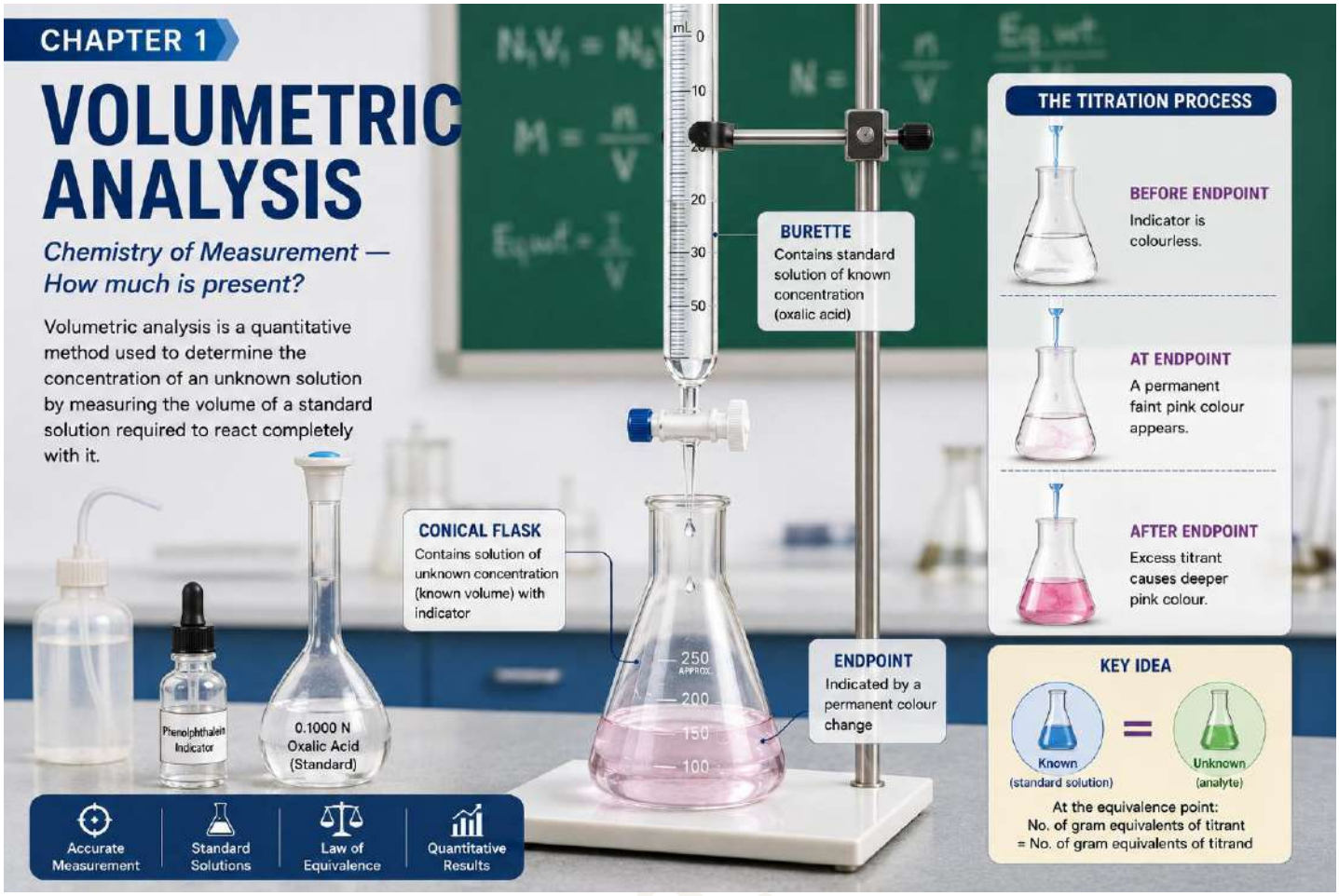

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🎯 Learning Outcomes

After the completion of the lesson, the students should be able to

1. Define and explain the terms volumetric and gravimetric analysis.
2. Define and calculate equivalent weights of (elements, acids, bases, salts, oxidising and reducing agents)
3. Define, express, and calculate the concentration of solutions in terms of percentage, g/l, molarity, molality, normality, formality, ppm, and ppb
4. Explain and apply the concept of the law of equivalence and the normality equation in chemical calculations.
5. Define, describe, explain, and distinguish primary and secondary standard substances.
6. Explain different types of titrations and their applications.
7. Define terms related to volumetric analysis, such as standard solution, normality factor, equivalence point, endpoint, indicator, and redox titration, etc.
8. Solve numerical and higher-level problems related to concentrations, dilutions, and titrations

Chemical analysis

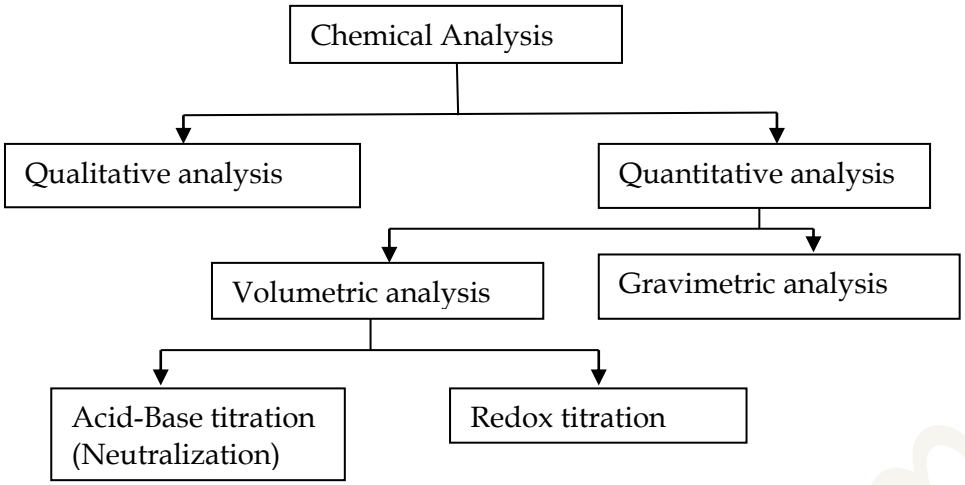
Imagine a doctor prescribing a medicine dose, a water-treatment plant monitoring fluoride levels, or a food scientist checking the acidity of fruit juice. In each case, it is important to know not only which substances are present but also how much of each is present.

This is the purpose of chemical analysis—the systematic process of identifying substances and determining their quantities.

One of the most important methods of quantitative chemical analysis is volumetric analysis, which uses the volume of a solution of known concentration to determine the concentration of another solution. In this chapter, you will learn how to determine unknown concentrations accurately using common laboratory apparatus.

Chemical analysis is of two types

1. **Qualitative analysis** mainly refers to detecting ions or radicals, generally in salts.
2. **Quantitative analysis** determines the quantity of a particular constituent present in a substance.



Qualitative Analysis

- Identifies *what* substances are present e.g., detection of ions, radicals

Quantitative Analysis

- Determines *how much* is present e.g., estimation of iron, chloride ions

Gravimetric and Volumetric analysis

Gravimetric Analysis:

- **Gravimetric analysis is a quantitative analytical method in which the amount of a substance is determined from an accurately measured mass.**
- In precipitation gravimetry, the substance is converted into a suitable precipitate, which is filtered, dried or ignited, and weighed
- The substance to be analysed is converted into an insoluble precipitate.

Involves: Precipitation → Filtration → Drying → Weighing

- Simple and inexpensive method.

e.g. $BaCl_2 + H_2SO_4 \rightarrow BaSO_4 \downarrow + 2\ HCl$

Volumetric Analysis: Volumetric analysis is a method of determining a solution's concentration by finding the volume which exactly reacts with a fixed volume of another standard solution.

Method	Based on	Process	Example
Gravimetric analysis	Mass measurement	precipitate → filter → dry → weigh	$BaSO_4$ precipitate from $BaCl_2 + H_2SO_4$
Volumetric analysis	Volume measurement	Titration using a burette & a pipette	Acid-base titration (HCl + NaOH)

Equivalent weight

Equivalent weight is a concept that tells us how much of a substance reacts with a standard reference amount. It is a bridge between mass and chemical reactivity.

1. Equivalent weight of an element:

It is the number of parts by weight of that element which combines with or displaces directly or indirectly 1.008 parts by weight of hydrogen, 8 parts by weight of oxygen, or 35.5 parts by weight of chlorine.

Equivalent weight is expressed in g/equiv. In numerical calculations, it is often treated simply as a numerical value without a unit.

The relation between Equivalent weight (E), atomic mass(A), and Valency (V) of an element

Consider an element with equivalent weight 'E', atomic mass 'A', and valency 'V'.

By the definition of valency,
An atom of the element combines with V atoms of hydrogen.
Or, V atoms of hydrogen combine with one atom of the element
Or, V x 1.008 parts by weight of H combines with A parts by weight of the element.
Or, 1.008 parts by wt. of H combines with A/V parts by wt. of the element.
Now, from the definition of equivalent wt.,

$$\text{Equivalent wt. of an element (E)} = \frac{\textbf{Atomic wt of the element (A)}}{\textbf{Valency (V)}}$$

2. Equivalent weight of compounds:

a. **Equivalent weight of acid: Equivalent weight of an acid is defined as the number of parts by weight of an acid that can supply 1.008 parts by weight of hydrogen ions**. In other words, it is the ratio of the acid's molecular mass to its basicity.

$$\text{Equivalent wt. of an acid} = \frac{\text{molecular wt}}{\text{basicity}}$$

Basicity: no. of moles of H^+ ions that 1 mole of the acid can furnish.

e.g.;

Acid	Basicity	Molecular wt.	Eq. wt.	Acid	Basicity	Molecular wt.	Eq. wt.
H_2SO_4	2	98	98/2 = 49	$(COOH)_2.H_2O$	2	126	126/2 = 63

Now you try:
Calculate the molecular weights, find basicity and determine the equivalent weights of:
CH_3COOH, HCl, HNO_3, and H_3PO_3

b. **Equivalent weight of base: Equivalent weight of a base is defined as the number of parts by weight of a base that can neutralise 1 gram equivalent of acid.** It is the ratio of molecular mass to acidity.

$$\text{Equivalent wt. of a base} = \frac{\text{molecular wt.}}{\text{acidity}}$$

Acidity: no. of moles of H^+ ions that 1 mole of the base can neutralise

e.g.,

Base	Acidity	Molecular wt.	Eq. wt.	Base	Acidity	Molecular wt.	Eq. wt.
NaOH	1	40	40/1=40	CaO	2	56	56/2=28

Now you try:
Calculate the equivalent weights of: $Ca(OH)_2$, NH_4OH, KOH, and CaO

c. **Equivalent weight of salt:** Equivalent weight of salt is defined as the ratio of the molecular weight of salt to the total no. of +ve or –ve charges.

$$\text{Equivalent wt. of a salt} = \frac{\text{molecular wt}}{\text{total +ve or −ve charge present in the cation or anion of the salt.}}$$

Salt	+ ve or – ve charge	Molecular wt.	Eq. wt.
NaCl	1	58.5	58.5/1 = 58.5
$Al_2(SO_4)_3$	6	342	342/6 = 57

Now you try:
Calculate the equivalent weights of the salts: Na_2CO_3, $CaCO_3$, KCl, $AlCl_3$ and CaO

d. **Equivalent weight of oxidising and reducing agents:** Equivalent weight of oxidising and reducing agents is the ratio of the molecular weight to the total change in oxidation number (total electrons lost or gained) during the chemical reaction.

$$\text{Equivalent wt. of the oxidizing agent or reducing agent} = \frac{molecular\ wt}{total\ change\ in\ oxidation\ number\ (ON)}$$

Here, the denominator (Basicity, Acidity, Total Charge, or ΔON) is collectively called the **n-factor**. **Equivalent weight depends on the particular chemical reaction.** It is calculated by dividing the molar mass by the appropriate n-factor for that reaction:

equivalent wt. = molecular wt./n-factor

a. **Equivalent weight of $KMnO_4$**:

i) In an acidic medium:

$$2\ KMnO_4 + 3\ H_2SO_4 \rightarrow K_2SO_4 + 2\ MnSO_4 + 3\ H_2O + 5\ [O]$$

(+7 in $KMnO_4$; +2 in $MnSO_4$)

$$\text{Eq. wt. of } KMnO_4 = \frac{molecular\ wt\ of\ KMnO4}{total\ change\ in\ oxidation\ number\ (ON)} = \frac{158}{(7-2)} = 31.6$$

ii) In basic medium:

$$2\ KMnO_4 + 2\ KOH \rightarrow 2\ K_2MnO_4 + H_2O + [O]$$

[Copy the above reaction, show all the oxidation numbers, then calculate the total change in oxidation number per molecule.]

$$\text{Eq. wt. of } KMnO_4 = \frac{molecular\ wt\ of\ KMnO4}{total\ change\ in\ oxidation\ number\ (ON)} = \frac{158}{(7-6)} = 158$$

iii) In neutral medium:

$2\ KMnO_4 + H_2O \rightarrow 2\ MnO_2 + 2\ KOH + 3\ [O]$ [Calculate yourself from the given reaction.]

❖ Equivalent weight of reductants: $C_2H_2O_4$, $FeSO_4$, Mohr's salt ($FeSO_4.(NH_4)_2SO_4.6H_2O$) etc.

a. Equivalent weight of oxalic acid:

$H_2C_2O_4 \rightarrow 2\ CO_2 + 2\ H^+ + 2\ e^-$

$$\text{Eq. wt. of oxalic acid} = \frac{\text{molecular wt of oxalic acid}}{\text{total change in oxidation number (ON)}} = \frac{90}{2} = 45$$

For oxalic acid crystals – $H_2C_2O_4.2H_2O$

$$\text{Eq. wt. of oxalic acid crystal} = \frac{\text{molecular wt of oxalic acid crystals}}{\text{total change in oxidation number (ON)}} = \frac{126}{2} = 63$$

b. Equivalent weight of Mohr's salt:

In Mohr's salt, the reducing agent is Fe^{2+}, which is oxidised to Fe^{3+}as:

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

Or, $Fe^{+2} \rightarrow Fe^{+3} + e^-$

In other words, Fe^{+2} loses one electron; the n-factor for Mohr's salt is 1.

$$\text{Eq. wt. of Mohr's salt} = \frac{\text{molecular wt of Mohr's salt}}{\text{total change in oxidation number (ON)}} = 392/1 = 392$$

Number of gram equivalents

Equivalent weight is mainly used in stoichiometric and volumetric calculations; in practice, we generally work with gram equivalents.

Gram equivalents is the ratio of the weight of the substance in grams to the equivalent weight.

$$\textbf{Number of gram equivalents} = \frac{\textbf{weight in gram}}{\textbf{equivalent weight}}$$

💡 Gram equivalents connect mass to chemical reactivity.

Worked Example

How many gram equivalents are in 20 g of NaOH?

Solution:

Molecular wt. of NaOH = 23+16+1 = 40; acidity = 1 (no. of OH-ions in 1 molecule)

Equivalent weight of NaOH = 40/1 = 40

Gram equivalents = 20 ÷ 40 = **0.5 gram equivalents**

Concentrations

- Concentration is the amount of a solute present in a definite quantity of the solution.
- A solution of known concentration is called a **standard solution**, whereas a solution of unknown concentration is called an **unknown solution**.
- The concentration of a solution is usually expressed in terms of Normality or Molarity in volumetric analysis. However, the concentration can also be expressed in percentage, grams per litre, formality, mole fraction, etc.

a. Gram per litre

It is defined as the amount of a solute in grams present in one litre of solution.

$$g/L = \frac{\text{mass of solute (g)}}{\text{volume of solution (L)}} = \frac{\text{mass(wt.) of solute (g)}}{\text{vol.of solution (mL)}} \times 1000$$

b. Normality

No. of gram equivalents of solute dissolved in a litre of solution.

Normality = no. of gram equivalents/ volume in litres

Number of gram equivalents = mass in grams/ equivalent wt.

$$\text{Normality} = \frac{\text{mass of solute in gram x 1000}}{\text{equivalent wt of solute x vol.of solution in ml}}$$

$$\text{Wt. in gram (of solute)} = \frac{\text{NEV}}{1000}$$

This last formula is useful to prepare standard solutions.

When one gram equivalent weight of solute is present in one litre of solution, it is called a **Normal** solution. (1N or N solution)

When half a gram equivalent weight of solute is present in one litre of solution, it is called a **SemiNormal** solution. (0.5N solution)

Try to define **Decinormal (0.1N or N/10)** and **Centinormal** solutions correspondingly.

Worked Example

1. What mass of Na_2CO_3 is required to make 50cc of its seminormal solution? 2

Solution:

$Na_2CO_3 + 2\,HCl \rightarrow 2\,NaCl + H_2O + CO_2$

Na_2CO_3 can be considered a base. In the above neutralisation reaction, we can see that 1 mole of it neutralises 2 moles of H^+ ions. Hence, its acidity is 2.

Now,

vol in ml = 50 ml(cc) normality = 0.5N

molecular wt. = 23 x 2 +12+16x 3= 106 amu eqv wt. = molecular wt./ acidity = 106/2 = 53

no. of gm eqvs = wt. in gm/53

We know,

normality = no of gram equivalents x 1000/ volume in ml

0.5 = wt. in g/53 x1000/50

wt. in g = 0.5 x 50 x 53/1000 = 1.325 g

Or, use the following formula directly,

N = wt. in g/E x (1000/ V) OR, Wt. in gram (of solute) = $\frac{\text{NEV}}{1000}$

Normality Factor (f):

Normality factor (f) tells how the actual concentration of a prepared solution compares with its intended concentration.

The ratio of the weight taken of the solute to the weight to be taken is called the normality factor.

Mathematically,

$$\text{Normality factor} = \frac{\text{wt taken}}{\text{wt to be taken}}$$

Hence, **Actual Normality = Given Normality × Normality factor**

It **saves time** by eliminating the need for exact weighing while giving the actual concentration.

Worked Example

To prepare N/10 Na_2CO_3, you need 5.30 g but actually weigh 5.36 g.

f = 5.36 ÷ 5.30 = 1.011

Actual normality = 0.1 × 1.011 = **0.1011 N**

c. Molarity (moles per litre)

A solution's **Molarity (M)** is the number of moles of solute dissolved in one litre of solution.

[Write the formula of molarity and express it in different useful forms, with the help of the corresponding formula of normality]

If the solution contains 1 mole, 1 gram-mole, or 1 gram-molecular weight of solute in 1 litre of its solution, then it is called a **molar solution**, or 1 M or M solution.

[Define **semimolar, decimolar** and **centimolar** solutions.**]**

Relation between Normality and Molarity

We have,

$$\text{Normality} = \frac{\text{wt in gram}}{\text{volume in litres x equivalent wt.}} \quad \text{Or, } \boxed{g/L = \text{Normality} \times \text{Eq. weight}} \quad (1)$$

Similarly,

$$\text{Molarity} = \frac{\text{wt in gram}}{\text{volume in litres x molecular wt.}} \quad \text{Or, } \boxed{g/L = \text{Molarity} \times \text{Molecular Weight}} \quad (2)$$

From equations (1) and (2)

$$\boxed{\text{Normality} \times \text{eq. weight} = \text{Molarity} \times \text{mol. Weight}} \ldots\ldots.(3)$$

But, Equivalent weight = $\frac{molecular\ weight}{acidity\ or\ basicity}$

Or, Molecular weight = eq. weight × acidity or basicity (4)

From equations (3) and (4),

Normality × eq. weight = molarity × eq. weight × acidity or basicity

Or, $\boxed{\text{Normality} = \text{Molarity} \times \text{acidity or basicity}}$…… (5) for acids and bases

For salt,

Normality = Molarity × No. of +ve or –ve charges……(6)

For oxidising and reducing agents,

Normality = Molarity × Total change in O.N……(7)

Think

Which is more concentrated? 1 M HCl or 2 M HCl; Obviously 2 M.

Then:

Which is more concentrated? 1 M H_2SO_4 or 1 N H_2SO_4

d. Percentage

- % solution (w/w) = $\frac{wt.of\ solute\ in\ gram}{wt.of\ solution\ in\ gm}\ x\ 100\ \%$
- % solution (v/v) = $\frac{vol.of\ solute\ in\ ml}{volume\ of\ solution\ in\ ml}\ x\ 100\ \%$
- % solution (w/v) = $\frac{wt.\ of\ solute\ in\ gram}{volume\ of\ solution\ in\ ml}\ x\ 100\ \%$

Gram/L = Percentage x 10

(This formula is applicable for %(w/v) or dilute solutions (density ~ 1 g/mL), & mostly percentage is given as w/v)

Worked Example

2. Calculate the Molarity of a 5% H_2SO_4 solution. **2**

Solution

5% (w/v) H_2SO_4 means 5 g H_2SO_4 in 100 mL solution. So,

Given,

wt. of H_2SO_4 = 5 g; vol. of solution = 100 ml

molecular wt. of H_2SO_4 = 1 x 2 + 32 + 16 x 4= 98

We know,

Molarity = no of moles x 1000 /vol in mL

Molarity = wt. in grams/molecular wt. x 1000 /vol in mL

= 5 /98 x 1000/100 = 5/98 x 10 = 50/98 = 0.5102 M

Normality = % x density or specific gravity x 10/eqv. Wt.

molarity = % x density x 10/molecular wt

e. Molality

Moles of solute per kg(1000g) of solvent. Unlike molarity, molality doesn't change with temperature.

$$\text{molality} = \frac{\textbf{no of moles of solute}}{\textbf{mass of solvent in kg}}$$

Molarity depends on volume, and volume can change with temperature. Molality depends on the mass of solvent, which does not appreciably change with temperature.

f. Formality

$$\text{Formality} = \frac{\textbf{no of gram formula units}}{\textbf{volume in litre}}$$

Since ionic compounds like NaCl do not exist as discrete molecules in solution, we use 'formula weight' instead of 'molecular weight', and its concentration is expressed as Formality.

g. ppm *(parts per million)*

ppm = (mass solute/mass solution) × 10^6

h. ppb *(parts per billion)*

ppb = (mass solute/mass solution) × 10^9

ppm and ppb units are used for very dilute solutions, such as pollutants in water or trace metals in blood.

Did You Know?

The safe limit for arsenic in drinking water, as set by WHO, is 10 ppb (micrograms per litre). Volumetric and instrumental methods help analysts measure these incredibly small concentrations — protecting millions of people from arsenic poisoning.

i. **Mole fraction**

$$\chi_A = \frac{nA}{nA+nB+\cdots}$$

🔵 Most important concentration units: Molarity, Normality, %, g/L

Primary & secondary standard Substances & solutions

❖ Standard solution:

A solution of known concentration is called the standard solution. It is of two types;

1. Primary standard solution:

The solution whose concentration is known and prepared by dissolving a suitable amount of **primary standard substance** in a solvent of definite volume is called a primary standard solution.

E.g., N/10 Oxalic acid solution, 1N Mohr's salt solution, N/2 Na_2CO_3 solution, etc.

2. Secondary standard solution:

The solution whose concentration is known by standardising it with the primary standard solution is called the secondary standard solution.

E.g., N/10 HCl solution, N/20 H_2SO_4 solution, N/10 $KMnO_4$ solution etc.

NaOH, HCl, and H_2SO_4 are NOT primary standards. NaOH absorbs CO_2 and moisture from the air; HCl and H_2SO_4 fumes make accurate weighing impossible

Requirements for a Primary Standard Substance:

- available readily in a very high **purity**.
- **stable** (not reactive to the atmosphere), **non-hygroscopic**
- The composition of the substance should not change in the solid state or solution state for a sufficiently long time.
- It should have a **high equivalent wt./molecular wt**., so that the relative weighing error is minimum.
- **Non-toxic and readily soluble** in the given solvent under the employed conditions.

Examples: Na_2CO_3, $(COOH)_2.2H_2O$, Mohr's salt $FeSO_4.(NH_4)_2SO_4.6H_2O$

A standard Na_2CO_3 solution is used to standardise HCl because HCl is not a primary standard. Oxalic acid is used to standardise $KMnO_4$.

⭐ **Remember**

Primary standard → weigh accurately → prepare solution directly.
Secondary standard → concentration determined by standardisation.

Law of equivalence and Normality equation

Usually, the concentration of the given solution is expressed in terms of Normality.

The volume and strength of a given solution can be mutually changed. If the volume is decreased, the strength must be increased proportionally, and vice versa. (Volume and Normality of the same solution are reciprocals of each other) E.g.;

100 ml of 1N HCl = 1 ml of 100N HCl
= 10 ml of 10N HCl
= 1000 ml of 0.1N HCl So, X ml of YN solution = (X.Y) ml of 1N solution

An equal volume of acid solution neutralises an equal volume of a basic solution of the same strength.
(1 gram equivalent of an acid solution can neutralise 1 gram equivalent of alkali solution)

E.g.; 1 gm. Eq. of HCl = 1 gm. Eq. of NaOH
35.5 gm of HCl = 40 gm. Of NaOH
1000 ml of 1N HCl = 1000 ml of 1N NaOH
1 ml of 1N HCl = 1 ml of 1N NaOH

Law of equivalence: This law states that the 1 g equivalent weight of one substance reacts completely with the 1 g equivalent weight of another. E.g., 36.5 g of HCl reacts completely with 40 g of NaOH.

At the equivalence point,

No. of gram equivalents of acid = no. of gram equivalents of base

We know that

Normality = no. of gram equivalents/volume in litres

So,

No. of gm eqv. = vol. in liter x normality

Therefore,

vol. of acid in litres x Normality of acid = vol. of base in litres x Normality of base

$$V_1S_1 = V_2S_2$$

Where,

V_1 = Volume of acid N_1 or S_1 = Strength of acid
V_2 = Volume of alkali N_2 or S_2 = Strength of alkali

This equation is called the **Normality equation**.

A critical Point to note for Numericals

The equation **$M_1V_1 = M_2V_2$ applies to dilution problems (not titration).**

In titration, use $N_1V_1 = N_2V_2$. In dilution, use $M_1V_1 = M_2V_2$ (or $N_1V_1 = N_2V_2$).

DO NOT CONFUSE

Dilution	Titration
No chemical reaction	Chemical reaction occurs
Same solute	Usually two reacting substances
$M_1V_1=M_2V_2$	$N_1V_1=N_2V_2$
Concentration changes	Unknown concentration is determined

Titration

Titration is a technique in which a solution of known concentration (the **titrant**) is carefully added from a burette to a measured volume of another solution (the **titrand**) in a conical flask until the completion of the reaction (**endpoint**), which is signalled by a colour change of an **indicator**.
The process is repeated until **concurrent** (more accurately called **concordant**) readings are obtained.

- ✓ **Titrant:** A solution, generally taken in a burette.
- ✓ **Titrand:** A solution, generally taken in a conical flask. (In a typical titration, the titrant has a known concentration and the titrand has an unknown concentration.)
- ✓ **Indicator**: A substance added to show the completion of a reaction by colour change.
- ✓ **Endpoint:** Completion of titration/reaction as indicated by the indicator.
- ✓ **Concurrent (concordant) reading:** The two or more similar consecutive readings obtained during titration.

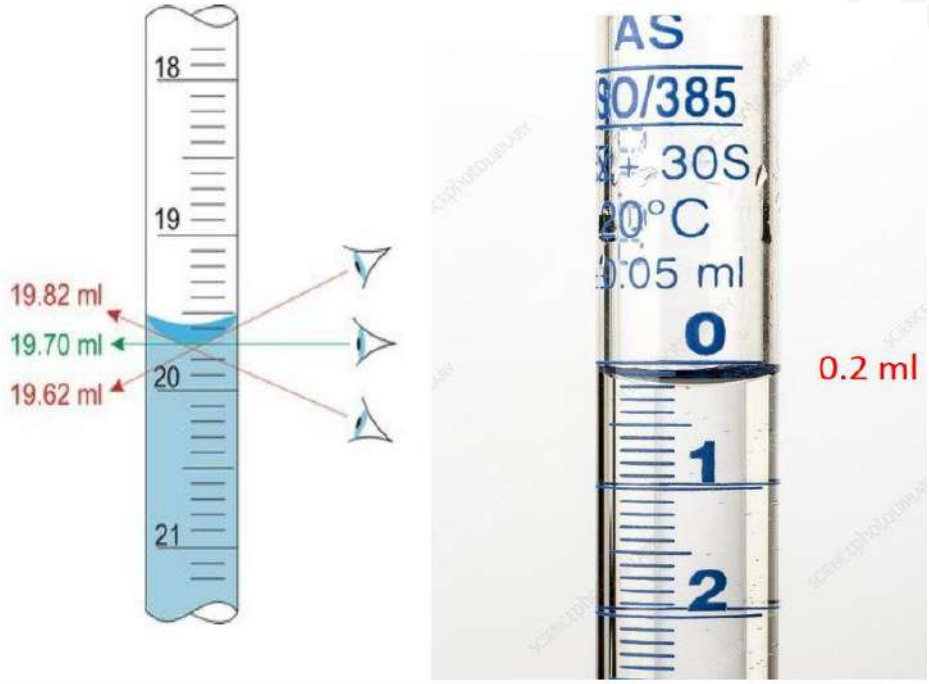


Figure: Correct way of taking a reading

Types of Titrations:

1. Acid-Base titration:

- A titration involving a reaction between an acid and a base.
- Used for determining the concentration of an acid by titrating it against a standard alkali solution and vice versa.
  - **Acidimetry:** Determining acid strength using a standard alkali.
  - **Alkalimetry:** Determining alkali strength using a standard acid.

E.g.; $NaOH + HCl \rightarrow NaCl + H_2O$

$Na^+ + OH^- + H^+ + Cl^- \rightarrow Na^+ + Cl^- + H^+ + OH^-$

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

2. Redox titration:

Involves oxidation & reduction (electron transfer) reactions. Here, one species loses an electron; another species gains it.
If the colour change of one of the reactants takes place at the endpoint, it's called a **self-indicator**.

E.g., the reaction between acidified $KMnO_4$ and oxalic acid solution, where $KMnO_4$ acts as a self-indicator (the pink colour of $KMnO_4$ gets discharged)

$$KMnO_4 + H_2SO_4 + (COOH)_2 \rightarrow K_2SO_4 + MnSO_4 + CO_2 + H_2O$$
(Pink) (Colourless)

The endpoint is indicated by the appearance of a permanent pale pink colour due to a slight excess of $KMnO_4$.

$KMnO_4$–Oxalic Acid Titration- an overview

Type	Redox	**Indicator**	$KMnO_4$ (self-indicator)
Titrant	$KMnO_4$	**Endpoint**	Permanent pale pink
Titrand	Oxalic acid (primary standard)	**n-factor of $KMnO_4$**	5 (ON change of Mn: 7→2)
Medium	Acidic	**Equivalent weight**	158/5 = **31.6 g/equiv**
Acid	Dilute H_2SO_4	**Warming**	To increase reaction rate

3. **Iodimetry:** direct titration using iodine as the titrant.
4. **Iodometry:** indirect determination of an oxidising agent by liberating iodine from iodide and titrating the iodine, commonly with sodium thiosulfate.
5. Argentometric titration: using Ag^+, commonly for halide ions
6. Complexometric titration: based on formation of a stable complex, commonly using EDTA (for metal ions)

Worked Example

3. **Experimental data obtained by titrating the decinormal solution of oxalic acid with potassium permanganate solution is given below.**

Experiment number	Volume of oxalic acid	Volume of $KMnO_4$ Burette reading (mL)	
		Initial	final
1.	10	0.00	11.50
2.	10	0.00	11.00
3.	10	0.00	11.00

a) Name the above titration.

Ans: **Redox titration**

b) Calculate the equivalent weight of $KMnO_4$.

Ans: **Equivalent weight = 158/5 = 31.5**

c) Calculate the normality of $KMnO_4$ from the above data.

Ans: **Given, for oxalic acid, V_1 = 10 ml N_1= 0.1 N (decinormal)**
for $KMnO_4$, V2= 11.00 mL N_2 = ?

For complete neutralisation, $N_1V_1 = N_2V_2$
Or, $N_2 = N_1V_1/V_2 = 10 \times 0.1/11.00 = 0.0909$ N

d) Why is dilute H_2SO_4 added to the conical flask containing standard oxalic acid before titrating with the $KMnO_4$ solution?

Ans: **$KMnO_4$ only acts as a strong oxidising agent in an acidic medium. In an acidic solution, the half-reaction for $KMnO_4$ is: $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 5H_2O$. Without sufficient H^+ ions (acid), this reduction won't occur properly, and the titration won't proceed accurately.**

e) Identify the titrant and titrand in this titration.

Ans**: Titrant: $KMnO_4$; Titrand: oxalic acid**

Endpoint, Equivalence point, and Neutral point

The completion of a reaction, as indicated by the indicator, is called the endpoint.

The point at which the equivalent quantity of the titrant is added to the titrand is called the equivalence point or theoretical endpoint.

Aspect	Equivalence point	End point
Definition	The point in the titration at which an equivalent quantity of titrand is exactly neutralised by titrant.	The point at which the indicator shows that the titration should be stopped, usually by a permanent colour change.
Visibility	Not visible in acid-base titration involving a burette and pipette system.	Visible in acid-base titration using a burette and pipette system.
Determination method	Determined by using instrumental methods.	Determined by observing the colour change of an indicator in the solution.
Reaction completion	The exact point where the reactants are completely reacted.	The practical point at which the completion of the reaction is indicated by the colour change.

Ideally, the endpoint should be very close to the equivalence point.

For strong acid-strong base titrations, the equivalence point, endpoint (with a suitable indicator), and the neutral point (pH 7) are practically the same.

Understand

Equivalence point = reaction says "complete." **Endpoint = indicator says "stop."**

Titration error: The difference between the endpoint and the equivalence point.

Common Errors During Titration (avoid these)

- Parallax error (eye-level reading)
- Overshooting the endpoint
- Air bubbles in the burette
- Unrinsed apparatus

Worked Numerical Example

4. 100 ml of a Na_2CO_3 solution contains 5.3 g of Na_2CO_3. If 10 ml of this solution is added to X ml of water to obtain a 0.01 M Na_2CO_3 solution, calculate the value of X. **4**

(Hint: find the concentration of the given solution first, then calculate for dilution)

First, Vol in ml = 100 ml; Wt in gm = 5.3 g

Molecular wt= 23 x 2 +12+16 x 3 = 106

Molarity = wt in gm/(vol in ml x molecular wt) x 1000

= 5.3 x 1000(100 x 106) = 0.5 M

Now

M_1= 0.5 M; M_2 = 0.01M; V_1= 10 ml; V_2= (10+x) ml

We know, for dilution, $M_1V_1 = M_2V_2$ (hence x = 490ml)

🔥 CORE IDEA/Summary of the Chapter

👉 Determine concentration using **titration (volume measurement)**

Concept	Formula/Key Point
Equivalent weight (element)	A / Valency
Equivalent weight (acid)	Molecular wt. / Basicity
Equivalent weight (base)	Molecular wt. / Acidity
Equivalent weight (salt)	Molecular wt. / Total charge
Equivalent weight (redox)	Molecular wt. / ΔON
Gram equivalent	Mass / E
Normality (N)	(Mass × 1000) / (E × V in ml)
Molarity (M)	(Mass × 1000) / (Molecular wt. × V in ml)
N = M × n-factor	n-factor = basicity/acidity/charge/ΔON
Normality equation	$N_1V_1 = N_2V_2$
Dilution	$M_1V_1 = M_2V_2$
Primary standard examples	Na_2CO_3, Oxalic acid, Mohr's salt
$KMnO_4$ in an acidic medium	E = 31.6, self-indicator
Titration error	Endpoint - Equivalence point

🎯 **End point** → colour change **Equivalence point** → exact reaction completion 👉 these should be as close as possible

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🧱 **PRIMARY STANDARD**

✓ **Properties:**

- High purity Stable /Non-hygroscopic High molecular/equivalent weight

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✨ **Study Tip:** This chapter is highly numerical. Practice deriving equivalent weights and applying $N_1V_1 = N_2V_2$ daily until it becomes second nature. In the CEE and Engineering entrance exams, at least 2 questions come directly from this chapter.

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