Introduction to Analytical Chemistry

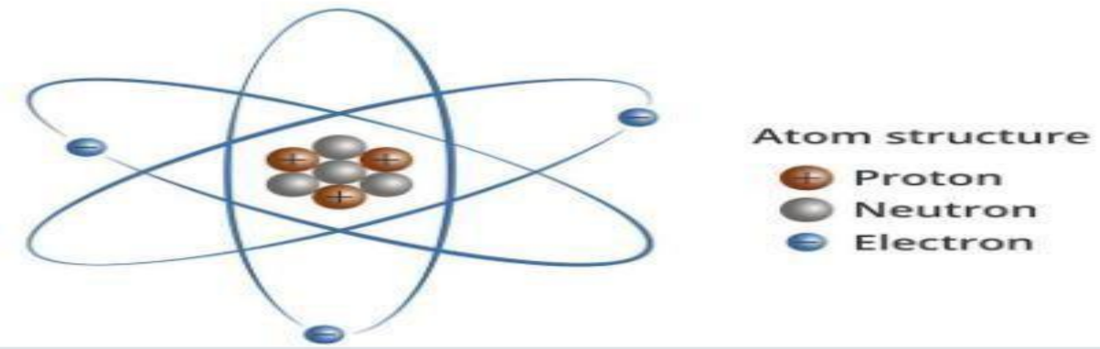
Analytical chemistry is the branch of chemistry that deals with identifying what substances are present in a sample (qualitative analysis) and how much of each substance exists (quantitative analysis). It is essential in environmental studies, medicine, materials science, and industry because it helps determine purity, composition, and chemical behavior.

Atom and Elements

An atom is the smallest unit of matter that retains the identity of a chemical element. Each atom consists of three main particles:

- Protons (positively charged)
- Neutrons (neutral)
- Electrons (negatively charged, orbiting around the nucleus).

An element is a pure substance made up of one kind of atom only. For example, hydrogen (H), oxygen (O), and carbon (C) are elements. Each element is defined by its atomic number (Z) — the number of protons in its nucleus.



Radioisotopes and Radioisomer Pollution

Radioisotopes are isotopes (atoms of the same element with different numbers of neutrons) that are unstable and emit radiation. Examples include Carbon-14, Iodine-131, and Uranium-238.

Radioisomers are radioactive isotopes of the same element that have nuclei in different energy states. They are used in medicine (imaging and therapy), industry, and agriculture. However, pollution with radioisotopes (radioisomer pollution) occurs when these radioactive materials enter the environment through:

- Nuclear power plant waste
- Medical and industrial waste
- Nuclear weapon testing

Such pollution can damage living tissues, cause genetic mutations, and contaminate soil and water for many years.

Pollution with Elements

Elemental pollution refers to contamination caused by heavy metals and toxic elements, such as lead (Pb), mercury (Hg), cadmium (Cd), and arsenic (As). These elements do not degrade and can accumulate in organisms, leading to serious health effects like:

- Nervous system damage (lead, mercury)
- Kidney and liver disorders
- Cancer (arsenic, cadmium)

Controlling elemental pollution involves chemical analysis of water, air, and soil using spectroscopy or chromatography to detect harmful levels.

Relation between Atoms, Molecules, and Energy (According to the New Atomic Theory)

According to modern atomic theory and Louis de Broglie’s hypothesis, electrons have both particle and wave properties. De Broglie proposed the equation:

$\lambda = h / mv$

Where:

- λ = wavelength of the electron

- h = Planck's constant
- m = mass of the particle
- v = velocity of the particle

This theory shows that energy and matter are related, and that electrons move in specific energy levels around the nucleus as standing waves — not fixed orbits. When atoms absorb or release energy, electrons move between these energy levels, producing spectral lines observed in atomic spectra.

Matter and Its Classification

Matter is anything that has mass and occupies space. It can exist in different physical states and forms:

1. Physical Classification:
   - Solid: fixed shape and volume
   - Liquid: fixed volume but variable shape
   - Gas: neither fixed shape nor volume
2. Chemical Classification:
   - Elements: made of one type of atom (e.g., O_2, Fe)
   - Compounds: made of atoms of different elements chemically combined (e.g., H_2O, CO_2)
   - Mixtures: physical combinations of substances (e.g., air, saltwater)

Analytical chemistry helps in identifying and quantifying the components of matter accurately.

Chemical Bonds:

There are many types of chemical bonds and forces that bind molecules together. The two most basic types of bonds are characterized as either ionic or covalent. In ionic bonding, atoms transfer electrons to each other.

Chemical Bonds can be divided into :

Covalent Bond

A **covalent bond** is formed when two atoms **share electrons** so that each atom can achieve a stable electron configuration (usually a full outer shell).

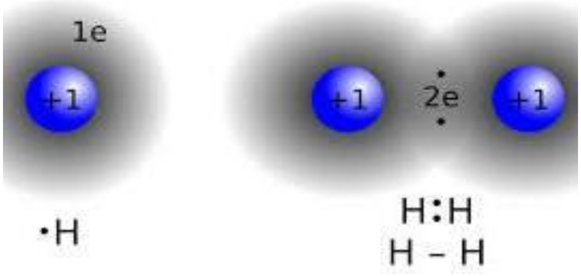
Types

1. **Non-polar covalent bond**
    - Electrons are shared **equally**.
    - Occurs between identical atoms.
    - Example:
        - H–H (H_2)
        - Cl–Cl (Cl_2)
2. **Polar covalent bond**
    - Electrons are shared **unequally** because one atom is more electronegative.
    - Creates partial charges δ^+ and δ^-.
    - Example:
        - H–O in H_2O
        - H–Cl in HCl

Properties

- Form molecules (gases, liquids, some solids)
- Low to moderate melting/boiling points

- Poor electrical conductivity
- Strong *intramolecular* bonds but weak *intermolecular* forces in many molecules



2. Ionic Bond

An **ionic bond** forms when electrons are **transferred** from one atom to another.

Mechanism

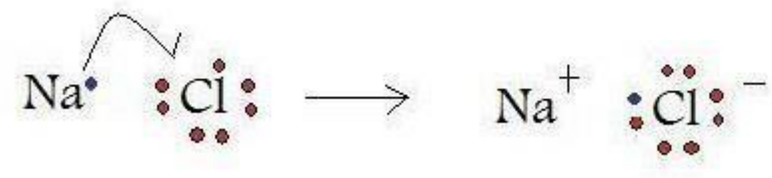
- A **metal** loses electrons → forms a **cation** (positive ion)
  Example: $Na \rightarrow Na^+$
- A **non-metal** gains electrons → forms an **anion** (negative ion)
  Example: $Cl \rightarrow Cl^-$
- The opposite charges attract strongly → **ionic compound**

Examples

- $NaCl$ (sodium chloride)
- MgO (magnesium oxide)
- $CaCl_2$ (calcium chloride)

Properties

- Solid crystalline structures
- Very high melting/boiling points
- Conduct electricity when molten or dissolved (ions move freely)
- Hard and brittle



3. Coordination (Dative Covalent) Bond

A **coordination bond** (dative bond) is a special type of covalent bond in which **both electrons come from one atom**.

How it forms

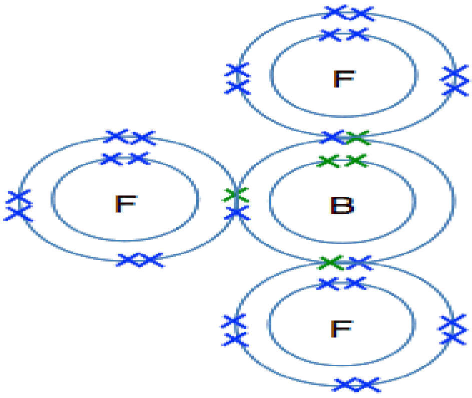
- One atom has a **lone pair** (donor)
- Another atom has an **empty orbital** (acceptor)
- The donor gives the pair → forms a bond

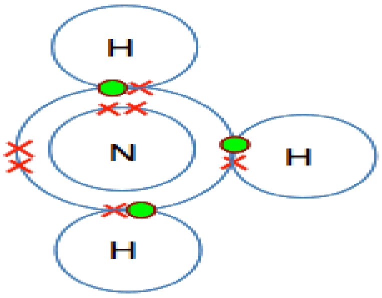
Examples

- NH_3 donating a lone pair to $H^+ \rightarrow NH_4^+$
- Complex ions:
    - $[Cu(NH_3)_4]^{2+}$
    - $[Fe(CN)_6]^{4-}$

Properties

- Very important in coordination chemistry
- Responsible for colors of transition-metal complexes
- After formation, it behaves like a normal covalent bond





4. Hydrogen Bond

A **hydrogen bond** is an **intermolecular force**, not a full covalent bond.
It occurs when:

- Hydrogen is covalently bonded to **O, N, or F**
- Hydrogen is attracted to a **lone pair** on another electronegative atom

Examples

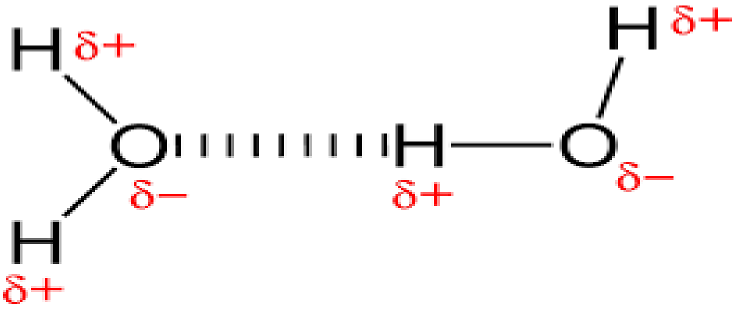
- Between water molecules
- In DNA base pairing (A–T and G–C)
- Between NH_3 molecules

Importance

- Responsible for high boiling point of water
- Stabilizes proteins and DNA
- Influences solubility and physical properties

Strength

- **Stronger** than Van der Waals forces
- **Weaker** than covalent bonds
- Typically 5–30 kJ/mol



The Analytical process

Analytical chemistry deal with determine chemical structure , type and quaint of the substance or mixture in sample.

Analytical chemistry divided to two type

a- Qualitative analysis: deal with constituents in the analytical sample.

b- Quantitative analysis: deal with determination quantitative substance in the sample.

Types of quantitative analysis:

1. Gravimeter analysis: usually involves the selective separation of the analytical by precipitation, form the weight of the precipitate and knowledge of chemical composition, the weight of analyst in the desired from is calculated.

1.Volumetric analysis:

The analytical react with a measured volume of reagent know concentration, in proces called titration.

2.Instrumental analysis : determine the amount of substance by measurement the physical or chemical properties like density, color and conductive .

Errors and statistics Accuracy:

The accuracy is the degree of agreement between the measured value and standard sample, other meaning is concordance between it and the true or most probable value (relative error) Precision :

Precision may by defined as the concordance a series of measurements of the same quantity .

Classification of errors :

The errors may be divided into :

A) Systematic Errors

These are errors that follow a specific system positive or negative, In other words, it is either an increase or a decrease, and it is possible to correct regular errors by creating mathematical relationships that represent the error.

1-instrumental errors : Impurities in reagents.

2-Methodic errors : Solubility of a precipitate, in complete reaction

3-Operative errors : loss of precipitate, in complete reaction 4- Personal errors :

B)Indeterminate errors (Random errors) :

Indeterminate errors are frequently called accidental or random, errors, such errors can be attributed to no known cause nor can they be predicted as to magnitude or direction for any single measurement standing alone.

Units for Expressing Concentration of Solutions

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

$$\text{Concentration} = \frac{\text{amount of solute}}{\text{amount of solution}}$$

Although the terms "solute " and "solution " are often associated with liquid samples, they can be extended to gas –phase and solid –phase sample as well. The actual units for reporting concentration depend on how the amounts of solute and solution are measured.

Molarity

Chemists primarily need the concentration of solutions to be expressed in a way that accounts for the number of particles that react according to a particular chemical equation. Since percentage measurements are based on either mass or volume, they are generally not useful for chemical reactions. A concentration unit based on moles is preferable**. The molarity (M) of a solution is the number of moles of solute dissolved in one liter of solution. To calculate the molarity of a solution, divide the moles of solute by the volume of the solution expressed in liters:**

$$\text{Molarity (M)} = \frac{\text{moles of solute}}{\text{liters of solution}} = \frac{\text{mol}}{\text{L}}$$

Note that the volume is in liters of solution and not liters of solvent. When a molarity is reported, the unit is the symbol M and is read as "molar". For example a solution labeled as 1.5M NH_3 is read as "1.5 molar ammonia solution".

Example: A solution is prepared by dissolving 42.23g of NH_4Cl into enough water to make 500 mL of solution. Calculate its molarity. N = 17 , H=1, Cl=35.5

mass = 42.23g NH_4Cl

Molar mass NH_4C l=53.50g/mol

Volume solution =500 mL = 0.5 L

$$\text{Molarity (M)} = \frac{\text{moles of solute}}{\text{liters of solution}}$$

$$\text{NO. of moles} = \frac{\text{mass}}{\text{M.wt}} = \frac{42.23\text{g}}{53.50\text{g/mol}} = 0.7893 \text{ mol}$$

$$\text{Molarity (M)} = \frac{0.7893 \text{ mol}}{0.5 \text{ L}} = 1.579 \text{ M}$$

W. M \ A chemist needs to prepare 3 L of a 0.25 M solution of potassium permanganate ($KMnO_4$). What mass of $KMnO_4$ does she need to make the solution? Answer = 119 g.

Normality

Normality expresses concentration in terms of the equivalents of one chemical species that react stoichiometrically with another chemical species. Note that this definition makes an equivalent, and thus normality, a function of the chemical reaction. Although a solution of H_2SO_4 has a single molarity, its normality depends on its reaction.

We define the number of equivalents, n, using a reaction unit, which is the part of a chemical species that participates in the chemical reaction. In a precipitation reaction, for example, the reaction unit is the charge of the cation or the anion that participates in the reaction; thus, for the reaction

$$Pb^{2+}{}_{(aq)}+2I^{-}{}_{(aq)} \rightleftharpoons PbI_2\ (s)$$

$n = 2$ for Pb^{2+} and $n = 1$ for I^{-}.

In an acid–base reaction, the reaction unit is the number of H^{+} ions that an acid donates or that a base accepts. For the reaction between sulfuric acid and ammonia

$$H_2SO_4\ (aq)+ 2\ NH_3(aq) \rightleftharpoons 2NH^{+4}(aq)+SO_2{}^{-4}$$

$n = 2$ for H2SO4 because sulfuric acid donates two protons, and $n = 1$ for NH_3 because each ammonia accepts one proton. For a complexation reaction, the reaction unit is the number of electron pairs that the metal accepts or that the ligand donates. In the reaction between Ag+ and NH_3

$$Ag^{+}(aq)+2NH_3(aq) \rightleftharpoons Ag(NH_3)^{+2}(aq)$$

n = 2 for Ag+ because the silver ion accepts two pairs of electrons, and n = 1 for NH3 because each ammonia has one pair of electrons to donate. Finally, in an oxidation–reduction reaction the reaction unit is the number of electrons released by the reducing agent or accepted by the oxidizing agent; thus, for the reaction

$$2Fe^{3}+(aq)+Sn^{2+(}aq)\rightleftharpoons Sn^{4}+(aq)+2Fe^{2+}\ (aq)$$

n = 1 for Fe^{3+} and n = 2 for Sn^{2+}. Clearly, determining the number of equivalents for a chemical species requires an understanding of how it reacts.

Normality is the number of equivalent weights, EW, per unit volume. An equivalent weight is the ratio of a chemical species' formula weight, FW, to the number of its equivalents, n.

$$EW= FW \backslash n$$

The following simple relationship exists between normality, N, and molarity, M,

$$N= n\times M$$

Molality

A final way to express the concentration of a solution is by its molality. The molality (m) of a solution is the moles of solute divided by the kilograms of solvent. A solution that contains 1.0mol of NaCl dissolved into 1.0kg of water is a "one-molal" solution of sodium chloride. The symbol for molality is a lower-case *m* written in italics.

$$\text{Molality} = \text{no. of moles} / \text{weight of solvent (kg)}$$

Weight, Volume, and Weight-to-Volume Ratios

Weight percent (w/w %), volume percent (% v/v) and weight-to-volume percent

1.(w/w %)= $\boldsymbol{Wt\ of\ solute\ gWt\ of\ solution\ g\ x\ 100}$

Example (a):

What is the weight percent of 25 g of sodium sulphate dissolved in 200 g of solution?

(w/w %)= $\boldsymbol{25g/200\ g\ x\ 100}$ = 0.125 x 100 =12.5%

Example (b):

Calculate the wt% for a solution prepared by dissolving 5 g of $AgNO3$ in 100 ml water

Water density = 1g/ml

ml of water=100 g of water = weight of solvent 100

(w/w %)= $\boldsymbol{Wt\ of\ solute\ g/Wt\ of\ solution\ g\ x\ 100}$

Weight of solution = solute + solvent = 5+100= 105 g

(w/w %)= $\boldsymbol{5\ g/105\ g\ x\ 100}$ =4.76%

2. (v/v %)= $\boldsymbol{v\ of\ solute\ mlv\ of\ solution\ ml\ x\ 100}$ .2

W.H. Calculate v/v% of a solution that was prepared by adding 50 ml of methanol to 200 ml water.

(wt/v %)= $\boldsymbol{wt\ of\ solute\ g/v\ of\ solution\ ml\ x\ 100}$. 3

Example (a):

Calculate wt/v % for 4g of NaOH dissolved in 500 ml solution.

wt/v%= $\boldsymbol{4\ g\ 500\ ml\ x\ 1\ \ \ 0}$ =0.8%

Parts per Million and Parts per Billion

Part per million (ppm) and parts per billion (ppb) are ratios giving the grams of solute to, respectively, one million or one billion grams of sample. For example, 450 ppm Mn in steel that is =steel contains 450 μg of Mn for every gram of steel.

If we approximate the density of an aqueous solution as 1.00 g/mL, or 1000 kg/m^3 then solution concentrations can be express in ppm or ppb using the following relationships.

Ppm = mg/ L = mg/1000 ml = mg/1000g = mg/kg or =1mg/1000000mg = ppm

ppb= μg/L = μg/1000ml= μg/1000g = μg/kg= 1 μg /1000000000 μg

Dilution Law (Dilution Equation)

Dilution is the process of reducing the concentration of a solution by adding more solvent (usually water). During dilution:

The amount of solute stays the same — only the volume changes.

The most important formula for dilution is:

$\mathbf{C_1V_1 = C_2V_2}$

Where:

- $\mathbf{C_1}$ = initial concentration
- $\mathbf{V_1}$ = initial volume
- $\mathbf{C_2}$ = final concentration
- $\mathbf{V_2}$ = final total volume

This equation works for:

✓ Molarity (M)
✓ Normality (N)
✓ Percent (%) solutions
✓ Any concentration unit, as long as it stays the same on both sides.

Why $C_1V_1 = C_2V_2$ Works?

Because the **moles before dilution = moles after dilution**.

Since moles = C × V:

$C_1V_1 = C_2V_2$

Worked Examples

1) Molarity (M) — Example

Problem: 42.23 g NH_4Cl is dissolved to make 500 mL of solution. Find the molarity.

Molar mass NH4Cl = 53.50 $g \cdot mol^{-1}$

Steps:

1. Calculate moles of solute:

   moles = mass / molar mass = 42.23 ÷ 53.50 = 0.7893 mol

2. Convert volume to liters: 500 mL = 0.500 L

3. Apply molarity formula:

   M = moles / liters = 0.7893 ÷ 0.500 = 1.5786 M

Answer: 1.58 M (rounded)

2) Molarity — Example

Problem: What mass of $KMnO_4$ (MW = 158 $g \cdot mol^{-1}$) is needed to prepare 3.00 L of 0.25 M solution?

Steps:

1. Moles required = M × V = 0.25 × 3.00 = 0.75 mol

2. Mass = moles × MW = 0.75 × 158 = 118.5 g

Answer: 118.5 g (≈ 119 g)

3)

Problem: 10.0 g NaOH (MW = 40.0 $g\cdot mol^{-1}$) dissolved to make 250 mL. Find molarity.

Steps:

1. Moles = 10.0 ÷ 40.0 = 0.250 mol

2. Volume = 250 mL = 0.250 L

3. M = 0.250 ÷ 0.250 = 1.00 M

Answer: 1.00 M

4) Example— Normality (N)

Problem: Convert 1.50 M H2SO4 to normality for acid–base reactions.

H_2SO_4 donates 2 H+ → n = 2

Steps:

1. N = M × n = 1.50 × 2 = 3.00 N

Answer: 3.00 N

5) Normality — Example

Problem: Convert 0.250 M Ba(OH)2 to normality (Ba(OH)2 provides 2 OH− → n = 2).

Steps:

1. N = 0.250 × 2 = 0.500 N

Answer: 0.50 N

6) Example— Molality (m)

Problem: 10.0 g KCl (MW = 74.5 $g\cdot mol^{-1}$) dissolved in 200 g water. Find molality.

Steps:

1. Moles solute = 10.0 ÷ 74.5 = 0.1342 mol

2. Mass of solvent in kg = 200 g = 0.200 kg

3. Molality m = moles / kg solvent = 0.1342 ÷ 0.200 = 0.6711 m

Answer: 0.671 m

7) Weight percent (w/w%) — Example

Problem: 5.00 g $AgNO3$ dissolved in 100.0 mL water (assume density 1.00 $g \cdot mL^{-1}$). Find % w/w.

Steps:

1. Mass solvent = 100.0 mL × 1.00 $g \cdot mL^{-1}$ = 100.0 g

2. Mass solution = solute + solvent = 5.00 + 100.0 = 105.0 g

3. % w/w = (mass solute / mass solution) × 100 = (5.00 ÷ 105.0) × 100 = 4.7619%

Answer: 4.76% w/w

8) Volume percent (v/v%) — Example

Problem: Add 50.0 mL methanol to water; final volume = 250.0 mL. Find % v/v.

Steps:

% v/v = (volume solute / total volume) × 100 = (50.0 ÷ 250.0) × 100 = 20.0% v/v

Answer: 20.0% v/v

9) ppm — Example

Problem: 2.0 mg Fe is dissolved in 500 mL water. Express concentration in ppm (assume density ≈1 $g \cdot mL^{-1}$).

Steps:

1. Convert volume to liters = 500 mL = 0.500 L

2. ppm ($mg \cdot L^{-1}$) = mg solute ÷ L solution = 2.0 ÷ 0.500 = 4.0 $mg \cdot L^{-1}$

3. 1 $mg \cdot L^{-1}$ ≈ 1 ppm (for dilute aqueous solutions) → 4.0 ppm

Answer: 4.0 ppm

10) Dilution Law (C1V1 = C2V2) — Example (molarity)

Problem: How many mL of 2.00 M NaCl are needed to prepare 500.0 mL of 0.500 M NaCl?

Steps:

1. Use C1V1 = C2V2

   C1 = 2.00 M, C2 = 0.500 M, V2 = 500.0 mL

2. V1 = (C2 × V2) ÷ C1 = (0.500 × 500.0) ÷ 2.00 = 250.0 ÷ 2.00 = 125.0 mL

Answer: 125.0 mL of 2.00 M, dilute to 500.0 mL.

11) Dilution Law — Example (ppm)

Problem: How much of a 1000 ppm stock is needed to make 100.0 mL of 50.0 ppm?

Steps:

1. C1 = 1000 ppm, C2 = 50.0 ppm, V2 = 100.0 mL

2. V1 = (C2 × V2) ÷ C1 = (50.0 × 100.0) ÷ 1000 = 5000 ÷ 1000 = 5.0 mL

Answer: 5.0 mL stock + dilute to 100.0 mL.

12) Dilution Law — Example (normality)

Problem: How much of 6.00 N HCl is needed to prepare 1.00 L of 1.50 N HCl?

Steps:

1. C1V1 = C2V2 → V1 = (C2 × V2) ÷ C1

V1 = (1.50 × 1000 mL) ÷ 6.00 = 1500 ÷ 6.00 = 250 mL

Answer: 250 mL of 6.00 N, dilute to 1.00 L.

Chemical Equilibrium:-

chemical equilibrium is the state in which both reactants and products are present in concentrations which have no further tendency to change with time, so that there is no observable change in the properties of the system. Usually, this state results when the forward reaction proceeds at the same rate as the reverse reaction. The reaction rates of the forward and backward reactions are generally not zero, but equal. Thus, there are no net changes in the concentrations of the reactants and products.

In a solution of acetic acid, two reactions occurring simultaneously

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

That is manning

$$CH_3COOH + H_2O \longrightarrow CH_3COO^- + H_3O^+ \ ...(1)$$

and

$$CH_3COO^- + H_3O^+ \longrightarrow CH_3COOH + H_2O \ .....2$$

Equilibrium constant

The equilibrium constant is the division of the products by the reactant, the general equation for a chemical equilibrium

$$aM + bN \rightleftharpoons cP + dQ$$

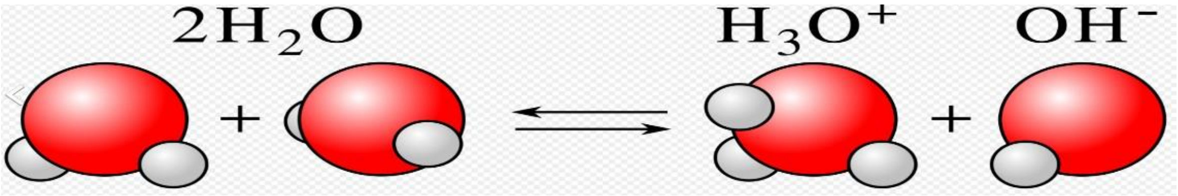
Express of the equilibrium constant for a chemical reaction

$$K_e = \frac{[P]^a[Q]^b}{[M]^c[N]^d}$$

Where the [P] and [Q] are products concentration, and [M] and [N] are reactant concentration ; and a, b,c and d are the stoichiometric coefficients from the balance reaction.

Ionization of water:

Aqueous solution always contain small amounts of hydronium and hydroxide ion as a consequence of the dissociation reaction



Water by itself ionizes to a very small extent to produce H3O+ and OH- ions. In such a self ionization reaction, one water molecule works as an acid to donate a proton to another water molecule (the base):

HOH + HOH$\longleftrightarrow$ OH- + H_2OH+

Since water contains an equal concentration of H+ and OH- ions, it serves as an excellent standard for acidity measurements.

When the [H2O] is constant, we have

$$Kw=[H3O+][OH-] \ldots\ldots\ldots.(1)$$

when [H+] =[OH-]

Kw is ion product constant,

[H3O+] [OH] is the product of ionic concentration

[H+] [OH-] is the product of ionic concentration

Kw = [H+] [OH-] when [H+] =[OH-] and assume y =[H+]

Hence y= [H+] =[OH-]

Substituting in equation 1 have

Kw= y^2 at 25 0C,

10^{-14} that meaning $y^2 = 1x10^{-14}$ and $y= 1x10^{-7}$

There for in pure water (neutral medium)

$[H+] =[OH-]= 1x10^{-7}$

In acidic medium [H+]> [OH-]

In basic medium [OH-] < [H+]

Measure of Acidity

- Acidity is measured in terms of [H+] present in a solution.
- The higher the concentration of H+ ions in the solution, the more acidic it is.
- Aqueous solution in which [OH-] = [H+] are said to be neutral; solutions in which [H+] > [OH-] are acidic; and conversely, solutions in which [OH-] > [H+] are basic or alkaline.
- Water is neutral, since it always produces an equal concentration of OH- and H+ ions. At room temperature the [OH-] and [H+] values are each 10^{-7}.
- In acidic solutions [H+] must be greater than 10^{-7} and in basic solutions [H+] must be less than $1.0*10^{-7.}$
- No matter how acidic a solution is, there will always be some OH- ions present, and every very basic solution always contains some H+ ions.

pH as a Measure of Acidity

- The numerical values for [H+] in most of the solutions we will discuss are very small ones, which are usually expressed as exponentials. These numbers are clumsy to use and awkward to speak about.
- The pH is directly related to the [H+] and is defined to be the negative logarithm of [H+] :

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

Measuring pH

- In laboratory several different methods are used to determine pH values depending upon the accuracy needed.
- For very crude measurements pH paper indicators may do, but for more accurate values pH meters and titration techniques are necessary.

PH and POH concept:

PH and POH are terms used to specify the hydrogen concentration and hydroxide concentration in aqueous solution,

$PH= -\log[H^+]$ ……. When the $[H^+]= 1x10-7$

$PH= -\log[1x10-7]$ and $POH = -\log[OH^-]$ So it $PH=7$ and $POH = 7$
$\log KW = \log[H^+] + \log[OH^-]$

$PKw= PH+ POH$

$14 = PH+ POH$

W.H. Sodium hydroxide is a strong base. 0.02M? Calculate the following values for each solution: (H3O+), (OH-) pH, pOH.if you know

$NaOH \rightleftharpoons Na^+ + OH^-$

We can find the concentration of hydroxide ions via stoichiometry. One hydroxide ion is created from each molecule of sodium hydroxide that dissociates.

$0.02M\ NaOH*1mol\ OH^{-}1mol\ NaOH=0.02M\ OH^{-}$

Since we have the concentration of hydroxide ions, we can solve for the POH of the solution.

$pOH=-\log[OH^{-}]=-\log(0.02)$

$pOH=1.70$

The question asks us to find the pH of the solution, so we will need to convert pOH to pH. To do so, we simply subtract the pOH from 14.

$pH+pOH=14\rightarrow pH=14-pOH$

$14-1.70=12.3$

The pH of the solution is 12.3. Because sodium hydroxide is a strong base, it makes sense that the pH is above 7.

Properties of Acids and Bases

- Acids

One property of acids is the sour taste many of them have. Acidic substances such as concentrated sulfuric acid, $H_2SO_4(aq)$, or hydrochloric acid, $HCl(aq)$, do have a sour taste, although they are much too reactive to test in this way.

- Acids react with certain metals to produce H_2 gas and salt. For instance, sulfuric acid reacts with magnesium metal to give hydrogen and the salt magnesium sulfate.

$Mg(s) + H2SO4(aq) \rightarrow H2(g) + MgSO4(aq)$

- Acids also react with metal oxides to form water and salt as products. For example, hydrochloric acid produces copper(II) chloride and water when it reacts with copper(II) oxide:

$CuO(s) + 2HCl (aq) \longrightarrow H2O + 2CuCl (aq)$

- Acids liberate CO2 from carbonates or from bicarbonates. For instance antacid tablets containing sodium bicarbonate, NaHCO3, are able to react with stomach acid, HCl, in this way:

$HCl(aq) + NaHCO3(aq) \longrightarrow CO2+H2O + NaCl(aq)$

- Acids undergoes a reaction with a dye called litmus to produce a red color. Dyes, such as litmus, that are used to test for acidity are called indicators.

- Bases

- Bases react with many salts of heavy metals to produce insoluble hydroxide precipitates in a double displacement reaction. For example, the base sodium hydroxide reacts with iron(III) nitrate to form the precipitate iron(III) hydroxide:

$FeNO3(aq) + 3NaOH(aq) \longrightarrow Fe(OH)3\downarrow + 3NaNO3 (aq)$

- Adding the indicator litmus to a base produces a blue color. Thus litmus paper dipped into a soapy solution turns blue.

Acid-Base Neutralizations

- The properties of both acids and bases are removed when an acid reacts with a base in a reaction called neutralization. The products of a neutralization reaction are a salt and water.

- For example, the reaction of NaOH, a base, with HCl, an acid, is a neutralization.

- $NaOH (aq) + HCl (aq) \rightarrow NaCl(aq) + H_2O$
- If the base is a carbonate or bicarbonate, the products also include CO_2 gas.

Proton Transfer

Theories that explain the behavior of acids and bases are based upon the differences in the chemical structure of these two types of compounds.

An acid-base theory proposed independently by J.N. Brönsted(1879-1947) in Denmark and T.M. Lowry(1874-1936) in England accounts for the acidic or basic properties of most compounds.

- The Brönsted-Lowry theory states that an acid is a compound that donates a proton and a base is a compound that accepts a proton.
- Thus, an acid is a proton donor; a base is a proton acceptor.
- According to the proton transfer theory, all acid-base reactions must involve both an acid and a base. Solvents may behave as acids or bases and must be included in acid-base reaction equations.

Strong Acids and Bases

- Strong acids and strong bases are 100 percent ionized.
- For instance, HCl is an example of a strong acid. That is, every HCl molecule dissolved in water donates a proton to a water molecule to form a hydronium ion, and no undissociated HCl molecules remain.

$HCl (g) + H_2O \rightarrow H_3O^+ + Cl^-$

- NaOH is one example of a strong base.

Weak Acids and Bases

- Weak acids and weak bases do not ionize completely, that is, not every molecule of a weak acid or a weak base dissociates. Equilibrium is established between the molecules of a weak acid or base and the ions that they produce.

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

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

Titration

- Titration is a method that is used to determine the concentration of a substance in a given solution sample by allowing the unknown sample to react completely with the solution that has a known concentration.

- The solution with the known concentration is called a standard solution.

- Titration is a particularly useful method of measuring acidity since acids can be completely neutralized by bases, and vice versa.

- For instance, suppose we want to find the concentration of a sample of HCl solution. A standard solution of NaOH can be added to the HCl solution of unknown concentration until all the HCl has been neutralized. This is called the equivalence point

- Indicators are selected that change color near the equivalence point. In a titration the point at which an indicator changes color is called the endpoint of the titration. Ideally, the endpoint and the equivalence point should be the same.

Ionization of Weak Electrolytes

Calculation of pH of Weak Acids and Weak Bases

1. Electrolytes and Ionization

An electrolyte is a substance that produces ions when dissolved in water and therefore conducts electricity.

Electrolytes are classified into:

- Strong electrolytes: completely ionize in water.

  Example: HCl, NaOH, NaCl

  $HCl(aq) \rightarrow H^+ + Cl^-$

- Weak electrolytes: partially ionize in water.

  Example: CH_3COOH, NH_3

Ionization of a weak electrolyte is reversible and reaches equilibrium.

Example (weak acid – acetic acid):

$CH_3COOH(aq) \rightleftharpoons H^+ + CH_3COO^-$

2. Ionization Constant

(a) Weak Acids – Ka

For a weak acid HA:

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

$Ka = [H^+][A^-] / [HA]$

Example:

$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$

$$Ka = [H^+][CH_3COO^-] / [CH_3COOH]$$

(b) Weak Bases – Kb

For a weak base B:

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

$$K_b = [BH^+][OH^-] / [B]$$

Example:

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

$K_b = [NH_4^+][OH^-] / [NH_3]$

3. pH and pOH

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

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

$pH + pOH = 14$

4. Calculation of pH of a Weak Acid

Example:

Calculate the pH of 0.10 M CH_3COOH.

$K_a = 1.8 \times 10^{-5}$

$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$

Let $x = [H^+]$

$K_a = x^2 / (0.10 - x) \approx x^2 / 0.10$

$1.8 \times 10^{-5} = x^2 / 0.10$

$x^2 = 1.8 \times 10^{-6}$

$x = 1.34 \times 10^{-3}$ M

$pH = -\log(1.34 \times 10^{-3}) \approx 2.87$

5. Calculation of pH of a Weak Base

Example:

Calculate the pH of 0.10 M NH_3.

$K_b = 1.8 \times 10^{-5}$

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

Let $x = [OH^-]$

$K_b = x^2 / (0.10 - x) \approx x^2 / 0.10$

$1.8 \times 10^{-5} = x^2 / 0.10$

$x = 1.34 \times 10^{-3} = [OH^-]$

$pOH = -\log(1.34 \times 10^{-3}) \approx 2.87$

$pH = 14 - 2.87 = 11.13$

Ionization of Weak Electrolytes

An electrolyte is a substance that produces ions in water and conducts electricity.

Strong electrolytes completely ionize in water:

$HCl(aq) \rightarrow H^+ + Cl^-$

Weak electrolytes partially ionize:

$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$

$Ka = [H^+][A^-] / [HA]$

$Kb = [BH^+][OH^-] / [B]$

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

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

$pH + pOH = 14$

Example 1:

0.10 M CH_3COOH, $Ka = 1.8 \times 10^{-5}$

$Ka = x^2 / (0.10 - x) \approx x^2 / 0.10$

$x = 1.34 \times 10^{-3}$

$pH = 2.87$

Example 2:

0.05 M HCOOH, $Ka = 1.8 \times 10^{-4}$

$Ka = x^2 / 0.05$

$x^2 = 9.0 \times 10^{-6}$

$x = 3.0 \times 10^{-3}$

$pH = -\log(3.0 \times 10^{-3}) = 2.52$

Example 3:

0.10 M NH_3, Kb = 1.8×10^{-5}

$x = 1.34 \times 10^{-3} = [OH^-]$

pOH = 2.87 → pH = 11.13

Example 4:

0.20 M CH_3NH_2, Kb = 4.4×10^{-4}

$Kb = x^2 / 0.20$

$x^2 = 8.8 \times 10^{-5}$

$x = 9.38 \times 10^{-3}$

pOH = 2.03 → pH = 11.97

Buffer Solutions

A buffer resists change in pH.

Acidic buffer = weak acid + its salt

Example: CH_3COOH / CH_3COO^-

Basic buffer = weak base + its salt

Example: NH_3 / NH_4^+

Henderson–Hasselbalch:

$$pH = pKa + \log([Salt]/[Acid])$$

$$pOH = pKb + \log([Salt]/[Base])$$

Example 5 (Acidic Buffer):

0.10 M CH_3COOH, 0.20 M CH_3COONa

pKa = 4.74

pH = 4.74 + log(2) = 5.04

Example 6 (Acidic Buffer):

0.20 M HCOOH, 0.10 M HCOONa

pKa = 3.75

pH = 3.75 + log(0.5) = 3.45

Example 7 (Basic Buffer):

0.30 M NH_3, 0.10 M NH_4Cl

pKb = 4.74

pOH = 4.74 + log(0.33) = 4.26

pH = 9.74

Example 8 (Basic Buffer):

0.10 M NH_3, 0.40 M NH_4Cl

pOH = 4.74 + log(4) = 5.34

pH = 8.66

How Buffer Solutions Work

When a **strong acid (H^+)** is added, it reacts with the **conjugate base**.

When a **strong base (OH^-)** is added, it reacts with the **weak acid**.

This minimizes the change in pH.

Uses of Buffer Solutions

1-In the Human Body

The blood buffer system maintains blood pH at approximately 7.4.

2. In Pharmaceutical Industry

Maintaining the pH of drugs

Increasing drug stability and effectiveness

3. In Chemical Laboratories

Used in **acid–base titrations

Preparation of solutions with fixed pH values

4. In Food Industry

Food preservation

Control of acidity and taste

5. In Biological and Biochemical Applications

Enzymes function at specific pH values

Used in microbial and cell culture media

Important Notes

* A buffer works best when:

$pKa = pH \Rightarrow [Salt] = [Acid]$

Buffers cannot be prepared using only **strong acids or strong bases

1. Volumetric Analysis

Volumetric analysis is a quantitative analytical method used to determine the concentration of an unknown solution by reacting it with a solution of known concentration (standard solution). The method is based on measuring the volume of one solution required to react completely with a known volume of another solution.

The process is called titration. In a titration, the standard solution (titrant) is added gradually from a burette to the unknown solution (analyte) until the reaction reaches completion, indicated by a color change or a measurable signal (end point).

Key Terms:

- Titration: Process of adding titrant to analyte.
- Titrant: Standard solution in burette.
- Analyte: Solution of unknown concentration.
- End Point: Point at which indicator changes color.
- Equivalence Point: Point where stoichiometric amounts have reacted.

Solved Problem:

A student titrates 25.0 mL of HCl with 0.100 M NaOH. The volume of NaOH used is 30.0 mL.

Find the molarity of HCl.

Solution:

$M1V1 = M2V2$

$M(HCl) \times 25.0 = 0.100 \times 30.0$

$M(HCl) = (0.100 \times 30.0) / 25.0 = 0.12\ M$

Exercises:

1. 20 mL of $H2SO4$ is neutralized by 40 mL of 0.5 M NaOH. Find the molarity of $H2SO4$.

2. 15 mL of HCl reacts with 25 mL of 0.2 M NaOH. Calculate the concentration of HCl.

2. Classification of Volumetric Analysis

Volumetric analysis is classified based on the type of reaction involved:

1. Acid–Base (Neutralization) Titrations
2. Precipitation Titrations
3. Oxidation–Reduction (Redox) Titrations
4. Complexometric Titrations

Each type depends on a specific chemical reaction that occurs quantitatively and rapidly.

3. Standard Solution

A standard solution is a solution with a precisely known concentration. It is prepared by dissolving an accurately weighed amount of a pure substance in a known volume of solvent.

Types:

- Primary Standard: Very pure, stable, non-hygroscopic (e.g., Na_2CO_3, $K_2Cr_2O_7$).
- Secondary Standard: Concentration determined by standardization (e.g., HCl, NaOH).

Solved Problem:

Calculate the mass of Na_2CO_3 needed to prepare 250 mL of 0.1 M solution.

Moles = $M \times V = 0.1 \times 0.250 = 0.025$ mol

Molar mass of Na_2CO_3 = 106 g/mol

Mass = $0.025 \times 106 = 2.65$ g

Exercises:

1. Calculate the mass of $K_2Cr_2O_7$ to prepare 500 mL of 0.05 M solution.
2. How many grams of NaOH are required to prepare 1 L of 0.2 M solution?

4. Neutralization Reactions

Neutralization is a reaction between an acid and a base to form salt and water.

General Equation:

Acid + Base → Salt + Water

Example:

$HCl + NaOH \rightarrow NaCl + H_2O$

Solved Problem:

25 mL of H_2SO_4 is titrated with 0.1 M NaOH. Volume used = 50 mL.

Find molarity of H_2SO_4.

Reaction:

$H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$

Moles NaOH = $0.1 \times 0.050 = 0.005$

Moles H_2SO_4 = $0.005 / 2 = 0.0025$

$M(H_2SO_4) = 0.0025 / 0.025 = 0.1$ M

Exercises:

1. 30 mL of HNO_3 reacts with 45 mL of 0.2 M NaOH. Find M of HNO_3.
2. 20 mL of HCl requires 18 mL of 0.15 M NaOH. Calculate M of HCl.

5. Precipitation Reactions

A precipitation reaction produces an insoluble solid (precipitate).

Example:

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

Solved Problem:

25 mL of NaCl is titrated with 0.1 M $AgNO_3$. Volume used = 20 mL.

Find M of NaCl.

Moles $AgNO_3 = 0.1 \times 0.020 = 0.002$

Stoichiometry 1:1 → Moles NaCl = 0.002

$M(NaCl) = 0.002 / 0.025 = 0.08$ M

Exercises:

1. 30 mL of KBr reacts with 24 mL of 0.2 M $AgNO_3$. Find M of KBr.
2. 50 mL of NaCl requires 40 mL of 0.1 M $AgNO_3$. Calculate M of NaCl.

6. Oxidation–Reduction Reactions

Redox reactions involve transfer of electrons.

Oxidation: Loss of electrons.

Reduction: Gain of electrons.

Example:

$MnO4^{-} + 5Fe^{2+} \rightarrow Mn^{2+} + 5Fe^{3+}$

Solved Problem:

20 mL of Fe^{2+} is titrated with 0.02 M KMnO4. Volume used = 10 mL.

Find M of Fe^{2+}.

Moles KMnO4 = $0.02 \times 0.010 = 0.0002$

Stoichiometry: 1 $MnO4^{-}$ reacts with 5 Fe^{2+}

Moles $Fe^{2+} = 5 \times 0.0002 = 0.001$

$M(Fe^{2+}) = 0.001 / 0.020 = 0.05$ M

Exercises:

1. 25 mL of Fe^{2+} requires 15 mL of 0.02 M KMnO4. Find M of Fe^{2+}.
2. 40 mL of oxalic acid is titrated with 0.05 M KMnO4 using 20 mL. Calculate concentration.

THEORY OF INDICATORS

An indicator is a chemical substance that changes color at or near the equivalence point in a titration. Indicators help determine the end point of a chemical reaction.

Indicator Reaction:

Most indicators are weak acids or bases that exist in two forms:

$HIn \rightleftharpoons H^+ + In^-$

Each form has a different color. The color change depends on pH.

Example:

Phenolphthalein:

HIn (colorless) $\rightleftharpoons H^+ + In^-$ (pink)

In acidic medium: colorless

In basic medium: pink

Properties of a Good Indicator:

1. Sharp color change.
2. Change occurs at equivalence point.
3. Does not react with analyte.
4. Stable and soluble.
5. Small quantity required.

Examples:

- Methyl orange: red in acid, yellow in base.
- Phenolphthalein: colorless in acid, pink in base.
- Bromothymol blue: yellow in acid, blue in base.

TYPES OF INDICATORS

1. Acid–Base Indicators:

Used in acid-base titrations.

Example: Phenolphthalein, Methyl orange.

2. Redox Indicators:

Change color when oxidized or reduced.

Example: Diphenylamine.

3. Adsorption Indicators:

Used in precipitation titrations.

Example: Fluorescein in $AgNO_3$ titrations.

4. Complexometric Indicators:

Used in EDTA titrations.

Example: Eriochrome Black T.

5. Natural Indicators:

Obtained from plants.

Example: Litmus, turmeric.

PRINCIPLES OF COLORIMETRY

Colorimetry is an analytical technique used to determine concentration by measuring light absorption.

Principle:

When light passes through a colored solution, part is absorbed.

The amount absorbed depends on concentration.

Components of Colorimeter:

1. Light source

2. Filter

3. Sample holder

4. Detector

5. Display

Applications:

- Determination of metal ions

- Water analysis

- Biochemical analysis

Example:

If a blue solution absorbs red light, intensity decreases with higher concentration.

BEER–LAMBERT LAW

Statement:

Absorbance is directly proportional to concentration and path length.

Formula:

$A = \varepsilon\, l\, c$

Where:

A = Absorbance

ε = Molar absorptivity

l = Path length (cm)

c = Concentration (mol/L)

Example:

If $\varepsilon = 200$ L/mol·cm, $l = 1$ cm, $c = 0.01$ mol/L:

$A = 200 \times 1 \times 0.01 = 2$

Graph:

Plot of Absorbance vs Concentration gives straight line.

Limitations:

- High concentration deviates.
- Turbid solutions.
- Chemical interactions.