5 \times 10^{-9}$$

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

$$K_{\text{sp}} = (x)(2x)^2 = 1.5 \times 10^{-9}$$

$$4[x]^3 = 1.5 \times 10^{-9} \quad *[\text{Ba}^{2+}]^3$$

$$x^3 = [\text{Ba}^{2+}]^3 = 3.75 \times 10^{-10} \text{ M}$$

$$X = S \text{ (solubility)} = [\text{Ba}^{2+}] = 7.2 \times 10^{-4} \text{ M}$$

$$\text{Or in mass terms: } S = (7.2 \times 10^{-4} \text{ M})(487 \text{ g/mol}) = 0.35 \text{ g/L}$$

Precipitation titrimetry, which is one of the oldest analytical techniques, is based on reactions that yield ionic compounds of limited solubility. The number of precipitating agents that can be used is limited because of the slow rate of formation of most precipitates. The most widely used precipitation reagent is silver nitrate, and precipitation titrimetry based on Ag^{+} (silver nitrate) as the titrant is called the **argentometric method**.

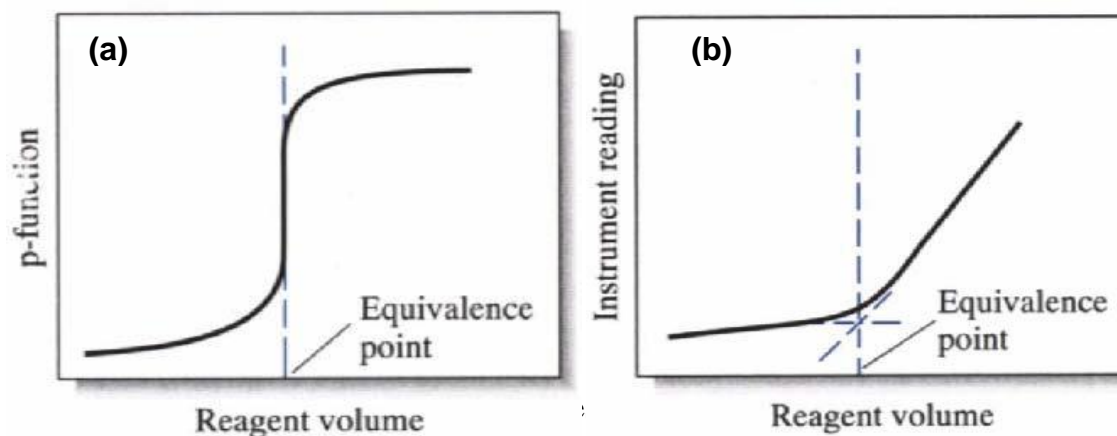
Silver nitrate titrations or Argentometric methods can be applied for: halides, halide-like anions (SCN^{-} , CN^{-} , CNO^{-}) several divalent anions, mercaptans, fatty acids, and several divalent and trivalent inorganic anions.



Titration curves for precipitation reactions are very similar to those involving strong acids and strong bases. Consequently, they can be derived in the exact same way. One need only substitutes the solubility product of the precipitate for the ion-product constant for the water.

Titration Curves in Titrimetric Methods

There are two types in drawing titration curves: (a) *Sigmoidal* curve and (b) *Linear-segment* curve. The following diagrams illustrates such a titration curve.



Both precipitation reactions and strong acids and strong bases reactions have a sharp inflection point. Furthermore, it is evident that at pre-equivalence and post-equivalence points, the p-function does not change very much. At the equivalence point, in contrast, a small volume of titrant corresponds to a large p-function change.

Endpoint

Endpoint can be found by:

1. A change in color due to the reagent, the analyte, or an indicator.
2. A change in the potential of an electrode that responds to the conc. of one of the reactants.

Titration curves: plots of a conc.-related variable as a function of reagent volume.

An example of sigmoidal titration curve is shown below for the precipitation reaction of AgNO_3 with 0.1000M KSCN:

Table 8.1 Concentration changes during a titration of 50.00 mL of 0.1000M AgNO_3 with 0.1000M KSCN

0.1000M KSCN, mL	$[\text{Ag}^+]$ mmol/mL	mL of KSCN to cause a tenfold decrease in $[\text{Ag}^+]$	pAg	pSCN
0.00	1.000×10^{-1}		1.00	
40.91	1.000×10^{-2}	40.91	2.00	10.00
49.01	1.000×10^{-3}	8.10	3.00	9.00
49.90	1.000×10^{-4}	0.89	4.00	8.00
49.99	1.000×10^{-5}	0.09	5.00	7.00
50.00	1.000×10^{-6}	0.01	6.00	6.00
50.01	1.000×10^{-7}	0.01	7.00	5.00
50.10	1.000×10^{-8}	0.09	8.00	4.00
51.01	1.000×10^{-9}	0.91	9.00	3.00
61.11	1.000×10^{-10}	10.10	10.00	2.00

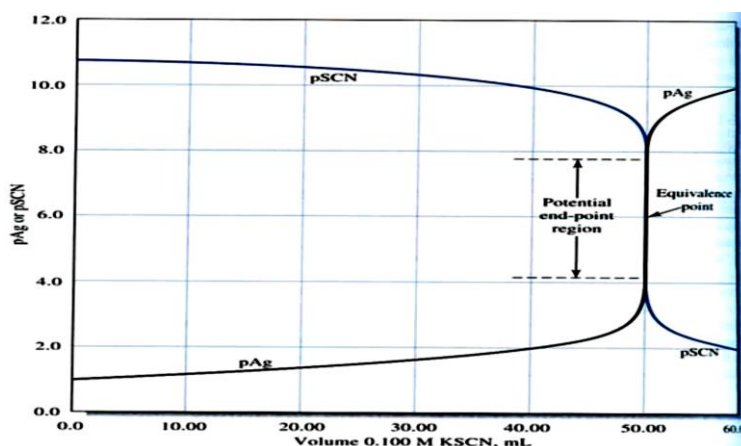


Figure 8.2 Titration curve for the titration of 50.00 mL of 0.1000 M AgNO_3 with 0.1000 M KSCN.



Precipitation Titration Curves Involving Silver Ion

Those curves have the same points as mentioned in acid-base and redox titrations:

- ◆ pre-equivalence points.
- ◆ equivalence point.
- ◆ post-equivalence point.

Factors Influencing End-Point Sharpness

Satisfactory endpoints require a change of two factors in p-function within ± 0.1 mL of the equivalence point

- a. reagent conc. : conc. $\uparrow \rightarrow$ sharpness \uparrow
- b. reaction completeness: product ppt $K_{sp} \downarrow \rightarrow$ sharpness \uparrow .

Figure 8.3 below shows the effect of product solubility on the sharpness of the endpoint. The change in the p-function at the equivalence point becomes greater as the solubility product becomes smaller. In other words, Δ p-function increases as the reaction between the analyte and the silver nitrate becomes more complete.

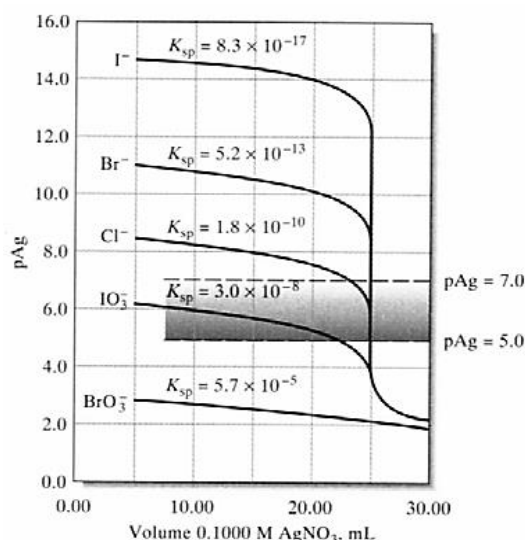


Figure 8.3 Effect of reaction completeness on precipitation titration curve, 50.00 mL of a 0.0500 M solution of the anion was titrated with 0.1000 M AgNO_3 .

Example 8-3: Perform calculations needed to generate a titration curve for 50.00 mL of 0.0500 M NaCl with 0.1000 M AgNO_3 .

Solution:



◆ **Initial point:** 0.000 M in Ag, and pAg is indeterminate.

◆ pre-equivalence points, **At 10.00 mL**

$$[\text{Cl}^-] \approx C_{\text{NaCl}} = \frac{\text{original no. mmol Cl}^- - \text{no. mol AgNO}_3}{\text{total volume of solution}}$$

$$= \frac{50.00 \times 0.0500 - 10.00 \times 0.100}{50.00 + 10.0} = 0.02500 \text{ M}$$

$$[\text{Ag}^+] = \frac{K_{sp}}{0.02500} = \frac{1.82 \times 10^{-10}}{0.02500} = 7.28 \times 10^{-9}, \text{ pAg} = -\log(7.28 \times 10^{-9}) = \underline{\underline{8.14}}$$

◆ **Equivalence point**

$$[\text{Ag}^+] = \sqrt{K_{sp}} = \sqrt{1.82 \times 10^{-10}} = 1.35 \times 10^{-5}, \text{ pAg} = -\log(1.35 \times 10^{-5}) = \underline{\underline{4.87}}$$

◆ post-equivalence point, **After Addition of 26.0 mL of Reagent**

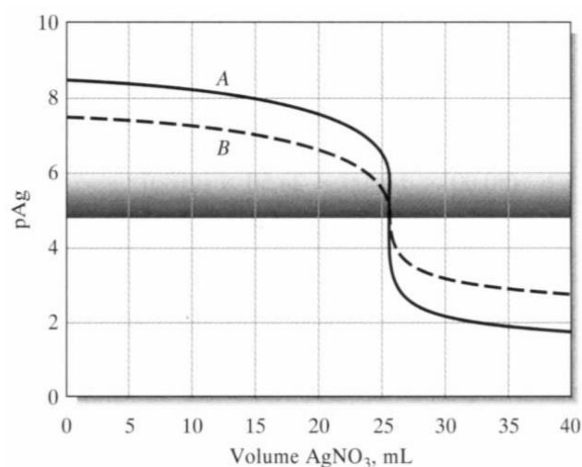
$$[\text{Ag}^+] \approx C_{\text{AgNO}_3} = \frac{(26.00 \times 0.1000 - 50.00 \times 0.0500)}{76.00} = 1.316 \times 10^{-3}$$

$$\text{pAg} = -\log(1.316 \times 10^{-3}) = \underline{\underline{2.88}}$$

Table 8.3 and Figure 8.4 below represent a titration of Cl^- (as NaCl) with AgNO_3 .

**Table 8.3** Changes in pAg in the titration of Cl⁻ with AgNO₃.

AgNO ₃ , mL	50.00 mL of 0.0500 M NaCl with 0.1000M AgNO ₃ , pAg value	50.00 mL of 0.00500 M NaCl with 0.01000M AgNO ₃ , pAg value
10.00	8.04	7.14
20.00	7.59	6.59
24.00	6.87	5.87
25.00	4.87	4.87
26.00	2.88	3.88
30.00	2.20	3.20
40.00	1.78	2.78

**Figure 8.4.** The shapes of titration curve for **A**, mL of 0.0500 M NaCl with 0.1000 M AgNO₃, and **B**, 50.00 mL of 0.00500 M NaCl with 0.01000 M AgNO₃.

Chemical Indicators for Precipitation Titration

Titrimetric methods have three types of indicators: self indicators, internal indicators, and external indicators (less common).

$A + R \rightarrow AR(s)$ analyte A with titrant R,

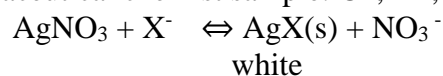
$In + R \rightarrow InR$ indicator In

For a color change to be seen, $[InR]/[In]$ must change by a factor of 10 to 100.

The endpoint produced by a chemical indicator usually consists of a color change. Once again, we see the relation between argentometric titrations and acid/base titrations, as the requirements for an indicator for the titrations are analogous. These requirements are namely: (1) the color change should occur over a limited range in the p-function of the reagent or the analyte, and (2) the color change should take place within the steep portion of the titration curve for the analyte. Three indicators that have widespread use in argentometric titrations are the Chromate ion, Fluorescein and Iron(III) ion.

1. Chromate Ion; The Mohr Method (Formation of a Second Precipitation)

1865 K. F. Mohr, a German pharmaceutical chemist sample: Cl⁻, Br⁻, CN⁻



End point: $2AgNO_3 + CrO_4^{2-} \rightleftharpoons Ag_2CrO_4(s) + 2NO_3^-$
yellow red ($K_{sp} = 1.1 \times 10^{-12} M^3$)

not for oxalate, I⁻, SCN⁻

Solubility: $Ag_2CrO_4 > AgX$

*Choice of indicator:

if indicator- I⁻ anion ($AgI K_{sp} = 8.3 \times 10^{-17} M^2$)

$AgCl K_{sp} = 1.82 \times 10^{-10} M^2$

$[Ag^+]_{ep} = (K_{sp})^{1/2} = (1.82 \times 10^{-10} M^2)^{1/2} = 1.35 \times 10^{-5} M$



if indicator- I⁻ anion conc. = 0.0025 M

AgI ppt formation

$$[Ag^+]_{\min} = 8.3 \times 10^{-17} M^2 / 0.0025 M I^- = 3.3 \times 10^{-14} M$$

pre-equivalence point : $Ag^+ \rightarrow AgI (s)$

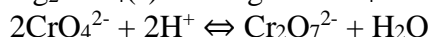
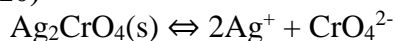
***Concentration of indicator [CrO₄²⁻]**

equivalence point: $[Ag^+] = [Cl^-] = 1.35 \times 10^{-5} M$

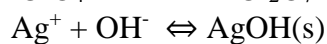
$$[CrO_4^{2-}] = K_{sp} / [Ag^+]^2 = 1.1 \times 10^{-12} / (1.35 \times 10^{-5})^2 = 6.6 \times 10^{-3} M$$

***pH : 6.5 ~ 10.3 (7~10)**

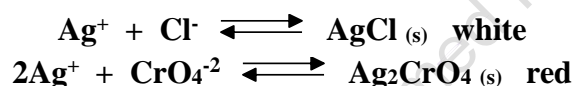
pH < 6.5



pH > 10.3



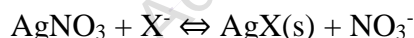
The chromate ion is employed as an indicator in the **Mohr method**. Sodium chromate can serve as an indicator for the argentometric titrations of chlorine, bromine, and cyanide ions, by reacting with silver to form silver chromate (Ag₂CrO₄). The brick red Ag₂CrO₄ precipitates at the equivalence point region and thus is a useful indicator. The Mohr method has an inherent systematic error that is correctable. At reagent concentrations lower than 0.1M, the chromate ion imparts an intense yellow color to the solution that hinders the identification of the red silver chromate. As a consequence, excess silver nitrate is required before precipitation can be detected and as a result, the volume is skewed. The correction that is often made to account for this error is making a blank titration of a chloride-free suspension of calcium carbonate. This volume can then be used to adjust the experimental results. The Mohr method will follow these reactions:



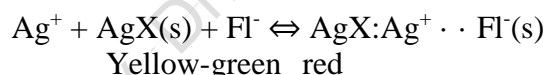
2. Adsorption indicators: The Fajans Method

1926, Polish chemist, K. Fajans

Advantages: rapid, accurate, and reliable



Endpoint:



Indicator: Fluorescein anion

* avoid ppt coagulation → ppt surface ↑

- adding dextrin or polyethylene glycol
- quick titration and avoid excessive stirring
- halide ion conc. : 0.005 ~ 0.025 M

*Fluorescein dyes: weak ionized acids

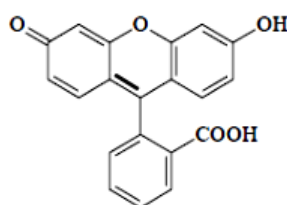
pH ↓ → [Fl⁻] ↓ → weak endpoint

pH ≥ 7, (dichlorofluorescein: pH ≥ 4).

*Photochemical decomposition : ppt → black

Indicator	pH	Sample
Fluorescein	≥ 7	Cl ⁻ , Br ⁻ , I ⁻ , SCN ⁻
Dichlorofluorescein	≥ 4	Cl ⁻ , Br ⁻ , I ⁻ , SCN ⁻
Tetrabromo fluorescein (called Eosin)	≥ 2	Br ⁻ , I ⁻ , SCN ⁻

The second popular indicator is Fluorescein, an adsorption indicator used in the **Fajans method**. An adsorption indicator is an organic compound that tends to be adsorbed onto the surface of the solid in a precipitation titration. In the ideal scenario, the adsorption occurs near the equivalence point and results in a color change. Fluorescein is a widely used adsorption indicator.

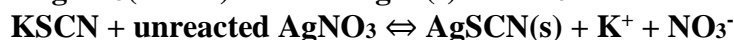


fluorescein

In aqueous solution partial dissociation into H_3O^+ and the negatively charged Fluorescein ion. The Fluorescein forms a bright red silver salt. These types of indicators give a rapid, accurate and reliable titration endpoint.

3. Iron(III) Ion; The Volhard Method (Formation a Colored Complex Compound)

1874 Jacob Volhard, a German chemist, (back titration): Iron(III) ion as indicator sample: halide ion, $\text{C}_2\text{O}_4^{2-}$, AsO_4^{3-} , SCN^-



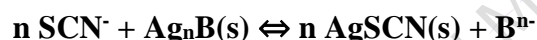
Endpoint: $\text{Fe}^{3+} + \text{SCN}^- \rightleftharpoons \text{Fe}(\text{SCN})^{2+}$ $K_f = \frac{[\text{Fe}(\text{SCN})^{2+}]}{[\text{Fe}^{3+}][\text{SCN}^-]} = 1050$
red

*pH : in acidic soln to prevent $\text{Fe}(\text{III}) \rightarrow \text{Fe}(\text{OH})_3(\text{s})$

*advantage: carbonate, oxalate & arsenate do not interfere.

*For Cl^- ion in blood serum, urine. (sample: HNO_3 digestion)

*Quantitativeness of the back titration



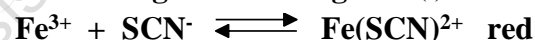
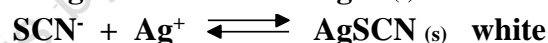
a. compare AgSCN and Ag_nB : molar solubility $\text{AgSCN}: 1.0 \times 10^{-6} \text{ M}$

b. Calculate $K_{\text{rxn}} = \frac{[\text{B}^{n-}]}{[\text{SCN}^-]^n} = \frac{K_{\text{sp of Ag}_n\text{B}}}{(K_{\text{sp of AgSCN}})^n}$

if AgSCN solubility < Ag_nB or $K_{\text{rxn}} > 1$

→ filter Ag_nB ppt or add liquid nitrobenzene.

The third indicator used is Iron(III) ion, used in the **Volhard method**. In this method, silver ions are titrated with a standard solution of thiocyanate ion, where Fe^{3+} serves as the indicator imparting a red color to the solution. This titration must be carried out in an acidic solution lest the $\text{Fe}(\text{III})$ precipitates out as a hydrated oxide. The reaction that accompany the Volhard method are:



The most important application of the Volhard method is for determining the presence of halide ions. An excess of silver nitrate is added to the sample and back-titrated with a standard thiocyanate solution.

A summary of differences among Argentometric methods are tabulated below

Table 8.2 Argentometric methods

Method	Mohr (Direct)	Fajans (Direct)	Volhard (Residual)
Titrant	AgNO_3	AgNO_3	$\text{AgNO}_3\text{-KSCN}$
Indicator	Na_2CrO_4	Fluorescein	Fe^{3+}
End point	$\text{Ag}_2\text{CrO}_4(\text{s})$ red ppt	$\text{AgX}:\text{Ag}^+ \cdot \cdot \text{Fl}^-$ (s) red ppt	$\text{Fe}(\text{SCN})^{2+}$ red solution
Titration pH	6.5 ~ 10.3	≥ 7	Acidic

Titration Curves for Mixtures of Anions

Titration can be done to determine several anions in the same solution. An example is a titration of 50.00 mL of a solution ($[\text{I}^-] = 0.0500\text{M}$ and $[\text{Cl}^-] = 0.0800\text{M}$) with 0.1000 M AgNO_3 .

-Initial Point:



$$\frac{[Ag^+][I^-]}{[Ag^+][Cl^-]} = \frac{8.3 \times 10^{-17}}{1.82 \times 10^{-10}} = 4.56 \times 10^{-7} \gg [I^-] = (4.56 \times 10^{-7})[Cl^-]$$

-When adding 25 mL of AgNO₃:

$$C_{Cl} = \frac{50.00 \times 0.0800 - ([25.00 \text{ mL} \times 0.1000 \text{ M}] - [50.00 \text{ mL} \times 0.0500 \text{ M}])}{(50.00 + 25.00) \text{ mL}} = 0.0533 \text{ M}$$

$$\text{Then } [I^-] = 4.56 \times 10^{-7} \times 0.0533 = 2.43 \times 10^{-8} \text{ M}$$

$$\text{no. mmol } I^- = 75.00 \text{ mL} \times (2.43 \times 10^{-8} \text{ mmol } I^-/\text{mL}) = 1.82 \times 10^{-6}$$

$$I^- \text{ unprecipitated} = \frac{1.82 \times 10^{-6}}{50.00 \times 0.0500} \times 100\% = 7.3 \times 10^{-5} \%$$

$$[Ag^+] = \frac{1.82 \times 10^{-10}}{0.0533} = 3.41 \times 10^{-9} \gg pAg = -\log(3.41 \times 10^{-9}) = 8.47$$

-After adding 30.00 mL AgNO₃

$$C_{Cl} = [Cl^-] = \frac{50.00 \times 0.0800 - (30.00 \times 0.1000 - 50.00 \times 0.0500)}{50.00 + 30.00} = 0.0438 \text{ M}$$

$$[Ag^+] = \frac{1.82 \times 10^{-10}}{0.0438} = 4.16 \times 10^{-9}$$

$$pAg = 8.38$$

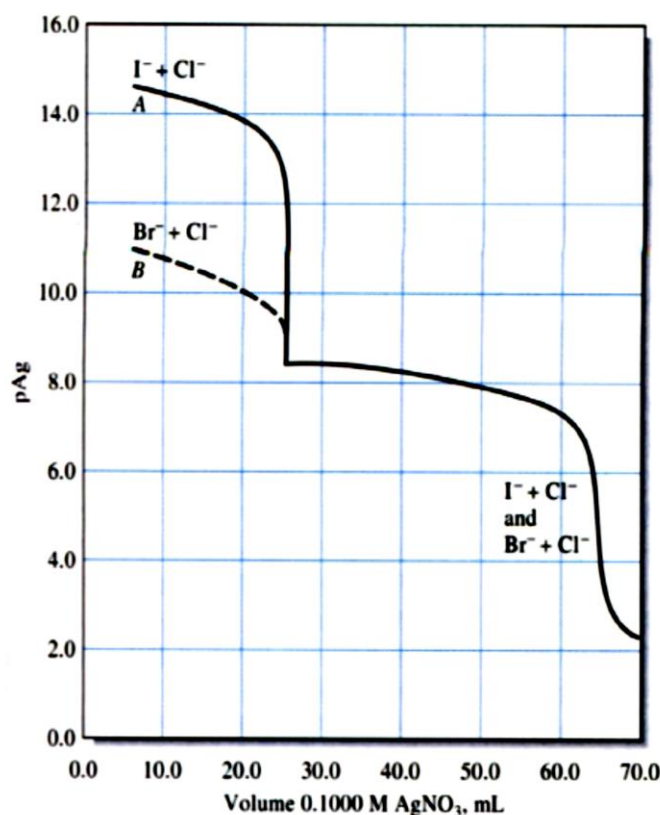


Figure 8.5. Titration curves for 50.00 mL of (A) a solution 0.0800 M in Cl⁻ and 0.0500 M in I⁻ or (B) Br⁻. K_{sp} of AgI = 8.3×10^{-17} ; AgBr = 5.2×10^{-13} ; AgCl = 1.8×10^{-10} .

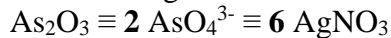
Example 8-4: The As in a 9.13-g sample of pesticide was converted to AsO₄³⁻ and precipitated as Ag₃AsO₄ with 50.00 mL of 0.02015 M AgNO₃. The excess Ag⁺ was then titrated with 4.75 mL of 0.04321 M KSCN. Calculate the % of As₂O₃ in the sample. (As₂O₃ M.wt. = 197.85)

Solution:

$$\text{no. mmol AgNO}_3 = 50.00 \text{ mL} \times 0.02015 \text{ mmol/mL} = 1.0075$$

$$\text{no. mmol KSCN} = 4.75 \text{ mL} \times 0.04321 \text{ mmol/mL} = 0.2052$$

$$\text{no. mmol AgNO}_3 \text{ consumed by AsO}_4^{3-} = 0.8023$$

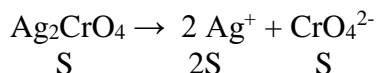


$$\% \text{ As}_2\text{O}_3 = 0.8023 \times (1/6) \times 0.1978/9.13 \times 100\% = 0.2987\%$$

Solved Problems;

Problem 8.1: What is the solubility product of Ag₂CrO₄ if its solubility is 6.50×10^{-5} mol/L?

Solution:





where $S = 6.5 \times 10^{-5}$ mol/L

$$K_{sp}(\text{Ag}_2\text{CrO}_4) = [\text{Ag}^+]^2[\text{CrO}_4^{2-}] = (2S)^2S = 4S^3 = 1.1 \times 10^{-12}$$

Problem 8.2: What is the solubility product of 0.214 g Hg_2SO_4 in 500 cm^3 of a solution?

Solution:

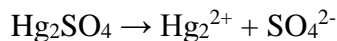
$$\text{Wt.}(\text{Hg}_2\text{SO}_4) = 0.214 \text{ g}$$

$$\text{M.wt.}(\text{Hg}_2\text{SO}_4) = 496 \text{ g/mol}$$

$$n(\text{Hg}_2\text{SO}_4) = 496 / 0.214 = 0.0004314 \text{ mol}$$

$$V(\text{Hg}_2\text{SO}_4 \text{ -solution}) = 500 \text{ cm}^3 = 0.500 \text{ dm}^3 = 0.500 \text{ L}$$

$$C = n/V = 0.0004314 \text{ mol} / 0.500 \text{ L} = 0.0008628 \text{ mol/dm}^3$$



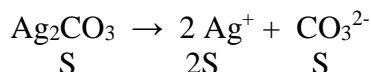
$$S \quad \quad \quad S \quad \quad \quad S$$

$$K_{sp}(\text{Hg}_2\text{SO}_4) = [\text{Hg}_2^{2+}][\text{SO}_4^{2-}] = S \times S = S^2$$

$$K_{sp}(\text{Hg}_2\text{SO}_4) = (0.0008628)^2 = 7.446 \times 10^{-7}$$

Problem 8.3: How many grams of Ag_2CO_3 are in 300 mL saturated solution at 25 °C?

Solution:



$$K_{sp}(\text{Ag}_2\text{CO}_3) = [\text{Ag}^+]^2[\text{CO}_3^{2-}] = (2S)^2 S = 4S^3$$

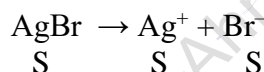
$$S = \sqrt[3]{\frac{K_{sp}(\text{Ag}_2\text{CO}_3)}{4}} = 1.17325 \times 10^{-4} \text{ mol/L}$$

That is, in 300 mL solution we have $(1.17325 \times 10^{-4} \text{ mol/L}) \times (0.300 \text{ L}) = 3.51975 \times 10^{-5} \text{ mol Ag}_2\text{CO}_3$.

M.wt. $\text{Ag}_2\text{CO}_3 = 275.748 \text{ g/mol}$, so wt. $\text{Ag}_2\text{CO}_3 = n_{\text{Ag}_2\text{CO}_3} \times \text{M.wt.}_{\text{Ag}_2\text{CO}_3} = (3.51975 \times 10^{-5} \text{ mol}) \times (275.748 \text{ g/mol}) = 0.009706 \text{ g}$.

Problem 8.4: What is the solubility of AgBr in pure water and in 0.1 M AgNO_3 ?

Solution:



In pure water:

$$K_{sp}(\text{AgBr}) = [\text{Ag}^+][\text{Br}^-] = S^2$$

$$S = \sqrt{K_{sp}(\text{AgBr})} = 1.00 \times 10^{-6} \text{ mol/L}$$

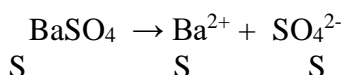
In 0.1 M AgNO_3 solution:

$$K_{sp}(\text{AgBr}) = [\text{Ag}^+][\text{Br}^-] = (S + 0.1) S \cong 0.1S$$

$$S = K_{sp}(\text{AgBr}) / 0.1 = 5.20 \times 10^{-11} \text{ mol/L}$$

Problem 8.5: How many grams of BaSO_4 can be dissolved in 1000 mL 0.001 M K_2SO_4 solution?

Solution:



$$K_{sp}(\text{BaSO}_4) = [\text{Ba}^{2+}][\text{SO}_4^{2-}] = S(0.001 + S) \cong 0.001S$$

$$S = [\text{Ba}^{2+}] = K_{sp}(\text{BaSO}_4) / 0.001 = 1.00 \times 10^{-7} \text{ mol/L}$$

That is $1.00 \times 10^{-7} \text{ mol Ba}^{2+}$ can be dissolved in 1000 ml (1.00 L) solution.

M.wt. $\text{BaSO}_4 = 233.392 \text{ g/mol}$, so

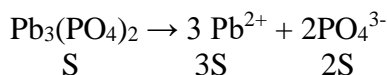
$$\text{wt.}_{\text{BaSO}_4} = n_{\text{BaSO}_4} \times \text{M.wt.}_{\text{BaSO}_4} = (1.00 \times 10^{-7} \text{ mol}) \times (233.392 \text{ g/mol}) =$$

$$2.334 \times 10^{-5} \text{ g.}$$

Problem 8.6: What is the solubility of $\text{Pb}_3(\text{PO}_4)_2$ in pure water and in 0.05 M $\text{Pb}(\text{NO}_3)_2$ solution?

Solution:

In pure water:



$$K_{sp}(\text{Pb}_3(\text{PO}_4)_2) = [\text{Pb}^{2+}]^3[\text{PO}_4^{3-}]^2 = (3S)^3(2S)^2 = 108S^5$$

$$S = \sqrt[5]{\frac{K_{sp}(\text{Pb}_3(\text{PO}_4)_2)}{108}} = 1.6925 \times 10^{-7} \text{ mol/L}$$

In 0.05 M $\text{Pb}(\text{NO}_3)_2$ solution:

$$K_{sp}(\text{Pb}_3(\text{PO}_4)_2) = [\text{Pb}^{2+}]^3[\text{PO}_4^{3-}]^2 = (0.05)^3 \times (2S)^2 = 5 \times 10^{-4} \times S^2$$

$$S = \sqrt{\frac{K_{sp}(\text{Pb}_3(\text{PO}_4)_2)}{5 \times 10^{-4}}} = 5.477 \times 10^{-15} \text{ mol/L}$$



Problem 8.7: Is there any precipitation (Ag_2SO_4) when we add 10 cm^3 of 0.05 mol/dm^3 AgNO_3 solution to 10.00 cm^3 of a 0.1 mol/dm^3 Na_2SO_4 solution?

Solution:

$$V(\text{AgNO}_3\text{-solution}) = 10 \text{ cm}^3 = 0.010 \text{ dm}^3$$

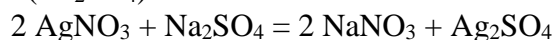
$$c(\text{AgNO}_3\text{-solution}) = 0.05 \text{ mol/dm}^3$$

$$V(\text{Na}_2\text{SO}_4\text{-solution}) = 10 \text{ cm}^3 = 0.010 \text{ dm}^3$$

$$c(\text{Na}_2\text{SO}_4\text{-solution}) = 0.1 \text{ mol/dm}^3$$

$$n(\text{AgNO}_3) = 0.01 \times 0.05 = 0.0005 \text{ mol}$$

$$n(\text{Na}_2\text{SO}_4) = 0.01 \times 0.1 = 0.001 \text{ mol}$$



$$V(\text{mixture}) = 20.00 \text{ mL} = 0.02 \text{ dm}^3$$

$$[\text{AgNO}_3] = 0.0005/0.02 = 2.5 \times 10^{-2} \text{ mol/dm}^3$$

$$[\text{Na}_2\text{SO}_4] = 0.001/0.02 = 5 \times 10^{-2} \text{ mol/dm}^3$$

$$K_{sp}(\text{Ag}_2\text{SO}_4) = 1.48 \times 10^{-5}$$

$$[\text{Ag}^+]^2 [\text{SO}_4^{2-}] = (2.5 \times 10^{-2})^2 \times 5 \times 10^{-2} = 3.125 \times 10^{-5}$$

$$K_{sp} = 1.48 \times 10^{-5} \quad ? \quad 3.125 \times 10^{-5}$$

As the result is larger than the K_{sp} value, there will be precipitate in the solution.

Problem 8.8: Is it possible to dissolve 10 mg AgNO_3 in 100 ml of 0.5 mol/dm^3 NaCl solution?

Solution:

$$V(\text{NaCl-solution}) = 100 \text{ mL} = 0.100 \text{ dm}^3$$

$$c(\text{NaCl-solution}) = 0.5 \text{ mol/dm}^3$$

$$n(\text{NaCl}) = 0.1 \times 0.5 = 0.05 \text{ mol}$$

$$\text{wt.}(\text{AgNO}_3) = 10 \text{ mg} = 0.01 \text{ g}$$

$$\text{M.wt.}(\text{AgNO}_3) = 169.9 \text{ g/mol}$$

$$n(\text{AgNO}_3) = 0.01/169.9 = 5.886 \times 10^{-5} \text{ mol}$$

$$c(\text{AgNO}_3\text{-sol}) = (5.886 \times 10^{-5})/0.1 = 5.886 \times 10^{-4} \text{ M}$$

$$K_{sp}(\text{AgCl}) = 1.83 \times 10^{-10}$$

$$[\text{Ag}^+] \times [\text{Cl}^-] = 5.886 \times 10^{-4} \times 0.5 = 2.943 \times 10^{-4}$$

$$2.943 \times 10^{-4} \quad ? \quad K_{sp}(\text{AgCl}) = 1.83 \times 10^{-10}$$

As the result is larger than the K_{sp} value, there will be a precipitate in the solution, so it is not possible to dissolve this amount of AgNO_3 in this solution.

Problem 8.9: 25.00 mL 0.11 M KCl solution is titrated with 0.105 M AgNO_3 titrant. Sketch the titration curve and calculate the pCl (and pAg) values at 0, 40, 100, and 140% degrees of titration.

Solution:

$$n_{\text{KCl}} = C_{\text{KCl}} \times V_{\text{KCl}} = (0.11 \text{ mol/L}) \times (0.025 \text{ L}) = 2.75 \times 10^{-3} \text{ mol KCl.}$$

At 100 % degree of titration, we added the same molar amount of AgNO_3 to the solution, so:

$$n_{\text{AgNO}_3} = 2.75 \times 10^{-3} \text{ mol}$$

$$\text{The volume of titrant at 100% degree of titration: } V_{\text{AgNO}_3} = n_{\text{AgNO}_3}/C_{\text{AgNO}_3} = 0.02619 \text{ L} = 26.19 \text{ mL}$$

0% degree of titration:

$$[\text{Cl}^-] = C_{\text{KCl}} = 0.11 \text{ mol/L} \rightarrow \text{pCl} = -\log[\text{Cl}^-] = 0.959$$

$$[\text{Ag}^+] = 0 \rightarrow \text{pAg} = -\log[\text{Ag}^+] = \text{undefined}$$

40% degree of titration:

$$40 \times (26.19 \text{ mL})/100 = 10.4762 \text{ mL AgNO}_3 \text{ solution is added. In this amount of solution,}$$

$$n_{\text{AgNO}_3} = (40 \times n_{\text{KCl}}) / 100 = 1.1 \times 10^{-3} \text{ mol AgNO}_3.$$

There is Cl^- excess compared to Ag^+ in the resulting solution, so

$$[\text{Cl}^-] = \frac{n_{\text{KCl}} - n_{\text{AgNO}_3}}{V_{\text{total}}} = \frac{(2.75 \times 10^{-3}) \text{ mol} - (1.1 \times 10^{-3}) \text{ mol}}{0.025 \text{ L} + 0.0104762 \text{ L}} = 0.046510 \text{ mol/L}$$

$$\rightarrow \text{pCl} = 1.332$$

$$K_{sp}(\text{AgCl}) = [\text{Ag}^+][\text{Cl}^-] \text{ so } [\text{Ag}^+] = \frac{K_{sp}(\text{AgCl})}{[\text{Cl}^-]} = 3.9346 \times 10^{-9} \text{ mol/L} \rightarrow \text{pAg} = 8.405$$

100% degree of titration: 26.19 mL AgNO_3 solution is added. The amount of $[\text{Cl}^-]$ and $[\text{Ag}^+]$ is the same in the solution, and $[\text{Cl}^-] = [\text{Ag}^+] = S = \sqrt{K_{sp}(\text{AgCl})} = 1.353 \times 10^{-5} \text{ mol/L}$

$$\rightarrow \text{pCl} = \text{pAg} = 4.869$$

140% degree of titration: $140 \times (26.19 \text{ mL})/100 = 36.666 \text{ mL AgNO}_3$ solution is added. In this amount of solution, $n_{\text{AgNO}_3} = (140 \times n_{\text{KCl}}) / 100 = 3.85 \times 10^{-3} \text{ mol AgNO}_3.$

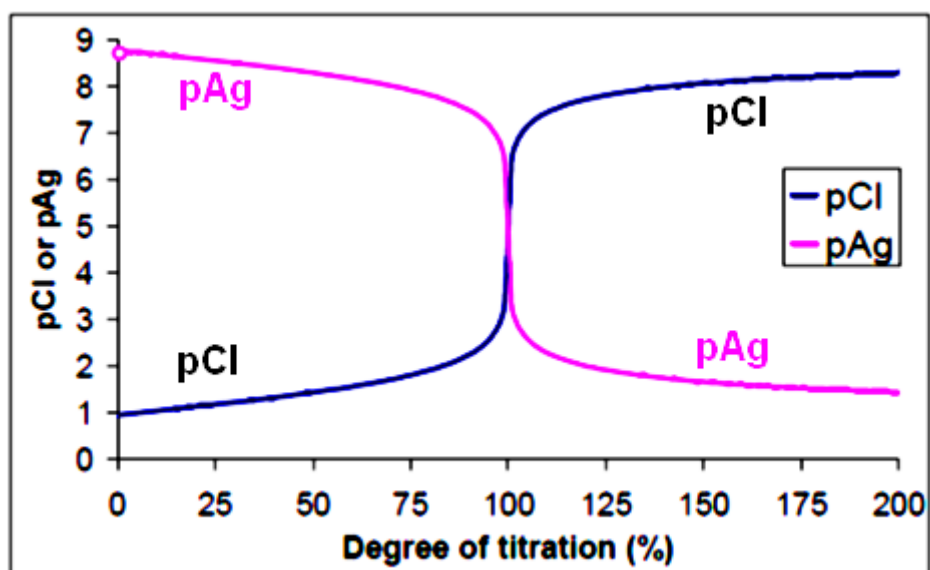
There is Ag^+ excess compared to the Cl^- in the resulting solution, so

$$[\text{Ag}^+] = \frac{n_{\text{AgNO}_3} - n_{\text{KCl}}}{V_{\text{total}}} = \frac{(3.85 \times 10^{-3}) \text{ mol} - (2.75 \times 10^{-3}) \text{ mol}}{0.025 \text{ L} + 0.036666 \text{ L}} = 0.017838 \text{ mol/L}$$



→ $pAg = 1.749$

$K_{sp}(AgCl) = [Ag^+][Cl^-]$ so $[Cl^-] = K_{sp}(AgCl) / [Ag^+] = 1.0259 \times 10^{-8} \text{ mol/L} \rightarrow pCl = 7.989$.



Titrimetric Analysis by Dr. Adel Ahmed Mohammed Saeed



9. COMPLEXATION EQUILIBRIA & TITRATIONS

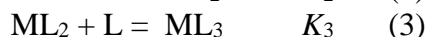
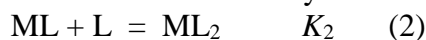
Complexation Equilibria

Complexation reactions are typically Lewis Acid-Base reactions. They involve a metal-ion (M) reacting with a ligand (L) to form a complex (ML) and are defined by formation constant, K_f , or stability constant, K_s , as shown in Equation:



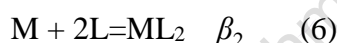
Metal-ion + Ligand = Complex

where we have omitted the charges on the ions in order to be general. Complexation reactions occur in a stepwise fashion and the reaction above is often followed by additional reactions:



Unidentate ligands invariably add in a series of steps as shown above. With multidentate ligands, the maximum coordination number of the cation may be satisfied with only one or a few added ligands. For example, Cu(II), with a maximum coordination number of 4, can form complexes with ammonia that have the formulas $Cu(NH_3)^{2+}$, $Cu(NH_3)_2^{2+}$, $Cu(NH_3)_3^{2+}$ and $Cu(NH_3)_4^{2+}$. With the **bidentate** ligand glycine (gly), the only complexes that form are $Cu(gly)^{2+}$ and $Cu(gly)_2^{2+}$.

The equilibrium constants for complex formation reactions are generally written as formation constants. Thus, each of the reactions 1 through 4 is associated with a stepwise formation constant K_1 through K_n . For example, $K_1 = [ML]/[M][L]$, $K_2 = [ML_2]/[ML][L]$, and so on. We can also write the equilibria as the sum of individual steps. These have overall formation constants designated by the symbol β . Therefore,



Multiple steps of these reactions can be combined using overall formation constants (β_n)



where

$$\beta_n = K_1 K_2 \dots K_n$$

Ligands:

May be conveniently classified on the basis of the number of points of attachment to the metal ion. Thus simple ligands, such as halide ions or the molecules H_2O or NH_3 , are **monodentate**, *i.e.* the ligand is bound to the metal ion at only one point by the donation of a lone pair of electrons to the metal. When, however, the ligand molecule or ion has two atoms, each of which has a lone pair of electrons, then the molecule has two donor atoms and it may be possible to form two coordinate bonds with the same metal ion.

Dentate: means having **toothlike**.

Tetradentate & hexadentate ligands are more satisfactory as titrants than ligands with a lesser number of donor groups for two reasons:

1. react more completely & sharper end points
2. tend to form 1:1 complexes

Macrocyclic: Metal ion+ cyclic organic compound.

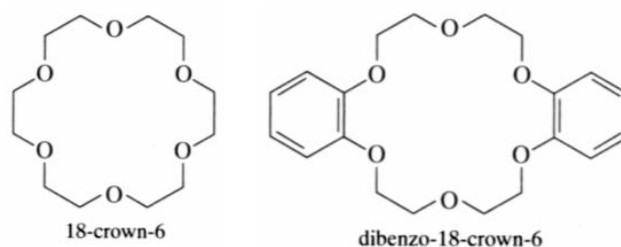


Figure 9.1. Some cyclic organic compounds

The formation of three five-membered rings, each including the metal ion; the process of ring formation is called **chelation** and like this complex is called a **chelate**.



Complexometric (Complexation) Titration

Complexometric titration (sometimes chelatometry) is a form of volumetric analysis in which the formation of a colored complex is used to indicate the end point of a titration. Complexometric titrations are particularly useful for the determination of a mixture of different metal ions in solution. An indicator capable of producing an unambiguous color change is usually used to detect the end-point of the titration. Complexometry: Volumetric method involves the reaction of metal with ligand to form a complex (with coordinate bond).

Complex formation is a type of acid-base reaction according to Lewis concept, where metal ion is Lewis acid (electron acceptor) and ligand is Lewis base (electron donor). Complexation reaction is the replacement of solvent molecules by ligand.

Complexometry

Titration against EDTA. EDTA = Complexon III = Sequesterene.

Compleximetry

Titration against any other complexing agent.

Reactions for Complexometric Titration

In theory, any complexation reaction can be used as a volumetric technique provided that:

- the reaction reaches equilibrium rapidly after each portion of titrant is added.
- interfering situations do not arise. For instance, the stepwise formation of several different complexes of the metal ion with the titrant, resulting in the presence of more than one complex in solution during the titration process.
- a complexometric indicator capable of locating equivalence points with fair accuracy is available.

In practice, the use of EDTA as a titrant is well established.

Ethylenediaminetetraacetic acid, EDTA, is an aminocarboxylic acid and forms strong 1:1 complexes with many metal ions (Figure 9.2).

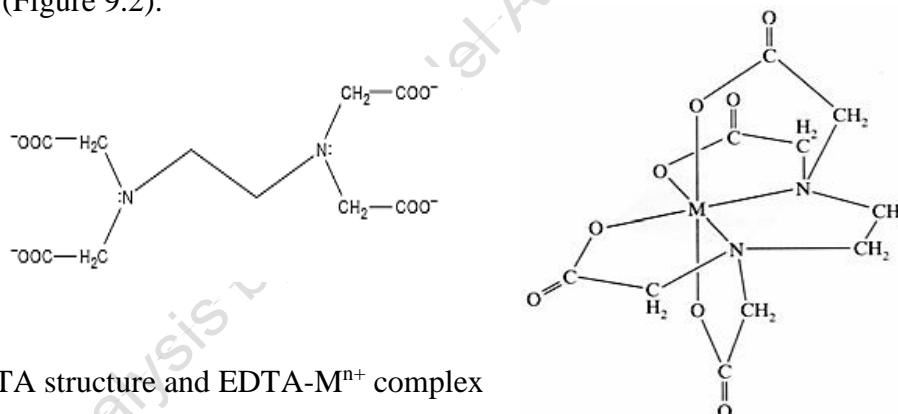


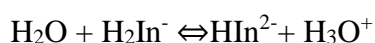
Figure 9.2. EDTA structure and EDTA-Mⁿ⁺ complex

Indicator for EDTA Titration

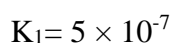
Reilley & Barnard: nearly 200 organic compounds

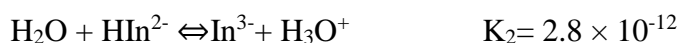
Examples:

Eriochrome Black T (EBT)	Calmagite

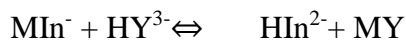


red blue





blue orange

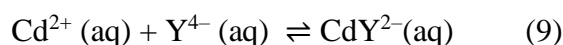


red colorless blue colorless

pH	color	predominant form
1 - 6.9	purple-red	H_2EBT^-
6.9 - 11.5	blue	HEBT^{2-}
11.5 - 14	orange	EBT^{3-}

2-Metal-EDTA Formation Constants

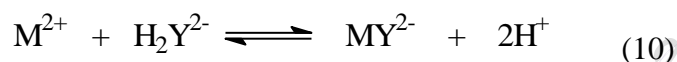
To illustrate the formation of a metal–EDTA complex consider the reaction between Cd^{2+} and EDTA



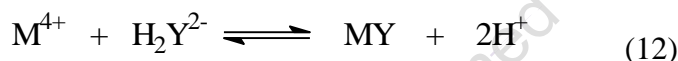
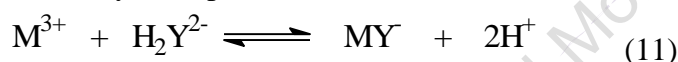
where Y^{4-} is a shorthand notation for the chemical form of EDTA. The formation constant for this reaction

$$K_f = \frac{[\text{CdY}^{2-}]}{[\text{Cd}^{2+}][\text{Y}^{4-}]} = 2.9 \times 10^{16}$$

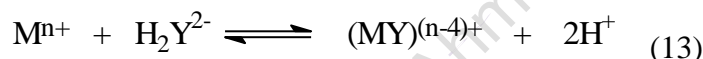
To simplify the following discussion EDTA is assigned the formula H_4Y : the dissolution salt is therefore $\text{Na}_2\text{H}_2\text{Y}$ and affords the complex-forming ion H_2Y^{2-} in aqueous solution; it reacts with all metals in 1:1 ratio. The reactions with cations, e.g. M^{2+} , may be written as:



For other cations, the reactions may be expressed as:



or



One mole of the complex-forming H_2Y^{2-} reacts in all cases with one mole of the metal ion and in each case, also, two moles of hydrogen ion are formed. It is apparent from equation (13) that the dissociation of the complex will be governed by the pH of the solution; lowering the pH will decrease stability of the metal-EDTA complex. The more stable the complex, the lower the pH at which an EDTA titration of the metal ion in question may be carried out. Table (9.1) indicates minimum pH values for the existence of EDTA complexes of some selected metals.

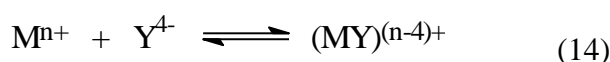
Table 9.1: Stability with respect to pH of some metal-EDTA complexes.

Minimum pH at which complexes exist	Selected metals
1-3	Zr^{4+} ; Hf^{4+} ; Th^{4+} ; Bi^{3+} ; Fe^{3+}
4-6	Pb^{2+} ; Cu^{2+} ; Zn^{2+} ; Co^{2+} ; Ni^{2+} ; Mn^{2+} ; Fe^{2+} ; Al^{3+} ; Cd^{2+} ; Sn^{2+}
8-10	Ca^{2+} ; Sr^{2+} ; Ba^{2+} ; Mg^{2+}

It is thus seen that, in general, EDTA complexes with metal ions of the charge number 2 are stable in alkaline or slightly acidic solution, whilst complexes with ions of charge numbers 3 or 4 may exist in solutions of much higher acidity.

Stability Constants of EDTA Complexes:

The stability of a complex is characterized by the stability constant (or formation constant) K :



$$K = \frac{[(\text{MY})^{(n-4)+}]}{[\text{M}^{n+}][\text{Y}^{4-}]} \quad (15)$$

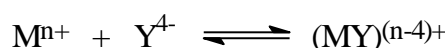
Some values for the stability constants (expressed as $\log K$) of metal-EDTA complexes are collected in Table 9.2:

**Table 9.2:** Stability constants (as log K) of metal-EDTA complexes.

Cation	log K	Cation	log K	Cation	log K
Mg ²⁺	8.7	Zn ²⁺	16.7	La ³⁺	15.7
Ca ²⁺	10.7	Cd ²⁺	16.6	Lu ³⁺	20.0
Sr ²⁺	8.6	Hg ²⁺	21.9	Sc ³⁺	23.1
Ba ²⁺	7.8	Pb ²⁺	18.0	Ga ³⁺	20.5
Mn ²⁺	13.8	Al ³⁺	16.3	In ³⁺	24.9
Fe ²⁺	14.3	Fe ³⁺	25.1	Th ⁴⁺	23.2
Co ²⁺	16.3	Y ³⁺	18.2	Ag ⁺	7.3
Ni ²⁺	18.6	Cr ³⁺	24.0	Li ⁺	2.8
Cu ²⁺	18.8	Ce ³⁺	15.9	Na ⁺	1.7

The "Apparent" or "Conditional" Stability Constant:

From equation (14):



$$K_{MY} = \frac{[MY^{(n-4)+}]}{[M^{n+}]\alpha_4 c_T}$$

$$K'_{MY} = \alpha_4 K_{MY} = \frac{[MY^{(n-4)+}]}{[M^{n+}]c_T}$$

only at the pH for which α_4 is applicable

where

$$\alpha_4 = \frac{[Y^{4-}]}{c_T}$$

c_T : [uncomplexed EDTA]

$$c_T = [Y^{4-}] + [HY^{3-}] + [H_2Y^{2-}] + [H_3Y^{-}] + [H_4Y]$$

Computing α_4 Values for EDTA Solutions

$$\alpha_4 = \frac{K_1 K_2 K_3 K_4}{[H^+]^4 + K_1 [H^+]^3 + K_1 K_2 [H^+]^2 + K_1 K_2 K_3 [H^+] + K_1 K_2 K_3 K_4}$$

$$\alpha_4 = \frac{K_1 K_2 K_3 K_4}{D}$$

$$D = [H^+]^4 + K_1 [H^+]^3 + K_1 K_2 [H^+]^2 + K_1 K_2 K_3 [H^+] + K_1 K_2 K_3 K_4$$

Table 9.3: Values of α_4 for EDTA in Solutions of Various pH

pH	α_4	pH	α_4	pH	α_4	pH	α_4
2.0	3.71×10^{-14}	5.0	3.54×10^{-7}	8.0	5.39×10^{-3}	11.0	0.85
3.0	2.51×10^{-11}	6.0	2.25×10^{-5}	9.0	5.21×10^{-2}	12.0	0.98
4.0	3.61×10^{-9}	7.0	4.8×10^{-4}	10.0	0.35	13.0	1.00

Example 9.1: Calculate the molar Y^{4-} conc. in a 0.0200 M EDTA solution that has been buffered to a pH of 10.00.

Solution:

At pH 10.00, α_4 is 0.35

$$[Y^{4-}] = \alpha_4 c_T = (0.35)(0.0200) = 7.0 \times 10^{-3} \text{ M}$$

Example 9.2: Calculate the equilibrium conc. of Ni^{2+} in a solution with an analytical NiY^{2-} conc. of 0.0150 M at pH(a) 3.0 and (b) 8.0

Solution:



$$[NiY^{2-}] = 0.0150 - [Ni^{2+}]$$



If we assume $[\text{Ni}^{2+}] \ll 0.0150$, $[\text{NiY}^{2-}] \approx 0.0150$

$$[\text{Ni}^{2+}] = [\text{Y}^{4-}] + [\text{HY}^{3-}] + [\text{H}_2\text{Y}^{2-}] + [\text{H}_3\text{Y}^-] + [\text{H}_4\text{Y}] = C_T$$

$$K'_{\text{NiY}} = \frac{[\text{NiY}^{2-}]}{[\text{Ni}^{2+}]c_T} = \frac{[\text{NiY}^{2-}]}{[\text{Ni}^{2+}]^2} = \alpha_4 K_{\text{NiY}}$$

$$(a) \text{ pH } 3.0 \rightarrow \alpha_4 = 2.5 \times 10^{-11}, \quad \frac{0.0150}{[\text{Ni}^{2+}]^2} = 2.5 \times 10^{-11} \times 4.2 \times 10^{18} = 1.05 \times 10^8$$

$$[\text{Ni}^{2+}] = \sqrt{1.43 \times 10^{-10}} = 1.2 \times 10^{-5} \text{ M}$$

$$(b) \text{ pH } 8.0 \rightarrow \alpha_4 = 5.4 \times 10^{-3}, \quad K'_{\text{NiY}} = 5.4 \times 10^{-3} \times 4.2 \times 10^{18} = 2.27 \times 10^{16}$$

$$[\text{Ni}^{2+}] = \sqrt{0.0150 / (2.27 \times 10^{16})} = 8.1 \times 10^{-10} \text{ M}$$

Example 9.3: Calculate the conc. of Ni^{2+} in a solution prepared by mixing 50.0 mL of 0.0300 M Ni^{2+} with 50.0 mL of 0.0500 M EDTA. The mixture is buffered to a pH of 3.00.

Solution:

$$C_{\text{NiY}^{2-}} = 50.0 \times 0.0300 / 100 = 0.0150 \text{ M}$$

$$c_{\text{EDTA}} = \frac{(50.0 \times 0.0500) \text{ mmol} - (50.0 \times 0.0300) \text{ mmol}}{100.0 \text{ mL}} = 0.0100 \text{ M}$$

assume $[\text{Ni}^{2+}] \ll [\text{NiY}^{2-}] \rightarrow [\text{NiY}^{2-}] = 0.0150 - [\text{Ni}^{2+}] \approx 0.0150$

$$C_T = 0.0100 \text{ M} \quad K'_{\text{NiY}} = \frac{0.0150}{[\text{Ni}^{2+}]0.0100} = \alpha_4 K_{\text{NiY}}$$

$$[\text{Ni}^{2+}] = \frac{0.0150}{0.0100 \times 1.05 \times 10^8} = 1.4 \times 10^{-8} \text{ M}$$

EDTA Titration Curves

If, in the titration of a strong acid, pH is plotted against the volume of the solution of the strong base added, a point of inflexion occurs at the equivalence point. Similarly, in the EDTA titration, if pM (negative logarithm of the 'free' metal ion concentration: $\text{pM} = -\log [\text{M}^{n+}]$) is plotted against the volume of EDTA solution added, a point of inflection occurs at the equivalence point; in some instances, this sudden increase may exceed 10 pM units. The general shape of titration curves obtained by titrating 10.0 mL of a 0.01 M solution of a metal ion M with a 0.01 M EDTA solution is shown in Figure 9.3. The apparent stability constants of various metal-EDTA complexes are indicated at the extreme right of the curve. It is evident that the greater the stability constant, the sharper is the end point provided the pH is maintained constant.

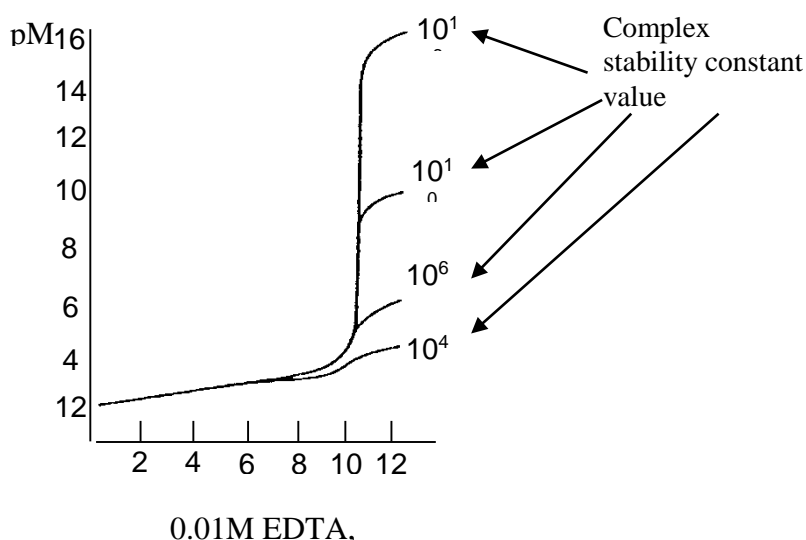


Figure 9.3. EDTA titration curves and the effect of K_{st} (complex stability constant).



Titration curves for 0.1 M Ca^{2+} versus 0.1 M EDTA at pH 7 and pH 10 are shown in Figure 9.4. This figure indicates the effect of pH on apparent stability constants and correspondingly on the shape of the titration curve.

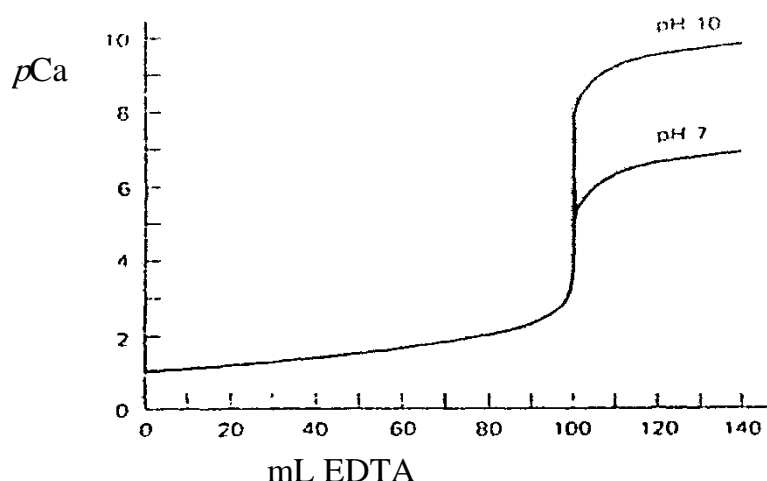


Figure 9.4. Titration curves of Ca^{2+} with EDTA at pH 7 and pH 10.

Titration Methods Employing EDTA

I. Direct Titration: (40 Cations)

In a direct titration, the analyte is titrated with standard EDTA. The analyte is buffered to an appropriate pH at which the conditional formation constant for the metal-EDTA complex is large enough to produce a sharp end point. Since most metal ion indicators are also acid-base indicators, they have different colors at different values of pH. An appropriate pH must be one at which the free indicator has a distinctly different color from the metal-indicator complex.

In many titrations an auxiliary complexing agent, such as ammonia, tartarate, citrate, or triethanolamine, is employed to prevent the metal ion from precipitating in the absence of EDTA. For example, the direct titration of Pb^{2+} is carried out in ammonia buffer at pH 10 in the presence of tartarate, which complexes with the metal ion and does not allow $\text{Pb}(\text{OH})_2$ to precipitate. The lead-tartarate complex must be less stable than the lead-EDTA complex, or the titration would not be feasible.

II. Back Titration:

Used when no suitable indicator is available, when the reaction between analyte and EDTA is slow, or when the analyte forms ppts at the pH required for its titration.

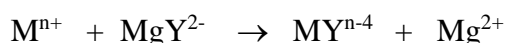
Titrant: EDTA and standard Mg^{2+} or Zn^{2+} solution.

MgEDTA or ZnEDTA complexes must be less stable than analyte-EDTA complexes.

In a back titration, a known excess of EDTA is added to the analyte. The excess EDTA is then titrated with a standard solution of a second metal ion. A back titration is necessary if the analyte precipitates in the absence of EDTA, if it reacts too slowly with EDTA under titration conditions, or if it blocks the indicator. The metal ion used in the back titration should not displace the analyte metal ion from its EDTA complex.

III. Displacement Titration:

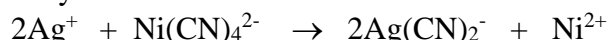
For metal ions that do not have a satisfactory indicator, a displacement titration may be feasible. In this procedure, the analyte usually is treated with excess $\text{Mg}(\text{EDTA})^{2-}$ chelate to displace Mg^{2+} , which is later titrated with standard EDTA.



Hg^{2+} is determined in this manner. The formation constant of $\text{Hg}(\text{EDTA})^{2-}$ must be greater than the formation constant for $\text{Mg}(\text{EDTA})^{2-}$, or else the above reaction will not work.

An interesting application is the titration of calcium. In the direct titration of calcium ions, solochrome black gives a poor endpoint; if magnesium is present, it is displaced from its EDTA complex by calcium, and an improved endpoint results.

Another example of the displacement titration; there is no suitable indicator for Ag^+ . However, Ag^+ will displace Ni^{2+} from the tetracyanonickelate ion:



The liberated Ni^{2+} can then be titrated with EDTA to find out how much Ag^+ was added.



IV. Alkalimetric Titration:

When a solution of disodium ethylenediaminetetra-acetate, $\text{Na}_2\text{H}_2\text{Y}$, is added to a solution containing metallic ions, complexes are formed with the liberation of two equivalents of hydrogen ions:



The hydrogen ions thus set free can be titrated with a standard solution of sodium hydroxide using an acid-base indicator or a potentiometric end-point. Alternatively, an iodate-iodide mixture is added as well as the EDTA solution and the liberated iodine is titrated with a standard thiosulphate solution.

The solution of the metal to be determined must be accurately neutralized before titration; this is often a difficult matter on account of the hydrolysis of many salts and constitutes a weak feature of alkalimetric titration.

V. Indirect titrations (determination of anions):

Anions that form precipitates with certain metal ions may be analyzed with EDTA by indirect titration. For example, sulfate can be analyzed by precipitation with excess Ba^{2+} at pH 1. The BaSO_4 precipitate is filtered and washed. Boiling the precipitate with excess EDTA at pH 10 brings the Ba^{2+} back into solution as $\text{Ba}(\text{EDTA})^{2-}$. The excess EDTA is back-titrated with Mg^{2+} .

Other Methods: Potentiometric Methods, Spectrophotometric Methods.

Masking agent: a complexing agent that reacts selectively with a component from interfering in an analysis.

ex: CN^- for Mg^{2+} and Ca^{2+}

analysis, in the presence of ions- Cd, Co, Cu, Ni, Zn and Pd ions.

Calculation of Titration Results

As an example 9.4, let's calculate the titration curve for 50.0 mL of 5.00×10^{-3} M Cd^{2+} with 0.0100 M EDTA at a pH of 10 and in the presence of 0.0100 M NH_3 . The formation constant for Cd^{2+} -EDTA is 2.9×10^{16} . At the following:

(a) Before adding EDTA (a) After adding 5.00 mL EDTA (c) At equivalence point (d) After adding 30.0 mL EDTA.

Plan:

- pH = 10, some EDTA is present in different forms.
- NH_3 is present: EDTA competes for Cd ions.
- Use α_4 at specific pH and values of $\alpha_{\text{Cd}^{2+}}$ at specific conc. of NH_3 (found in Tables).

Calculations:

Calculate The Conditional Formation Constant:

$\alpha_{\text{Y}^{4-}}$ is 0.35 at a pH of 10, and $\alpha_{\text{Cd}^{2+}}$ is 0.0881 when the concentration of NH_3 is 0.0100 M. Using these values, we calculate that the conditional formation constant is:

$$\begin{aligned} K_f' &= \alpha_{\text{Y}^{4-}} \times \alpha_{\text{Cd}^{2+}} \times K_f \\ &= (0.35) (0.0881) (2.9 \times 10^{16}) = 8.9 \times 10^{14} \end{aligned}$$

Calculate The Volume of EDTA At Equivalence Point:

Because K_f' is so large, we treat the titration reaction as though it proceeds to completion. The first task in calculating the titration curve is to determine the volume of EDTA needed to reach the equivalence point. At the equivalence point, we know that

$$\text{Moles EDTA} = \text{moles Cd}^{2+} \quad (\text{because the mole ratio is 1:1})$$

or

$$M_{\text{EDTA}} V_{\text{EDTA}} = M_{\text{Cd}} V_{\text{Cd}}$$

Solving for the volume of EDTA



$$V_{\text{EDTA}} = \frac{M_{\text{Cd}} V_{\text{Cd}}}{M_{\text{EDTA}}}$$

$$\therefore V_{\text{EDTA}} = \frac{(5.00 \times 10^{-3} \text{ M})(50.0 \text{ mL})}{0.0100 \text{ M}} = 25.0 \text{ mL}$$

shows us that 25.0 mL of EDTA is needed to reach the equivalence point.

(a) Before adding EDTA:

To calculate the concentration of free Cd^{2+} we use equation 9.14.

$$[\text{Cd}^{2+}] = \alpha_{\text{Cd}^{2+}} \times C_{\text{Cd}}$$

$$= (0.0881) (5.00 \times 10^{-3}) = 4.405 \times 10^{-4} \text{ M}$$

Thus, pCd is

$$\text{pCd} = -\log [\text{Cd}^{2+}] = -\log (4.405 \times 10^{-4}) = 3.36$$

(b) After adding 5.00 mL EDTA

Before the equivalence point, Cd^{2+} is in excess, and pCd is determined by the concentration of free Cd^{2+} remaining in the solution. Not all the untitrated Cd^{2+} is free (some are complexed with NH_3), so we will have to account for the presence of NH_3 .

For example, after adding 5.0 mL of EDTA, the total concentration of Cd^{2+} is

$$C_{\text{Cd}} = \frac{\text{moles excess Cd}^{2+}}{\text{total volume}} = \frac{M_{\text{Cd}} V_{\text{Cd}} - M_{\text{EDTA}} V_{\text{EDTA}}}{V_{\text{Cd}} + V_{\text{EDTA}}}$$

$$C_{\text{Cd}} = \frac{(5.00 \times 10^{-3} \text{ M})(50.0 \text{ mL}) - (0.0100 \text{ M})(5.0 \text{ mL})}{50.0 \text{ mL} + 5.0 \text{ mL}} = 3.64 \times 10^{-3} \text{ M}$$

To calculate the concentration of free Cd^{2+} we use the equation:

$$\alpha_4 = \frac{[\text{Y}^{4-}]}{c_T}$$

$$[\text{Cd}^{2+}] = \alpha_{\text{Cd}^{2+}} \times C_{\text{Cd}}$$

$$= (0.0881) (3.64 \times 10^{-3} \text{ M})$$

$$= 3.21 \times 10^{-4} \text{ M}$$

Thus, pCd is

$$\text{pCd} = -\log [\text{Cd}^{2+}] = -\log (3.21 \times 10^{-4}) = 3.49$$

(c) At equivalence point:

At the equivalence point, all the Cd^{2+} initially present is now present as CdY^{2-} .

The concentration of Cd^{2+} , therefore, is determined by the dissociation of the CdY^{2-} complex. To find pCd we must first calculate the concentration of the complex.

$$[\text{CdY}^{2-}] = \frac{\text{initial moles Cd}^{2+}}{\text{total volume}} = \frac{M_{\text{Cd}} V_{\text{Cd}}}{V_{\text{Cd}} + V_{\text{EDTA}}}$$

$$[\text{CdY}^{2-}] = \frac{(5.00 \times 10^{-3} \text{ M})(50.0 \text{ mL})}{50.0 \text{ mL} + 25.0 \text{ mL}} = 3.33 \times 10^{-3} \text{ M}$$

Letting the variable x represent the concentration of Cd^{2+} due to the dissociation of the CdY^{2-} complex, we have



$$K_f'' = \frac{[\text{CdY}^{2-}]}{C_{\text{Cd}}C_{\text{EDTA}}} = \frac{3.33 \times 10^{-3} - x}{(x)(x)} = 8.94 \times 10^{14}$$

$$\therefore x = C_{\text{Cd}} = 1.93 \times 10^{-9} \text{ M}$$

Once again, to find the $[\text{Cd}^{2+}]$ we must account for the presence of NH_3 ; thus

$$[\text{Cd}^{2+}] = \alpha_{\text{Cd}^{2+}} \times C_{\text{Cd}}$$

$$= (0.0881) (1.93 \times 10^{-9} \text{ M})$$

$$= 1.70 \times 10^{-10} \text{ M}$$

giving pCd as 9.77.

(d) After adding 30.0 mL EDTA:

After the equivalence point, EDTA is in excess, and the concentration of Cd^{2+} is determined by the dissociation of the CdY^{2-} complex. Examining the equation for the complex's conditional formation constant, we see that to calculate C_{Cd} we must first calculate $[\text{CdY}^{2-}]$ and C_{EDTA} . After adding 30.0 mL of EDTA,

these concentrations are:

$$[\text{CdY}^{2-}] = \frac{\text{initial moles Cd}^{2+}}{\text{total volume}} = \frac{M_{\text{Cd}} V_{\text{Cd}}}{V_{\text{Cd}} + V_{\text{EDTA}}}$$

$$[\text{CdY}^{2-}] = \frac{(5.00 \times 10^{-3} \text{ M})(50.0 \text{ mL})}{50.0 \text{ mL} + 30.0 \text{ mL}} = 3.13 \times 10^{-3} \text{ M}$$

$$C_{\text{EDTA}} = \frac{\text{moles excess EDTA}}{\text{total volume}} = \frac{M_{\text{EDTA}} V_{\text{EDTA}} - M_{\text{Cd}} V_{\text{Cd}}}{V_{\text{Cd}} + V_{\text{EDTA}}}$$

$$C_{\text{EDTA}} = \frac{(0.0100 \text{ M})(30.0 \text{ mL}) - (5.00 \times 10^{-3} \text{ M})(50.0 \text{ mL})}{50.0 \text{ mL} + 30.0 \text{ mL}} = 6.25 \times 10^{-4} \text{ M}$$

Substituting these concentrations into complex's conditional formation constant equation and solving for C_{Cd} gives

$$\frac{[\text{CdY}^{2-}]}{C_{\text{Cd}}C_{\text{EDTA}}} = \frac{3.13 \times 10^{-3}}{C_{\text{Cd}}(6.25 \times 10^{-4})} = 8.94 \times 10^{14}$$

$$C_{\text{Cd}} = 5.60 \times 10^{-15} \text{ M}$$

Thus,

$$[\text{Cd}^{2+}] = \alpha_{\text{Cd}^{2+}} \times C_{\text{Cd}}$$

$$= (0.0881) (5.60 \times 10^{-15} \text{ M})$$

$$= 4.93 \times 10^{-16} \text{ M}$$

and pCd is 15.31. Figure 9.5 and Table 9.4 show additional results for this titration.

Table 9.15 Data for Titration of $5.00 \times 10^{-3} \text{ M}$ Cd^{2+} with 0.0100 M EDTA at a pH of 10.0 and in the Presence of 0.0100 M NH_3

Volume of EDTA (mL)	pCd
0.00	3.36
5.00	3.49
10.00	3.66
15.00	3.87
20.00	4.20
23.00	4.62
25.00	9.77
27.00	14.91
30.00	15.31
35.00	15.61
40.00	15.78
45.00	15.91
50.00	16.01

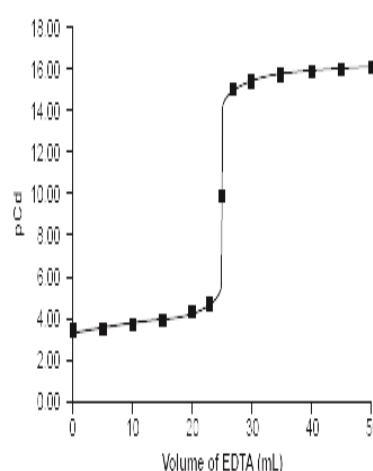


Figure 9.27 Complexometric titration curve for 50.0 mL of $5.00 \times 10^{-3} \text{ M}$ Cd^{2+} with 0.0100 M EDTA at a pH of 10.0 in the presence of 0.0100 M NH_3 .



The Determining of Water Hardness

Water "hardness": the capacity of cations (Ca, Mg, and heavy-metal ions) in the water to replace the Na or K ions in soaps and form sparingly soluble products.

Hardness expressed in terms of the conc. of CaCO_3 equivalent to the total conc. of all multivalent cations in the sample.

Titrant: EDTA, pH: 10 \rightarrow NH_3 buffer

Indicator: Calmagite or EBT + Mg-EDTA, End-point color: pink-red \rightarrow blue

Calculation of Titration Results

Conc. of EDTA titrant expressed in

(a). **Molarity (M)**

$$\text{EDTA (M)} = \frac{\text{mmole of EDTA}}{\text{mL}} = \frac{\text{mole of EDTA}}{\text{L}}$$

(b). **Titer** or EDTA for a certain ion or compound

$$\text{EDTA titer} = \frac{\text{mg of species}}{\text{mL EDTA}} = \frac{\text{g of species}}{\text{L EDTA}}$$

Example 9.5: Exactly 0.1001 g of pure CaCO_3 (100.1 g/mol) is dissolved in 100.0 mL of water.

A 10.0-mL aliquot is titrated with 9.00 mL of EDTA. Calculate the molarity of the EDTA and its titer for CaCO_3

Solution:

$$\text{M of EDTA} = \frac{100.1 \text{ mg} \times \frac{10}{100} \times \frac{1 \text{ mmol}}{100.1 \text{ mg}}}{9.00 \text{ mL}} = 0.0111 \text{ M}$$

$$\text{EDTA titer} = \frac{100.1 \text{ mg} \times \frac{10}{100}}{9.00 \text{ mL}} = 1.112 \text{ mg/mL}$$

Example 9.6: A 50.00-mL water sample requires 12.00 mL of 0.0100 M EDTA.

Calculate the hardness of this sample as ppm CaCO_3 (100.1 g/mol).

Solution: $\text{mg CaCO}_3 = (12.00 \text{ mL}) (0.0100 \text{ M}) (100.1 \text{ mg /mmole}) = 12.01 \text{ mg}$
 $\text{ppm CaCO}_3 = 12.01 \text{ mg} / 0.0500 \text{ L} = 240.2 \text{ ppm}$