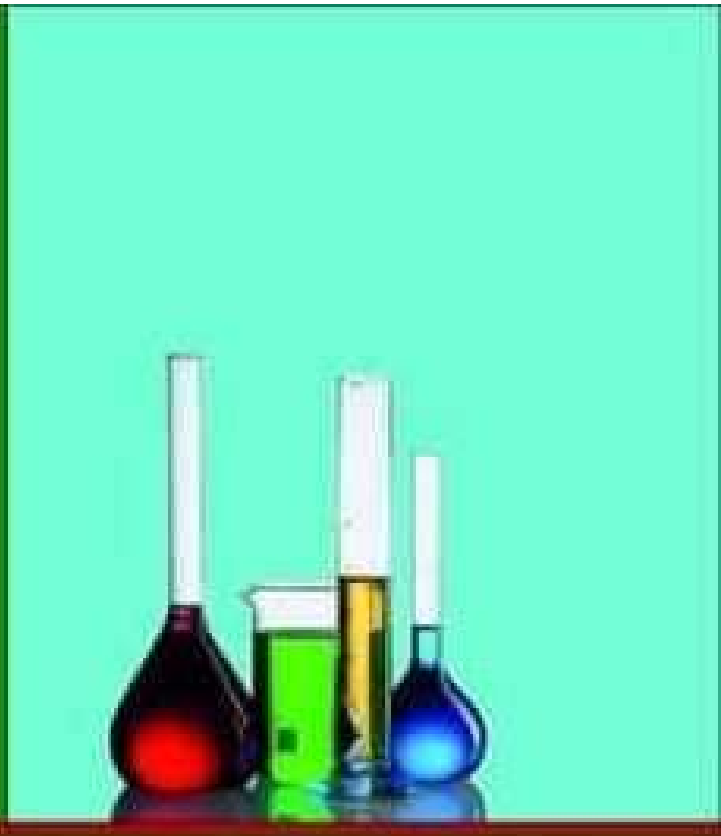
Fundamental Chemistry For Medical Sciences



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Fundamental Chemistry for Medical Sciences
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Fundamental Chemistry

FOR

MEDICAL SCIENCES

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الطبعة الأولى

لإبداء أي ملاحظات تعمل على تطوير الكتاب في الطبعات القادمة ان شاء الله

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PREFACE

This text is designed for college students majoring in medical sciences. It covers most major area of analytical chemistry (volumetric analysis, gravimetric analysis, and spectrophotometric analysis), organic chemistry and biochemistry. At the Beginning of the book starts with introduction chapter one, it describes the relationship between chemistry and medical sciences. Section I contains nine Chapters that treat general concepts of volumetric analysis which are including expressing of concentration of solutions, titration techniques, acid base equilibria, precipitation titration, type of indicator, inorganic and organic reagents, redox titration and gravimetric analysis. Instrumental analysis such as spectrophotometric method was studied in chapter ten. Other feature of the text includes the general organic chemistry in section II is illustrated the types of organic compounds, nomination and types of the reactions. While the section III contain a principle of biochemistry, which are biomolecules, enzymes, electrolytes, uric acid, vitamins, urea and creatinine. The application of all activities in these fields is practically in good laboratory practice which is listed in section IV.

There are questions and answers are listed at end of each chapter. The review of much information's as units, periodic table and balancing redox reaction and others have been placed in appendix. Regarding to my experience by giving lectures in chemistry, pharmacy and radiology technology, I came up with this book, specifically for the first grade studies to break down topics to be simple and easy to understand, which shows equations with answers, samples and tables.

I have focused on some of the subjects that relate to medical sciences, such as analytical chemistry, organic chemistry and biochemistry. The suggestions of a number of colleagues have assisted immeasurably in revision of this text. I especially thank, (Dr. Amer Salih Mahdi, Prof. Dr. Ramzie R. Alani, Prof. Dr. Fatin Fadhel Alkazazz, Prof. Dr. Abudl Jabar Kh. Atia, Prof. Dr. Salam A. H. Almeri, Dr. Muntadhar Salih Sultan, Mrs Ruba Fahmi Abbas (Al-Mustensiryah University), Prof. Dr. Sasdiyah Ahmed Dhaheir (Baghdad University), Dr. Riyadh Hassan Mohammed Ali, Dr. Bashar Mudhaffar Abudllah (Al-Rafedian University College) who read the entire manuscript and offered several helpful comments.

Jameel M. Dhabab

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INTRODUCTION RELATIONSHIP BETWEEN CHEMISTRY AND MEDICAL SCIENCES

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INTRODUCTION: RELATIONSHIP BETWEEN CHEMISTRY AND MEDICAL SCIENCES

Introduction

The chemistry is particular branch of science, holds the key which alone can unlock the gate to really fundamental knowledge of the hidden causes of medical sciences.

This chapter Includes; fundamental branches of chemistry, also has a summary of the topics that are the basis of this knowledge. It focuses on three branches as analytical chemistry, organic chemistry and biochemistry, because these branches are wide relating with medical sciences such as medicine, dentistry, pharmacy, radiology techniques and others.

Chemistry and Medical Sciences

Chemistry; A branch of science that deals with the study of the composition, structure, properties, changes of matter, and the energy changes that accompany these processes. Chemistry is the study of the composition of substances and the changes that they undergo. in particular, chemistry is the study of elements (substances containing only one kind of atom) and the compounds (substances containing combined elements) they form. Chemists work with reactions between substances to create plastics, medicines, dyes, and many other materials useful in our modern world. They study what substances are made of, and how they can be altered or combined to create new materials. 92 elements occur in nature, and another 17 have been created in nuclear laboratories. Several million compounds have been synthesized by chemists.

Main branches of chemistry;

Analytical chemistry: branch of chemistry involved with studying the properties of materials or developing tools to analyze materials.

Organic chemistry: branch of chemistry deals with the chemistry of carbon and living things. This type of chemistry is important to the petrochemical, pharmaceutical, and textile industries. All living organisms contain at least some amount of carbon in their body.

Biochemistry: branch of chemistry concerned with the chemical reactions that occur inside living organisms. This type of chemistry utilizes the concepts of organic and physical chemistry to make the world of living organisms seem much clearer. Some people also consider biochemistry as physiological chemistry and biological chemistry. The scientists that study biochemistry are called biochemists. They study such things as the properties of biological molecules, including proteins, lipids, carbohydrates, and nucleic acids. Other topics they focus on are the chemical regulation of metabolism, the chemistry of vitamins, and biological oxidation.

Physical chemistry: branch of chemistry that applies physics to the study of chemistry. Quantum Mechanics and Thermodynamics are examples of physical chemistry disciplines.

Theoretical chemistry: applies chemistry and physics calculations to explain or make predictions about chemical phenomena.

Nuclear chemistry: chemistry of subatomic particles and nuclear reactions

Inorganic chemistry: branch of chemistry that deals with the structure and interactions between inorganic compounds, which are any compounds that aren't based in carbon-hydrogen bonds.

Uses of Chemistry in Medical sciences;

Chemistry is the most important science in the preparation for a career in medical sciences. Using chemistry to improve health of patients and to prepare future physicians.

There are many projects applied in practical medical sciences for example:

1-**Stoichiometry**; it is including;

a- Management of fluids and electrolytes

b- Solutions, Such as Normal Saline: 154 mEq Na+ / L and D10W: 10% glucose solution.

2-**Electrolytes**; they are Current concentrations to needed concentrations.

3- **Electrochemistry**;

a- Sodium ions (Na^+) have higher concentrations outside cell membrane via Na+/K+ pump.

b- Electrical gradient across the cell membrane of -70 mV Nerve conduction and action potentials.

4- **Gas laws and diffusion;**

O_2 and CO_2 diffuse in alveoli in lungs and the capillary beds in tissues until they reach equilibrium

5- **Solubility;**

a- It Will certain chemicals be able to diffuse through the cell membrane lipid bilayer.

b- How will the concentration of chemicals (drugs) are distributed through body.

c- Tissues that are aqueous verses lipid.

d- What tissues do you want the drug to be highly concentrated.

6- **Kinetics;**

a- How rapidly are chemicals we give patients degraded in the body.

b- Half-life of drugs.

7- **Acid-Base;** it contains:

a- pH balance to maintain homeostasis.

b- Buffers in the body such as -HCO_3^-

8- **Metals;** they are important role in live such as;

a- Iron in Hemoglobin and O_2 transport

b- Copper in Immune system health

c- Zinc in Wound healing, smell and taste

9-**Nuclear chemistry**; it is including Isotopes that are used for imaging studies for example Technetium $Tc_{99,}$ which is emission Gama ray and Isotopes used for therapy as Radioactive Iodine $I_{131.}$

10- for Antacid - **Acid base** neutralization.

11- **Buffer system**, without which a glass of coke would be fatal. Controls acid base excursions.

12- **Chelation**, a means of treating heavy metal poisoning using EDTA or BAL to bind then and render soluble to pee out.

13- **dissolution**, of uric acid so it does not precipitate stones in your joints and kidneys as it has a god given right to.

14- **Ethanol**, the treatment for Methanol poisoning by competitive inhibition of enzymes involved in toxic formaldehyde formation

15- Fishy odour of amines in certain, gyne Infections.

16- for Gout – see term13 for why it occurs when kidney fails, producing monoclinic crystals that kamikaze ingesting phagocytes.
17- for Henderson -Hassel Bach Equation.
The Henderson–Hassel Balch equation focusing on the titration curve of a weak acid with a strong base. Over much of the titration range, the calculation of pH relies on the Henderson–Hassel Balch equation;

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

Were k_a is the dissociation constant of the week acid, $pk_a = -\log k_a$ and [HA] and $[A^-]$ are molarities of week acid and its conjugated base.

Importance of chemistry in medical sciences:

1- In knowing the actual composition of the drug and Decrease the toxic effect.
2- For sterilization and sanitation.
3- In the diagnosis of a disease.
4- To regulate the distribution of medicine inside the body compartments.
5- To study the mechanism of disease.
6- Chemistry also plays a central role in making biomaterials such as artificial joints, implants, heart valves and skin patches filled with hormones or other medicines.
7- Efforts to engineer artificial organs, like a liver, pancreas or bladder also hinge on chemistry.

In this book, we focused on some branches of chemistry that are taught in some medical departments in private education, such as departments of pharmacy, radiology and sonography techniques, medical lab techniques, and dentistry.

The important branches of chemistry in medical sciences;

There are three branches of chemistry which are wide link with deferent type of medical sciences;

Analytical chemistry

It is the study of the separation, identification, and quantification of the chemical components of natural and artificial materials. Analysis gives an indication of the identity of the chemical species in the sample, and quantitative analysis determines the amount of certain components in the substance. Analytical chemistry contributes to the safety of the food we eat and the water we drink and the medicines used to treat diseases. In the field of medicine, it helps physicians diagnose diseases by analysis of blood gas, enzymes, bacteria, and other medical samples. And in pathology, It is helping to understand the disease through its molecular makeup. The use of devices, statistics, analytical chemistry and computers makes analytical chemists necessary for medical research and pharmaceutical development. It is also used in law enforcement through forensic science.

The most important step in diagnosing diseases with analytical chemistry is how to obtain a representative sample after having the right information about the sample by analyst. It can be illustrated with the following steps;

1. A chemical analysis is usually performed on only a small portion of the materiel to be characterized.
2. The material to be characterized can be:

a- In the case of biological fluids, the condition which the collected sample must undergo are very important. For ex., the patient should fast for a number of hours before a blood test.

b- Blood samples may be analyzed as whole blood or separated to yield plasma and serum. Serum: is the fluid separated from the clotted blood. Plasma: is the fluid separated from the unclothed blood. The difference is that plasma contains fibrinogen.

3. Handling and storing samples: Certain precautions must be taken to prevent alternation or contamination of the sample. For ex., storing the sample in the proper light, temperature and container.

The stability of samples must be considered. For ex., preservations added to the blood must not interfere with the sample.

Analytical chemistry plays an important role in nearly all aspects of chemistry. There are many fields that depend on analytical chemistry. For ex., Medicine; analytical chemistry is the basis for clinical laboratory tests which help physicians diagnose disease. The nutritional value of food is determined by chemical analysis for major components such as protein and carbohydrates.

Diagrams below declare the relationship between analytical chemistry and deferent science. the diagram bellow declair relationship between analytical chemistry with different sciences.

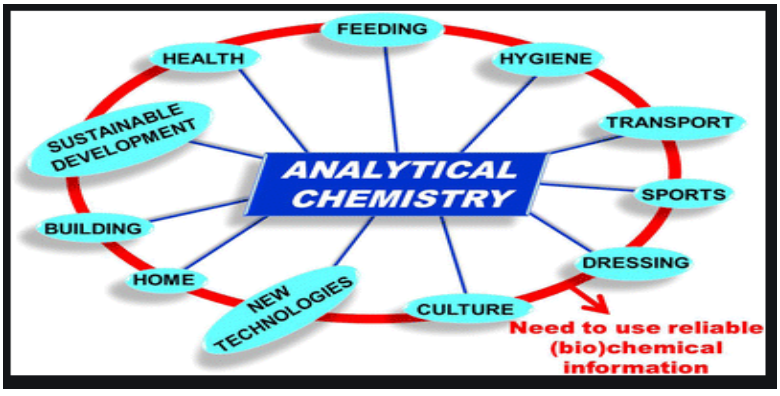


Figure 1-1, relationship between analytical chemistry and other sciences.

Analytical chemistry is applied in medical sciences such as;
The concentrations of O_2 and of CO_2 in blood samples, analyzing blood gases, enzymes, bacteria, and other medical samples.
There are experienced the great strides in improved health practices and products used in medicine today with the presence of analytical chemists.

Organic Chemistry

Organic chemistry is a chemistry subdiscipline involving the scientific study of the structure, properties, and reactions of organic compounds and organic materials, i.e., matter in its various forms that contain carbon atoms.
There are three generally accepted sources of organic compounds:
1- Living organisms; the chemical compounds of living things are known as organic compounds because of their association with organisms and because they are carbon-containing compounds. Among the numerous types of organic compounds, four major categories are found in all living things: carbohydrates, lipids, proteins, and nucleic acids
2- Invention/Human ingenuity; Antibiotics, aspirin, vanilla flavoring, and heart drugs are examples of substances that no longer have to be obtained directly from nature, they are manufactured in laboratories from organic starting materials. Each year over 250,000 new chemical compounds are discovered and many of these are products of scientists' imaginations, exploration. Plastics are excellent examples of substances that are the product of invention, they are not found anywhere in nature.
3- carbonized organic matter; Carbonization is the term for the conversion of an organic substance into carbon or a carbon-containing residue through pyrolysis or destructive distillation. For **Example**: the generation of coal gas and coal tar from raw coal. Fossil fuels from vegetable matter, coal to produce coke. The charcoal making process, etc.
Organic compounds form the basis of all earthly life. They are structurally diverse. The range of application of organic compounds is enormous. They either form the basis of, or are important constituents

of, many products including plastics, drugs, petrochemicals, food, explosive material, and paints.

Organic chemistry is a chemistry of carbon compounds. **Example:** methane, DNA, urea, DDT (insecticide), penicillin, nicotine, aspirin etc. But not all carbon compounds are organics. **Example:** carbonate (CO_3^{2-}; cyanide (CN^-), bicarbonate ($HCO3^-$), carbon dioxide and carbon monoxide.

The role played by organic chemist in pharmaceutical industry continues to be one of the main drivers in the drug discovery process.

The chemistry has contributed to life processes and to the efforts to advance the quality of life as well as to the development of society from synthetic, medicinal, biopharmaceutical and industrial point of view (Figures 1–1).

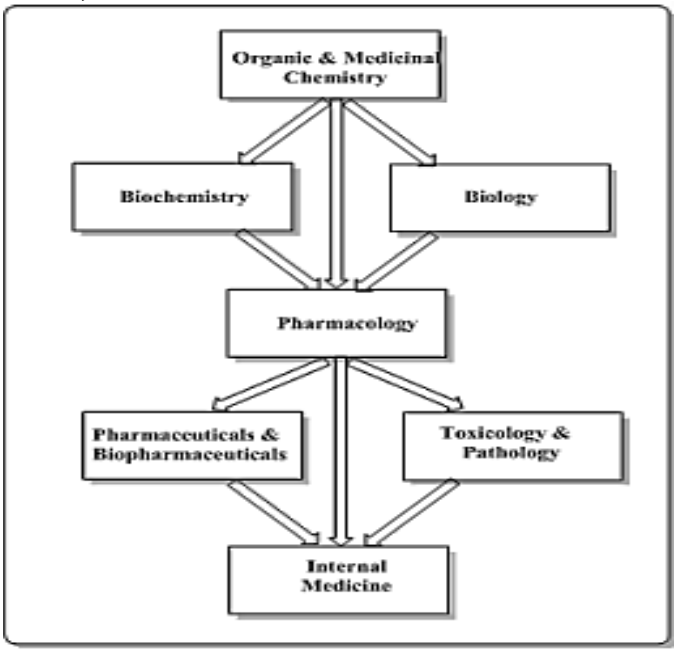


Figure 1-1Ramifications of Organic, Medicinal and Pharmaceutical Chemistry

Biochemistry

Biochemistry sometimes called **biological chemistry**; is the study of chemical process within and relating to, living organisms. By controlling information flow through biochemical signaling and the

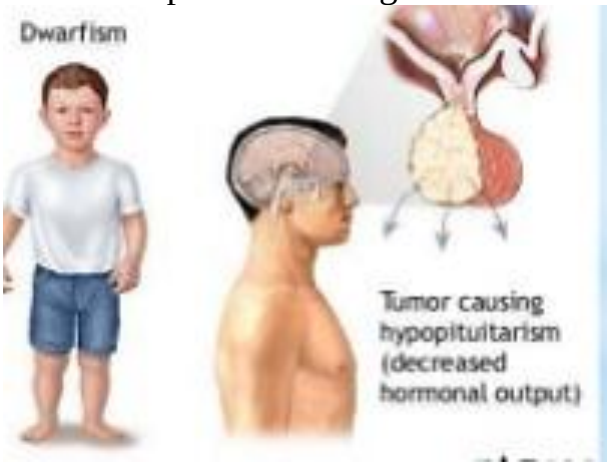
flow of chemical energy through metabolism, biochemical processes give rise to the complexity of life.

Importance of biochemistry in medical sciences;

1- The biochemistry helps us understand the pathology of any the biochemical changes and related disease is studied physiological alteration in the body through biochemical changes.

2- Many people rely in taking multivitamin and minerals for better health. The function and role of the vitamins is described only by biochemistry.

3- There are many disorders due to hormonal imbalance in specially women and children. The formation of hormones in the normal body function is taught in biochemistry by which the physician can understand the concerned problem during treatment.



4- Importance of biochemistry in Nursing Biochemistry is of great use within the field of nursing, with many practical applications that can assist you in becoming a better nurse.

5- Using biochemistry can be helpful knowing the chemical in the nursing profession, allowing reactions of drugs to nurses to determine how much the human body and medicine should be prescribed or mixing said drugs given to each patient they encounter.

6- The influence exercised by the environment is reflected both in morphological structure, and chemical structure of organisms. Organic matter is formed, transformed and is degraded in any living organism (plant, animal or microorganism).

7- Biochemical processes play an important role in many branches of food industry and especially in the process of processing raw materials, plant or animal kind. Another example is the enzymes involved in various processes which help to improve crops.

8- Importance of biochemistry in nutrition such as water, it is necessary for maintenance of health and optimum intake of many chemicals like vitamins, minerals, and essential fatty acids.

9- The nutrients value of food material can also be determined by biochemical tests.

10- Importance of biochemistry in pharmacy; it is Gives an idea of its constitution, its change of degradation with varying temperature and how drugs are metabolized by biochemical reactions in presence of enzymes.

Biochemistry in general deals with body substance like enzymes, hormones, carbohydrates, amino acids, fats, proteins, DNA, RNA, pigments etc.

The role of biochemistry and its importance in various fields is as described in following: physiology, pathology, nutrition deficiency, kidney function test, the change in pH, the colour of urine, blood test, liver function tests, serum cholesterol test, blood test, drug metabolism and others.

SECTION ONE
ANALYTICAL CHEMISTRY

CHAPTER TWO

Expression of Concentration of Solutions

SECTION ONE
ANALYTICAL CHEMISTRY

CHAPTER TWO
EXPRESSION OF CONCENTRATION OF SOLUTIONS

Introduction

Analytical chemistry studies and uses instruments and methods used to separate, identify, and quantify matter. In practice, separation, identification or quantification may constitute the entire analysis or be combined with another method. Analytical chemistry involves the quality control such as analysis of the pharmaceuticals.

It is divided into two parts:

1- Qualitative analysis … (what?).

2- Quantitative analysis… (how much?)

Qualitative analysis is identifies analytes by using separations such as precipitation, extraction, and distillation. Identification may be based on differences in color, odor, melting point, boiling point, radioactivity or reactivity.

Quantitative analysis; it is determining the numerical amount or concentration and uses mass or volume changes to quantify amount. Instrumental methods may be used to separate samples, using chromatography, electrophoresis or field flow fractionation. Then qualitative and quantitative analysis can be performed, often with the same instrument and may use light interaction, heat interaction, electric fields or magnetic fields. Often the same instrument can separate, identify and quantify an analyte.

Quantitative analytical chemistry. It is divided into three techniques:

1- Volumetric analysis

2- Gravimetric analysis

3- Instruments analysis

Stoichiometry

What is Stoichiometry; Using a balanced chemical equation to determine how much reactant or product is consumed or produced in a chemical reaction.

$2\ H_2\ (g) + O_2\ (g) \rightarrow 2\ H_2O\ (l)$

How many moles of H_2O are produced from the reaction of 2 moles of H_2?

How many moles of O_2 are required to produce 4 moles of H_2O?

Stoichiometry Formula Weight (FW); Sum of the atomic weights for the atoms in a chemical formula. So, the formula weight of calcium chloride, $CaCl_2$, would be

Ca: 1(40.1 amu) + Cl: 2(35.5 amu) = 111.1 amu

Note: amu, atomic mass unit (symbols: Da or u) is a unit of mass

These are generally reported for ionic compounds.

Stoichiometry Molecular Weight (MW); Sum of the atomic weights of the atoms in a molecule.

For the molecule ethane, C_2H_6, the molecular weight would be

C: 2(12.0 amu) + H: 6(1.0 amu) = 30.0 amu

Stoichiometry Percent Composition; One can find the percentage of the mass of a compound that comes from each of the elements in the compound by using this equation:

%element =(number of atoms) (atomic weight)/
(FW of the compound) x 100

Stoichiometry Percent Composition So the percentage of carbon in ethane is

$$\%C = \frac{(2)(12.0\ \text{amu})}{(30.0\ \text{amu})}$$

$$= \frac{24.0\ \text{amu}}{30.0\ \text{amu}} \times 100$$

$$= 80.0\%$$

Where, amu = atomic mass unit

Stoichiometry of Moles

The mole is the unit of measurement of the amount of matter in chemistry. As it is a basic unit of the international system of units (SI). One mole of carbon-12 atoms has 6.02214076×10^{23} atoms (Avogadro's constant) and a mass of 12 grams. The term "mol" came from the German word for Mole, as Wilhelm Ostwald was the first to

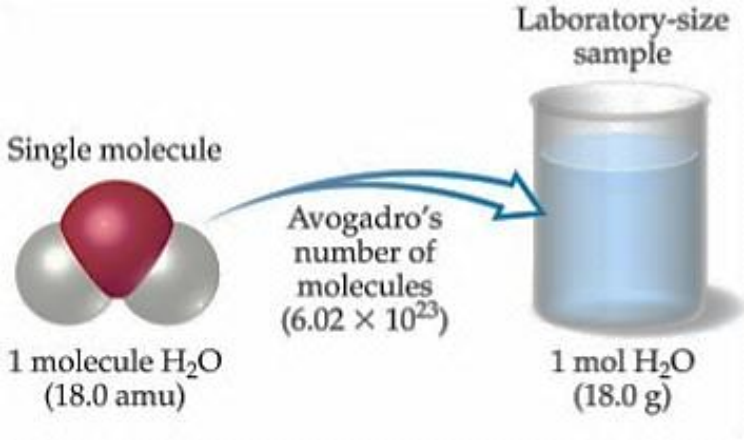
give this name in 1893. For example, in the following chemical reaction;

$2H_2O \rightarrow O_2 + 2H_2$

Two moles of water are decomposed into two moles of molecular hydrogen and one mole of molecular oxygen.

Stoichiometry Avogadro's Number:

6.02×10^{23}, 1 mole of 12C has a mass of 12 g

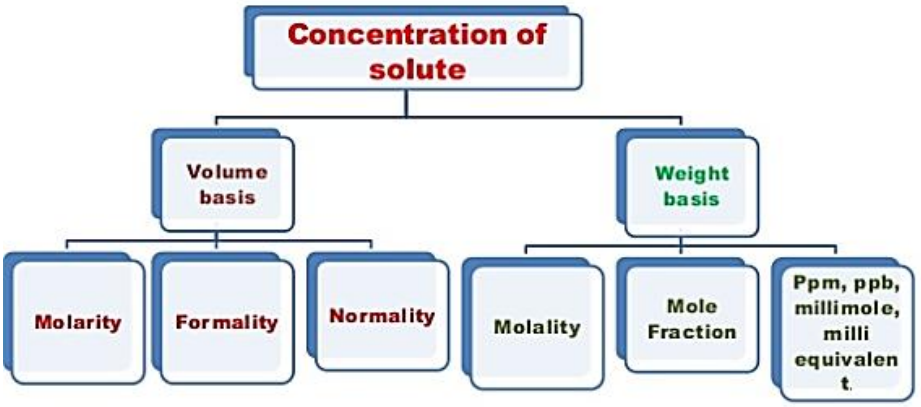


Volumetric Analysis

Principles of volumetric analysis:

Volumetric analysis deals with the measurement of volume of solutions involved in the chemical reactions which ultimately lead to the determination of the amount of the constituents of the substance.

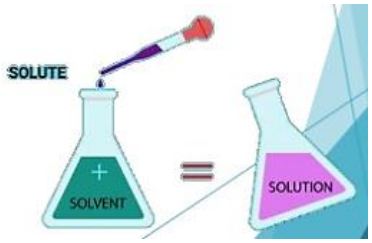
Different ways of expressing the concentration of the solutions. The amount of the substance present in the definite quantity of the solution is called concentration of the solutions. There are many ways of expressing the concentration of the solution. the flowing diagram illustrated these ways;



Concentration

The concentration of a solution may be defined as the weight of solute in a given amount of solution or solvent. (Concentration Amount of solute dissolved in given amount of solution);

$$c = \frac{\textbf{amount of solute}}{\textbf{amount of solution}}$$



Method of expressing of concentration;

There are several different methods to quantitatively describe the concentration of a solution. In all the techniques of quantitative analysis the use of solutions requires some basis for the expression of solution concentration such as molarity, normality, part per million and others.

The concentration of the solution can be expressed in any of the following ways.

a) Molarity: The number of moles of solute per liter of solution;

$$\boldsymbol{M = \frac{Wt}{Mwt} \times \frac{1000}{V(ml)} \ldots (2-1)}$$

b) Normality: the number of gram- equivalent weights of solute per liter of solution.

$$N = \frac{Wt}{eq.wt} \times \frac{1000}{V(ml)} \ldots . (2-2)$$

Ex1: What is the molarity and normality of 0.25 g of $NaHCO_3$ in 100 ml of solution, Mass of $NaHCO_3$=0.25 g, molar mass of $NaHCO_3$=84 g/mol.

Sol.: Volume of solution = 100 ml = 100/1000 = 0.1 L

Molarity= mass of solute/ Molar mass of solute L of solution.

$$M = \frac{Wt}{Mwt} \times \frac{1000}{V(ml)}$$

$$M = \frac{0.25}{84} \times \frac{1000}{100(ml)}$$

M = 0.0298

N = *n* × M (where *n* is an integer) … (2−3)

N= 1 × M = 0.0298

Or; apply this equation;

$$N = \frac{Wt}{eq.wt} \times \frac{1000}{V(ml)}$$

Note; to calculate equivalent weight of compounds in later paragraphs.

c) Part per million (ppm): number of milligrams of solute in one liter of solution;

$$ppm = \frac{mass\ of\ solute}{mass\ of\ solution} \times 10^6 \ldots (2-4)$$

or;

$$ppm = \frac{grams\ of\ solute}{mL\ of\ solution} \times 10^6 \ldots (2-5)$$

To convert from molarity and normality to ppm, below equation number **3 and 4** respectively.

$$M = \frac{PPM}{1000 \times Mwt} \ldots (2-6)$$

$$N = \frac{P.P.M}{1000 \times eq.wt} \ldots (2-7)$$

ppm= M x M.wt x1000

ppm= N x eq.wt x1000

Ex2: An atmospheric chemist reports that one dm^3 (L) of air in an urban are contained $3.5x10^{-4}cm^3$(ml) of CO. what was the concentration of CO in ppm?

$$pm = \frac{volume\ of\ \text{CO}\ in\ cm^3}{volume\ of\ air\ in\ cm^3} \times 10^6 \ldots (2-8)$$

$$pm = \frac{3.5 \times 10^{-4}\ cm}{10^3\ cm^3}\ 10^6 = 0.35$$

d) Percentage composition (part per hundred): it is the number of grams of solute per 100 grams of solution.

$$\text{Percentage(per cent)} = \frac{W}{W + Wo} x\ 100 \ldots (2-9)$$

In another hand;

1. Per cent W/W = Weight of solute/ Weight of solution X 100

18 Ka = 750 / 1000

$$\frac{75\ g\ gold}{100\ g\ alloy} = 75\ \%\ m/m$$

2. Per cent V/V = Volume of solute/ Volume of solution X 100

$$\frac{\text{5 ml acetic acid}}{\text{100 ml of vinegar}}$$

3. Per cent W/V= Weight of solute/ Volume of solution X 100

$$\frac{\text{0.243 g Sodium fluoride}}{\text{100 ml of tooth paste}}$$

For examples;
1 %= 1gm of KCl … in 100 ml of water.
10 % = 10 gm of KCl … in 100 ml of water.
100 % = 100 gm of KCl … in 100 ml of water.

e) Molality; moles of solute/kg solvent.

$$\boldsymbol{Molality(m) = \frac{moles\ of\ solute}{kilograms\ of\ solvent} \ldots (2-10)}$$

Ex. 3: Ethanol is an excellent solvent. It is used to prepare tinctures and in the extraction of medicinal compounds from plants. For this purpose, either pure ethanol or its aqueous solutions are used. A solution is prepared by mixing 1.00 g of ethanol (C_2H_5OH) with 100 g of water. Calculate Molality of this solution.

Sol.

Mass of C_2H_5OH = 1.00 g

Molar mass of C_2H_5OH = 46 g/mol

$$\text{Moles of } C_2H_5OH = \frac{1.00\ g}{46\ g/mol} = 2.17 \times 10^{-2}\ mol$$

$$\text{Mass of water} = 100\ g = 100/1000 = 0.1\ kg$$

$$\text{Molality of solution} = \frac{\text{Moles of } C_2H_5OH}{\text{Kg of water}}$$

$$\text{Molality of solution} = \frac{2.17 \times 10^{-2}\ mol}{0.1\ kg}$$

Molality of solution= 0.217 m

f- Mole Fraction (X); the ratio of the number of moles of a given component to the total number of moles of a solution.

$$\boldsymbol{Mole\ Fraction\ solute = X1 = \frac{n1}{n1 + n2}}$$

$$\boldsymbol{Mole\ Fraction\ solvent = X2 = \frac{n2}{n1 + n2}}$$

$$\boldsymbol{X1 + x2 = 1 \ldots (2 - 11)}$$

Where; n_1= moles of solute, n_2= moles of solvent, below table 2-1 show brief of units of concentration.

Table 2-1 show brief of units of concentration.

Name	Units	Symbol
Molarity	Moles solute/liters solution	M
Formality	No.FWs solute/liters solution	F
Normality	No.EWs solute/liters solution	N
Molality	Moles solute/kg solvent	*m*
Weight %	g solute/100g solution	%w/w
Volume %	mL solute/100mL solution	%v/v
w/v %	g solute/100 mL solution	%w/v
ppm	g solute/10^6 solution	ppm
ppb	g solute/10^9 g solution	ppb
ppt	g solute/10^{12} g solution	ppt

Equivalent Weight of Compounds

1- For acids: The gram-equivalent weight is known as the weight of the acid which supplies (1.008) grams of hydrogen as the hydrogen ion H^+. Therefore, the gram-equivalent weight of HCl acid is 1 mole and H_2SO_4 is 1/2 and H_3PO_4 is 1/3 or in other words one molecule of HCl prepares one hydrogen ion and one part of H_2SO_4 prepares two ions and one part of H_3PO_4 supplies three ions.

2- Substances that follow the behavior of the acid: The gram's weight of these substances is their weight in grams that have an equivalent to one gram of an atom of hydrogen like a hydrogen ion. One hydrogen ion H^+ equivalent to one a hydroxyl ion (OH^-).

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

3- Substance that acts as an acidizing neutralizing power of two hydrogen ions because it interacts quantitatively with 2OH-. The SO_3 equivalent weight is 1/2 mole.

$$\text{Eqwt } SO_3 = \frac{\text{Mwt } SO_3}{2}$$

$SO_3 + 2OH^- \rightarrow SO_4^{2-} + H_2O$

The equivalent weight of P_2O_5 (phosphorus pentoxide) is 1/6 mol.

$$\text{Eqwt P2O5} = \frac{\text{Mwt P2O5}}{6}$$

$P_2O_5 + 6NaOH \rightarrow 2Na_3PO_4 + 3H_2O.$

For bases: Equivalent Weight to grams and containing one gram equivalent of (0H -) (17.008 gm), according to the following rules.

Table 2-2 show the deferent of Equivalent Weight

bases	weight gram base	Equivalent Weight
KOH	1 Mole	**or** $\frac{\textbf{Mwt KOH}}{\textbf{1}}$
$Ca(OH)_2$	1/2 Mole	**or** $\frac{\textbf{Mwt Ca(OH)}_2}{\textbf{2}}$
$AL(OH)_3$	1/3 Mole	**or** $\frac{\textbf{Mwt Al(OH)}_3}{\textbf{3}}$

4- For substances that exhibit base behavior: some bases do not contain a hydroxyl ion (OH-) for that gram-equivalent law is their weight in grams that are equivalent to an atomic weight of a hydrogen ion or equivalent in their equal strength to 17.008 g of OH^-

Gram's weight to calcium oxide (CaO) is 1/2 mol because it interacts with two hydrogen ions. These two ions are equivalent to two OH^-.

$CaO + 2H^+ \rightarrow Ca^{2+} + H_2O$

$$\text{Eq.wt CaO} = \frac{\text{M wt CaO}}{2}$$

$Fe_2O_3 + 6H^+ \rightarrow 3H_2O + 2Fe^{3+}$

$$\text{Eq. wt } Fe_2O_3 = \frac{\text{M wt } Fe_2O_3}{2}$$

5- Factors that act the behavior as reducing agents: The gram equivalent weight is their weight in grams that equals the reducing strength of 1/2 mol of hydrogen gas (where H_2 is the reducing agent). It can be defined based on the number of electrons lost from the interaction with the oxidizing agents.

$$\text{Eq.wt of a reactant} = \frac{\text{molecular weight}}{\text{No of electrons lost per molecule}}$$

oxalate ion $C_2O_4^{2-}$

The oxalate ion is a reduced ion that oxidizes to (CO_2) with the loss of (2) electrons.

$C_2O_4^{2-} \rightarrow 2CO_2 + 2e$

$$\text{eq.wt} = \frac{\text{M wt}}{2}$$

6- Substances that is behavior as oxidizing agent: Gram equivalent weight is their weight in grams equivalent to the oxidation force of them for 1.008 gms of hydrogen ions. Where the behavior of H^+ as oxidizing agent. It is find with a metal ion like Zn to convert it to Zn^{2+} or 8.00 g of oxygen can be defined, the number of electrons Acquired by the oxidizing agent.

$$\text{eq.wt of a reactant} = \frac{\text{molecular weight}}{\text{no of electrons gained per mole}}$$

$KMnO_4$ potassium permanganate is a strong oxidizing agent. in an acidic medium it reduces by a reducing agent by acquiring five electrons per molecule for that equivalent.

$$\text{eq.wt} = \frac{KMnO_4}{5}$$

As for the base medium: the equivalent gram weight is $KMnO_4$ = 1/3 mole for Mno_4^-. it is reducing to MnO_4^- then reduced to MnO_2 by acquiring three electrons.

$$\text{eq.wt} = \frac{\text{Mwt}\,KMnO_4}{3}$$

7- Salts:

A) Basic salts: the equivalent weight is the weight that by interacting with one proton (H +).

$$\text{eq.wt} = \frac{\text{Mwt}\,NO_2CO_3}{2}$$

$$Na_2CO_3 + 2H^+Cl^- \rightarrow H_2CO_3 + 2NaCl$$

$Na_2B_4O_7$

$$\text{eq.wt} = \frac{\text{Mwt}\,Na_2B_4O_7}{2}$$

$$Na_2B_4O_7 + 2HCl \rightarrow 2NaCl + 4\,H_3BO_3$$

B) Acidic salts: weight that liberates or acquires one proton (H +).

Equivalent weight of Salts

KCl 1mole or $\frac{mwt\ kcl}{1}$

$BaCl_2$ 1/2 mole or $\frac{\text{Mwt BaCl2}}{2}$

$FeCl_3$ 1/3 mole or $\frac{MwtFeCl3}{3}$

$KHSO_4$ 1 mole or $\frac{\text{Mwt KHSO4}}{1}$

$KH(IO_3)_2$ 1mole or $\frac{\text{Mwt KH(IO3)2}}{1}$

$(NH_4)_2SO_4$ 1/2 mole or $\frac{\text{Mwt (NH4)2SO4}}{2}$

$Ca_3(PO_4)_2$ 1/6mole or $\frac{MWt\ Ca3(PO4)2}{6}$

Ex4: calculate the equivalent weight (eq. wt) each of the following substances when they act as oxidizing agents:

a) H_2O_2

b) I_2

c) $KMnO_4$

d) $K_2Cr_2O_7$

e) $K_3Fe(CN)_6$

Sol.:

a) H_2O_2 can act as an oxidizing agent and also a reducing agent. As reducing agent, it is oxidized free oxygen and water.

$5H_2O_2 + 2MnO_4^- + 6H_3O^+ \rightarrow 5O_2 + 2Mn^{2+} + 14H_2O$

The average change in oxidation number of each oxygen atom in hydrogen peroxide molecule is form -1 to 0. Total change for the molecules is 2.

equivalent weight= $H_2O_2/2$= 34.02/2=17.01g

as oxidizing agent, it is reduced to water

$H_2O_2 + 2H_3O^+ + 2e \rightarrow 4H_2O$

The total change for molecule is 2, equivalent weight is 17.01g

b) I_2: iodine is reduced to iodide with one unite change in oxidation number for each iodine atom or two units change for molecule. There for the equivalent weight is the half the formula weight $I_2 \rightarrow 2I^-$

equivalent weight= $I_2/2$ = 253.8g/2 = 126.9 g

c) $KMno_4$ the permanganate ion is reduced to the manganous ion in the present of an acid, and to MnO_2 in the alkaline solution.

$MnO_4^- + 8H_3O^+ + 5e \rightarrow Mn^{+2}(MnO) + 12H_2o$

The change of oxidation number of manganese is from +7 to +2

Equivalent weight= $KMnO_4/5$ = 158.03g/5=31.61gm

In alkaline solution, the permanganate ion is reduced to mno2 with change in oxidation number of 3(from +7 to +4)

$MnO_4^- + 2H_2O + 3e \rightarrow MnO_2 + 4OH^-$

Equivalent weight = 158.03/3 = 52.68 gm

d) $K_2Cr_2O_7$: the dichromate ions are reduced in acid solution to chromic ion

$Cr_2O_7^- + 14\ H_3O^+ + 6e \rightarrow 2Cr_3^+ + 21H_2O$

The change in oxidation number of each chromium atom is from +6 to +3, or the change of the dichromate ion, since contain 2 chromium atoms is 6.

Equivalent weight = $K_2Cr_2O_7/6$ = 294.21g/6 =49.03gm

e) $K_3Fe(CN)_6$

The ferricyanide ions are capable of being reduced to ferrocyanide ions.

$Fe(CN)_6^{3-} + e \rightarrow Fe(CN)_6^{4-}$

The change in oxidation number of the ion is from (+3 to +2)

Equivalent weight = $K_3Fe(CN)6/1$ = 329.3/1= 329.3gm

Calculations Involving Normality and Molarity

Ex5: Calculate the normality and molarity of a solution contain 10.60 grams of a sodium carbonate (Na_2CO_3) in one liter of the aqueous solution = Mwt Na_2CO_3 = 106 g/mole.

Sol.: wt 1000

$$\mathbf{M = \frac{wt}{Mwt} x \frac{1000}{V(ml)}},$$

Mwt = 106

$$\mathbf{M = \frac{10.60}{106} x \frac{1000}{1000} = 0.1 molar}$$

The equivalent weight of Na_2CO_3 is 1/2 of its Mwt, sin the molecule. Reacts quantitatively with two hydrogens.

$Na_2Co_3 + 2H^+ \rightarrow 2Na^+ + H_2CO_3$

Gram. equivalent Wt of Na_2CO_3 =1/2 mole, or 106/2 = 53

$$\mathbf{N = \frac{wt}{wt} x \frac{1000}{V(ml)}}$$

$$\mathbf{N = \frac{10.6}{53} x \frac{1000}{1000}} = 0.2 \text{ N}$$

0.1 M of Na_2CO_3 solution = 0.2 N

or 1M of Na_2Co_3 **sol** = 2 N, or in other words:

N = RM ... (2-6)

= 2 x 0.1 M = 0.2 M

Ex6: calculate the number of grams present in 1 liter of

a) 0,2000 N HCl (M.wt =36.46) solution.

b) 0.2000 N $Ba(OH)_2$ (M.wt =171.2) solution.

c) 0.1000 N $H_2C_2O_4$. $2H_2O$ (M.wt = 126.1) solution.

Sol.:

a) For HCI

molecular weight = equivalent wight =36.46

$$\mathbf{N = \frac{wt}{36.46} x \frac{1000}{1000}}$$

$$\mathbf{N = \frac{wt}{Eq.wt} x \frac{1000}{1000}}$$

$$\mathbf{0.200 = \frac{wt}{36.46} x \frac{1000}{1000}}$$

Wt = 7.292 gm

Here is a new relationship for calculating the number of grams of substance in a standard solution.

No. grams = (volume in liters) x (Normality) x (Eq.wt)

= (1 L) x (0.2000 eq /L) x (36.46 g

= 7.292 grams of HCl

b) for $Ba(OH)_2$

equivalent weight of $Ba(OH)_2$ in grams = 1/2 mole =1/2 x 171.4 g

= 85.7 g.

No. grams of $Ba(OH)_2$ = (1 L) (0.2000 eg/L) (857 g/.eq)

= 17.14 grams of $Ba(OH)_2$

C) for $H_2C_2O_4.2H_2O$

Equivalent wt of $H_2C_2O_4$ = 1/2 mole = 1/2 x 126.1 = 63.05

(1 L) (0.1000 g.eq 1L) (63.05 glg.eq) =6.305 grams of $H_2C_2O_4$

Ex7: How many grams of Na OH are needed to prepare 150 ml of 0.2 N NaOH solution (Mwt NaOH) = 40 gm/ mole.

Sol.:

$$\mathbf{Eq.wt = \frac{Mwt}{No.equivalent} = \frac{40}{1}} = 40 \text{ gm/mole}$$

$$\mathbf{0.2 = N = \frac{wt}{150} x \frac{1000}{Eq.wt}}$$

$$\text{Wt} = \frac{\mathbf{0.2 \times 40 \times 150}}{\mathbf{1000}} = 1.2 \text{ gm}$$

Ex8: How many grams of $BaCl_2.2H_2O$ are needed to prepare 1.5 liter of 0.1 MBa^{2+} and calculate the numbers of moles of Ba^{2+} and Cl^- in this solution, Mwt = 245 gm/mole.

Sol.:

a) Mwt $BaCl_2.2H_2O$ = 137.5 + 71 +18x2 = 245 gm/mole

$$\mathbf{M = \frac{wt}{Mwt} x \frac{1000}{1500}}$$

$$\mathbf{0.1 = \frac{wtx1000}{245x1500}}$$

wt = 36.75 gm should be dissolved in 1500ml to be get 0.1 M of solution.

b) no of moles of Ba^+ = R × M × V

= 1× 0.1 × 1500/ 1000 = 0.15 mole

No of mole g Cl^-= R × M × V

= 2× 0.1 × 1500/1000 = 0.3 mole

Ex9: calculate the number of ppm of NaCl in the solution prepared by dissolving 2 gmms of NaCl in 1.5 liter of water, Mwt NaCl =58 gm/mol.

Sol.:

$$\mathbf{N = \frac{wt}{Mwt} x \frac{1000}{v}}$$

$$\mathbf{N = \frac{2x1000}{58x1500} = 0.023}$$

$$\mathbf{N = \frac{ppm}{Eq.wt\,x\,1000}}$$

ppm =N ×eq.wt ×1000 = 0.023 × 58 ×1000 =1334

Normality, Molarity and specific Gravity of liquids

If the specific weight of a solution and percentage of its weight are known, it is possible to calculate its concentration by normality or molarity according to the two equations below.

$$N = \frac{Sp.G \times w\% \times 1000}{Eq.wt} ...(2-12)$$

$$M = \frac{Sp.G \times w\% \times 1000}{Mwt} ...(2-13)$$

Not: Sp.Gravity = density

Ex10: calculate the molarity and normality of a concentrated hydrochloric acid whose specific gravity is 1.20 when it contains 3.11% HCl by weight, Mwt HCl = 36.46 g/mole.

Sol.:

$$N = \frac{Sp.G \times w\% \times 1000}{Eq.wt}$$

Eq.wt = Mwt/1 =36.46/1 = 36.46

$$\frac{1.2 \times 0.3911 \times 1000}{36.45} = 12.8 \text{ N HCl}$$

Since 1M HCl = 1NHCl

Molarity = 12.8 M

Ex11: a concentrated sulfuric acid (H_2SO_4) has a specific gravity of 1.700 when it contains 77.17 % H_2SO_4 by weight. Calculate the molarity and normality of this acid. Mwt H_2SO_4 =9.8

Sol.:

$$M = \frac{1.7 \times 0.7717 \times 1000}{98.08}$$

13.37 moles 1 liter = 13.37 M.

If 1 mole of H_2SO_4 =2 gram – equivalent weight of H_2SO_4,

1 M = 2 N

and 13.17 M = 13.17 * 2 N/M = 26.74 N

Another law can be used to obtain the same result:

$$N = \frac{Sp.G \times w\% \times 1000}{Eq.wt}$$

Dilution Calculations

The number of gram–equivalents or milligram –equivalents in a solution of definite normality does not change upon dilution. When a standard solution is diluted, its normality win decrease while the volume is increasing, but the product of V and N remains constant. Dilution is one of the methods for preparing solutions of the desired normalities.

V1 × N1 = V2 × N2 … (2- 14)

V1 and N1 are the original volume and normality respectively.

V2 and N2 are the volume and normality of the same solution after dilution.

V1 × M1 = V2 × M2 … (2- 15)

The important point here is that in the standard case, the number of grammatical equivalents on both sides of the equation is the same, and the number of millimoles or moles on both sides of the equation become the same or remain the same as well.

Ex12: How many milliliters of 12 N HCl should be diluted to 500 ml to obtain a normality of 0.25 N?

Sol.:

$V_1 \times N_1 = V_2 \times N_2$

V1 (12 mg – eq/ml) = (500 ml) (0.25 mg – eq/ml)
V1 = 10.4 ml of 12 N HCl

Ex13: preparing 500 ml of 0.1 M solu of $K_2Cr_2O_7$ from 0.25 M of its concentrated solution, what is the volume of 0.1 M $K_2Cr_2O_7$ required to prepare or dilute to 500 ml?

Sol.:

$M_1 \times V_1 = M_2 \times V_2$
(0.25 M mole/ml) (V1) = (0.1 M mole/ ml) × (500 ml)
V1 =200 ml.
Note =M ×V(ml) = no. of mmole

Normality of solution prepared by mixing similar components.

When some special solvents are mixed, the general number of millimoles in the final solution equals the sum of the equivalents of the all components.

Ex14: If mix HCl or NaOH Or $K_2Cr_2O_7$ it is;

(V1) (N1) + (V2) (N2) + … (VX) (NX) = (Vy) (Ny) … (2-12)

mg.eq in Soln.1 | mg.eq in soln.2 | mg.eq in soln.x | mg.eq in resulting.

$V1 + V2 \ldots + V_X$ where V_y is the total volume.

$N1 + N2 \ldots + N_X$ where N_y is the final normality.

This equation applies when mixing two similar materials and when there is no interaction between them.

Ex15: If 100 ml of 6.2000 N HCl solution are added to 500ml of 100 N HCl solution, what will be the normality of the resulting solution.

Sol.:

(V1) (N1)+ (V2) (N2) = (V3) (N3)
(100ml) (0. 2000mg.eq/ml) +(500ml) (0. 1000mg.eq/ml) =(600ml) (N2)

$$\mathbf{N_3 = \frac{20.00\,mg.eq + 50.00\,mg.eq}{600\,ml\ \ HCl}}$$

= 0.1166 mg.eq/ml = 0.1166N of

Question and Answer

Q1. 20.0 mL of 0.10 M hydrochloric acid (HCl) reacts with 20.0 mL of 0.30 M potassium hydroxide (KOH) solution. The concentration of potassium ions in the resultant solution, in mole per litre, is

a. 0.10
b. 0.15
c. 0.20
d. 0.3

Sol. $HCl(aq) + KOH(aq) \rightarrow KCl(aq) + H_2O(l)$; $K^+(aq)$ is a spectator ion

$KOH(aq) \rightarrow K+(aq) + OH-(aq)$

$n(K^+) = n(KOH) = 0.30 \times 20.0 \times 10^{-3} = 6.0 \times 10^{-3}$ mol

Total volume = 40.0 mL

$c(K^+) = 6.0 \times 10^{-3} / 40.0 \times 10^{-3} = 0.15$ mol L^{-1} (option B)

Q2. 25.00 mL of a 0.100 M solution of HCl is added to 25.00 mL of a 0.180 M solution of NaOH.

The concentration of $OH^-(aq)$ remaining in the solution, in M, is

a. 0.0400
b. 0.0500
c. 0.0800
d. 0.1000

Sol. a. $HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H2O(l)$

$n(HCl) = c(HCl)V(HCl) = 0.100 \times 25.00 \times 10^{-3} = 2.50 \times 10^{-3}$ mol

$n(NaOH) = c(NaOH)V(NaOH) = 0.180 \times 25.00 \times 10^{-3} = 4.50 \times 10^{-3}$ mol

$n(NaOH)$ reacting $= n(HCl) = 2.50 \times 10^{-3}$ mol

$n(NaOH)$ remaining $= 4.50 \times 10^{-3} - 2.50 \times 10^{-3} = 2.00 \times 10^{-3}$ mol

$[OH^-]$ remaining = $n(OH^-)$ remaining/ V(mixture)

$= 2.00 \times 10^{-3/} 50.00 \times 10^{-3}$

= 0.0400 M

Q3. 20.0 mL of 0.10 M hydrochloric acid (HCl) reacts with 20.0 mL of 0.30 M potassium hydroxide (KOH) solution.

The concentration of potassium ions in the resultant solution, in mole per liter, is

a. 0.10
b. 0.15
c. 0.20
d. 0.30

Sol. $HCl(aq) + KOH(aq) \rightarrow KCl(aq) + H_2O(l)$; $K^+(aq)$ is a spectator ion

$KOH(aq) \rightarrow K^+(aq) + OH^-(aq)$

$n(K^+) = n(KOH) = 0.30 \times 20.0 \times 10^{-3}$

$= 6.0 \times 10^{-3}$ mol

Total volume = 40.0 mL

$c(K^+) = 6.0 \times 10^{-3} / 40.0 \times 10^{-3}$

$= 0.15$ mol L^{-1} (option B)

Q4. The concentration of K^+ ions in 100 mL of 0.0500 M K_2CO_3 solution, in g/ L is:

a. 0.196
b. 0.391
c. 1.96
d. 3.91

Sol. d. $K_2CO_3(aq) \rightarrow 2K^+(aq) + CO_3^{2-}(aq)$

$c(K^+) = 2 \times 0.0500$

$0.100 =$mol L^{-1}

$0.100 =$mol $L^{-1} \times 39.1$ g/mole

$= 3.91$ g L^{-1}

Q5. 15.0 mL of 10.0 M HCl is added to 60.0 mL of deionised water. The concentration of diluted acid is:

a. 3.33 M
b. 2.50 M
c. 2.00 M
d. 0.500 M

Sol. c. n(HCl) present = 10.0 mol $L^{-1} \times 15.0 \times 10^{-3}$ L = 1.50×10^{-3} M

Volume of diluted acid = 15.0 + 60.0

= 75.0 mL

c(diluted acid) = 1.50×10^{-3} mol $\div 75.0 \times 10^{-3}$ L = 2.00 M

Alternatively, since the volume of the acid increases by a factor of 5 (15.0 mL to 75.0 mL) the concentration decreases by a factor of 5 from 10.0 M to 2.00 M.

Option B is consistent with calculating the concentration of the diluted acid based on the volume of diluted solution being 60.0 mL.

Q6. How many significant figures are present in the number 10.450?

a. three

b. four

c. five

d. none of these

Define or give a mathematical equation for the following terms:

Sol.

A Primary Standard: A chemical that is of sufficient purity and stability that it can be weighed and used directly in an analytical procedure without further standardization.

A back titration: A titration method in which a known excess of titrant is added to an analyte, and then the excess titrant is determined. The difference between the known amount of titrant and the amount of titrant that remains is then used to determine that amount of analyte

Q7. How many millileters of 0.100M KI are needed to react with 40.00 ml of 0.0400 M $Hg_2(NO_3)$ if the reaction is:

$Hg^{2+} + 2I^- \rightarrow Hg_2I_2(s)$

Sol. 40 ml ×.04M $Hg_2(NO_3)_2$ = 1.6 mmole $Hg(NO_3)_2$ = 1.6 mmoles Hg_2^{2+}

1.6 mmoles Hg^+ x 2 mole/ L/1 mole Hg^+ = 3.2 mmole/L

Molarity= mole/liter; 0.1M = 3.2 mmole/V(mL); V= 32 mL KI.

Q8. The principal reason that solid sodium hydroxide is not used as a primary standard for acid-base titrations is that it:

a. absorbs water from air.

b. has a low molar mass.

c. reacts slowly with many acids.

d. ionizes in water.

Q8. "Qualitative results" refer to:

a. Results that can be observed during an experiment.

b. Results those are difficult to observe during an experiment.

c. Results that require numerical data.
d. none of these is correct.

Q9. What piece of laboratory equipment is best-suited for accurately measuring the volume of a liquid?
a. graduated cylinder
b. beaker
c. Erlenmeyer flask
d. more than one of the above

CHAPTER THREE

TITRATION OF ACID-BASE

CHAPTER THREE
TITRATION OF ACID-BASE

Introduction

A technique for determining the concentration of a solution by measuring the volume of one solution needed to completely react with another solution. Titration process involves addition of solution of known conc. from burette to the measured volume of analyte.

Principle of titration

It is based on the complete chemical reaction between the analyte and the reagent (titrant) of known concentration.

Analyte + Titrant → Product

Terms used in titration

Analyte: The solution of unknown concentration but known volume.

Titrant: The solution of known concentration.

Standard solution: A solution of known concentration is called the standard solution.

Types of standard solution;

1- Primary standard- It has certain properties;

(a) Extremely pure.

(b) Highly stable.

(c) Can be weighed easily. For e.g. Na_2CO_3, KHP

2- Secondary standard- It has certain properties:

(a) Less pure than primary standard.

(b) Less stable than primary standard.

(c) Cannot be weighed easily. For e.g. NaOH, HCl

Solution of exactly known concentration and composition:

Table 3-1 Types of standard solution.

A **standard solution** has **known molarity**.
A **primary standard** is made by **weighing** a **pure solid** and diluting in a volumetric flask.
A **secondary standard** requires a titration to calibrate its concentration. It was made using an acid or base with **suspect purity**.

Not suitable	Example	Reason
Arrhenius bases	NaOH	Hydroscopic
Strong acids	HCl	volatile liquids or gases
Suitable		
solid bronsted bases	Na_2CO_3	pure solid
solid weak acids	$H_2C_2O_4$	pure solid

Primary Standard	Secondary Standard
$H_2C_2O_{4(s)}$	$H_2SO_{4(l)}$
$Na_2CO_{3(s)}$	$NH_{3(g)}$
$C_6H_5COOH_{(s)}$	$NaOH_{(s)}$
$KC_6H_5COO_{(s)}$	$HCl_{(g)}$

Preparing a Primary Standard

Ex1: Calculate the mass of $H_2C_2O_4 \cdot 2H_2O$ require to prepare 100.0 mL of 0.100 M standard solution.

Mass of acid = 0.1000 L x 0.1000 mole/1L x 126.06 g/1mole
=1.261 g

Standardization: The process whereby it the concentration of a standard solution is determined by titration of a primary standard.

Equivalence Point: Point where the amount of two reactants are just equivalent.

End point: Point at which the reaction is observed to be complete, this point is usually observed with the help of indicator.

Titration requirements as follows;

1- The chemical reaction must be stoichiometric (chemically balanced).
2- The reaction must be rapid.
3- The reaction must be specific.

4-The chemical reaction must show obvious change in its properties, such as change in its color, electrical properties, pH, etc. ….
5- It must be an available method for determining the end point.
6- It should proceed for to completion

example:

$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$

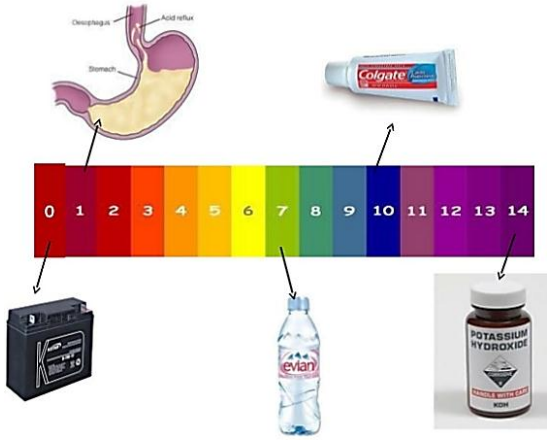
Indicators

It is an organic material which their color changes at a known pH. a system to cause a chemical reaction, or added to test if a reaction occurs. The terms reactant and reagent are often used interchangeably-however; a reactant is more specifically a substance consumed in the course of a chemical reaction. Indicator- It is a natural or synthetic organic material whose color changes according to its pH value.
The following table shows the most popular signs and pH that change color;

Table 3-2 types of indicator

Indicator	Approximate pH Range for Color Change	Color Change	pK_a	Useful range
Methyl Orange	2.8-3.8	Red to orange	3.7	3.1-4.4
Methyl red	3.8-4.4	Red to yellow	5.1	4.2-6.3
Bromothymol	6.0-7.9	Yellow to blue	7.0	6.0-7.6
phenophalene	6.0-9.6	Colorless to pink	9.3	8.2-10.0
Thymol blue	8.0-9.6	Yellow to blue	8.9	8.5-10.5

Or
1- strong acid - strong base, pH = 7 Bromothymol blue.
2- strong acid - weak Base, pH < 7 Methyl orange.
3- weak acid - strong Base, pH > 7 Phenophthalne.



Ex2: Titration calculation

For acid - base titration, at equivalence point

No of hydrogen ions from acid = No of moles of (OH^-) at base solution when;

No of mole of (H^+) at acid sol = No of (H^+) moles in mole (one) of acid x volume of acid x molarity of the acid = (R_1 x V_1 x M_1)

And;

No. of mole of (OH^-) abas solution = No of (OH^-) moles in one mole of the base × molarity = $R_2 \times V_2 \times M_2$

So at end point.

$R_1 \times V_1 \times M_1 = R_2 \times V_2 \times M_2$ … (3-1**)**

Or;

$N_1 \times V_1 = N_2 \times V_2$ … (3-2)

Ex3: It was found that (15 ml) of H_2SO_4 solution equalized by adding (10 ml) of 0.1M $Mg(OH)_2$ solution, what is the molarity of H_2SO_4 solution.

Sol.: At end point acid base

$$\mathbf{R_1 \times V_1 \times M1 = R_2 \times V_2 \times M_2}$$

$$\mathbf{\frac{2 \times 15}{1000} \times M_1 = 2 \times \frac{10}{1000} \times 0.1}$$

$$\mathbf{\frac{2 \times 10}{1000} \times 0.1}$$

$$\mathbf{M1 = \frac{2 \times 15}{1000} = 0.060}$$

Ex5: 10 ml of H_2SO_4 was titrated against 0.4 M NaOH solution. How many ml of NaOH was consume at end point (neutralization point).

Sol.:

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

$M_1\ V_1\ R_1 = M_2\ V_2\ R_2$

$0.1 \times \frac{10}{1000} \times 2 = 0.4 \times V_2 \times 1$

$V_2 = 0.005$ L = 5.0 ml of NaOH

Ex4: 20 ml of acid solution of 0.1 M is equal to 30ml of 0.2M of NaOH solution. Calculate number of moles of H^+ at one mole of the acid which is substituted during the reaction.

Sol.: Acid = base

$M_1\ V_1\ R_1 = M_2\ V_2\ R_2$

$0.1 \times 20/1000 \times R = 0.2 \times 30/1000 \times 1$

$$R = \frac{0.2 \times 0.03 \times 1}{0.1 \times 0.02} = 3$$

Ex5: calculate the weight of the acid in the above example knowing that it is M.Wt = 98.

Sol.:

$$wt = \frac{M * Mwt * 20}{1000} = wt = \frac{0.1 * 98 * 20}{1000} = 0.196\ \text{g}$$

Ex6: when 25.00 ml of an acid (CH_3COOH) were titrated with 0.100 N sodium hydroxide (NaOH) solution, 30.55 ml of the base were needed. Calculate normality of the acid.

Sol.:

No. of m.eq of NaOH = No. of meq of CH_3COOH

$(V_{base})\ (N_{base}) = (V_{acid})\ (N_{acid})$

(35.55ml) (0.1000 meq/ml) = (25.00 ml) (N acid)

N = 0.1222 meq/ml, the normality of CH_3COOH

Partial Competition of Titration Reaction

When an unequal number of gravimetric equivalents of acids are mixed with the bases or oxidizing agents with the reducing agent, the number of gram equivalents to them is the difference between them before and after mixing.

Ex7: what will be acidic or basic the solution resulting by mixing 50ml 0.20N HCl with 25ml 0.59 N of the NaOH solution? what will be the N of the solution with respect to the excess substance left and the salt formed?

Sol.:

(50ml)(0.20meq/ml) =10meq of HCl before mixing

(25ml) (0.50meq/ml) =12.5 meq of NaOH before mixing

$HCl + NaOH \rightarrow NaCl + H_2O$

10meq + 12.5meq $\rightarrow$10meq + 2.5 meq of excess of NaOH in the solution.

50ml + 25ml = 75ml, total volume of solution

12.5meq - 10meq= 2. 5 meq of NaOH in excess

(75ml) (normality) = 2.5 meq

Normality = 2.5meq/75ml = 0.033meq/ml, the normality of NaOH solution.

There are 10meq NaCl in 75ml of the solution thus,

(75ml) (normality) =10 meq/ml, the normality of NaCl.

N= 10meq/75ml = 0.133meq/ml, the normality of salt solution.

Normality and Percentage Composition

The purity of the substance or the percentage of its presence in the sample can be calculated by the titration process of the known weight (or the solution for a known weight of the sample) with a suitable standard solution. Where the weight of the material sought in the sample can be measured to calculate the number of grammatical equivalents of the material, and the percentage of the substance in the form is divided weight over the weight of the original sample multiplied by 100.

If N_t and V_t are the vaolium and standard for titrant, X is the weight of the material, then the percentage of the material in the sample is calculated according to the equation below;

$$(V_t)\,(N_t) = \frac{\text{Wt of X}}{\text{Meq wt of X}} \quad \ldots(3\text{-}3)$$

$$\text{Wt of X} = (V_t)\,(N_t)\,(\text{Meq wt X}) \ldots (3\text{-}4)$$

$$\%X = \frac{\text{Wt of X}}{\text{Wt of sample containing X}} X100$$

Ex8: A soluble chloride sample weighing 0.3520 gram, is dissolved in water.

(a) Calculate the percentage chlorine in the sample if it required 20.50ml of 0.10 N silver nitrate (Ag NO_3) solution for the complete titration?

(b) What will be the percentage NaCl, assuming that Cl is present in the sample as sodium salt?

Sol.: (a) No. of meq of Cl = No of meq of $AgNO_3$

Wt of Cl = (20.50 ml) (0.1000 meq/ml)(35.46 mg/eq)

= 72.69 mg of Cl = 0.07269 gram of Cl.

One can also say that

No of meq of Cl = no of meq of $AgNO_3$

Wtof Cl= (20.50 ml) (0.10 meq/ml) (0.03546 meq)

= 0.0726gm of Cl in the sample.

= 0.07269 gm

Percent Cl = $\frac{0.07269\ gm}{0.352\ gm} \times 100$ =20.65% Cl in the sample

(c) Number of meq of NaCl =number of meq of $AgNO_3$

Wt of NaCl = (25.50ml) (0.10meq/ml) (0.05845g/meq)

Wt of NaCl =0.1198 grams.

Percent NaCl = $\frac{0.1198\ gm}{0.352\ gm} \times 100$ =34.3% NaCl in the sample

Molarity and Percentage Composition

We noticed that the previous example can calculate the anlyate A percentage of the analytical substance (anayle A) with a ratio of 1:1 mol with the titrant of the general formula

$$\%A = \frac{\text{Mg analyle}}{\text{Mg sample}} X100$$

$$\%A = \frac{\text{M (m moles/ml) x ml x Mwt analyle (mg/m mole)}}{\text{Mg sample}} X100 \ldots \text{(3-6)}$$

But there is a lot of materials that do not reacte at a ratio of 1: 1 mol, and therefore simple calculations in the above example cannot be applied to all reactions. A formula for calculations applied to equilibrium reactions can be expressing the general reactions is:

$aA + bB \rightarrow p$

Since A is the anylate, the B is titrant and P represent the products:

Mmoles A = mmoles B $\frac{a}{b}$(mmoles a/ mmoles b)

Mmoles A = M_B (mmoles/ml) X mLB x $\frac{a}{b}$(mmples a/mmole b)

As mg A = mmole A × Mwt A(mg/mmole)

mg A =M_B (mmoles/ml)× $\frac{a}{b}$(mmoles a/mmples b)x Mwt A

It is possible to modify the percentage of the anylate in the sample by titrating a known weight of the sample with a standard solution, the following equation;

$$\%A = \frac{\text{MB (m moles/ml) x ml B x (a/b) x Mwt (mg/m mole)}}{\text{Mg sample}} X100$$

The measured concentration of solution B can be calculated by titrating a known number of millimoles from the primary standard A as follows:

$$M_B = \frac{\text{(mg A/ Mwt A) x (b/a)}}{\text{mL B}} \ldots (3-7)$$

Ex9: 0.4671 gm of a sample containing $NaHCO_3$ was dissolved and titrated with HCl. (40.72 ml) of the acid was required to equivalence. Knowing that (37.86 ml) of the same acid (HCl) was need in another titration process with o.1676 gm of Na_2CO_3 (pure) calculate the percentage of $NaHCO_3$ in the original sample.

Sol.:

$2H^+ + Co_3^{2-} \rightarrow H_2O + CO_2$

$bB + aA \rightarrow P$

To calculate the molarity of HCl from the above equation, applying the following law;

$$M_{HCl} = \frac{(\frac{mg\ Na2CO3}{\text{Mwt Na2CO3}})\text{x } 2/1}{\text{ml HCl}}$$

$$= \frac{(187.6\text{vmg}/105.99(\text{mg/mmole})) \text{ x } 2 \text{ (mmoles HCl/mmole } Na_2CO_3}{37.86 \text{ ml}}$$

$= 0.09350$ mmoles/ml

$$\% \text{ NaHCO3} = \frac{M_{HCl}\text{x ml HCl x } 1/1 \text{ x Mwt } NaHCO_7}{\text{mg sample}} \text{ x } 100$$

$$= \frac{0.09350\text{mmoles/ml x } 40.72\text{x } 1\text{x}84.01 \text{ mg/m mole}}{467.1 \text{ mg}} \text{ x } 100$$

$= 68.48$ %

Ex10: acidic solution containing Fe^{2+} was titrated with 40.2 ml of 0.0205 M of $KMnO_4$ solution. How many milligrams of Fe are existing in the sample?

Sol.:

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

Five times of iron millimoles reacted with the permanganate for that;
mmoles Fe = mg Fe/ Mwt Fe
= M $KMnO_4$ x ml $kMnO_4$ x ml $KMnO_4$x 5/1

Mg Fe = M $kMnO_4$ x ml $KMnO_4$ x 5 x Mwt Fe
= 0.0206 mmoles/ml x 40.2ml x5x55.8 mg/mmole
= 231 mg

It is noted here that the law is a modification of the previous law

$$\%X(A) = \frac{(Vt)\,(Nt)\,(meqwt\ of\ A)}{Wt\ of\ sample\ containing\ A} X100...(3-8)$$

$$\%A = \frac{(Vt)\,(Mt)x\ (a/b)\ x[Mwt\,(mg/mmole)\,]}{Wt\ of\ sample\ in\ mg\ containing\ A} X100...(3-9)$$

$Aa + Bb \rightarrow P$, A = analyte, B =titrant

Back Titration

In back titration an accurately known amount of a reagent is added to analyte in such a way that some excess of the added reagent is left. This excess is then titrated to determine its amount.

$aA_{(Titrant_1)} + bB_{(analyte)} \rightarrow Products + A_{(excess)}$

Then back titration of $A_{(excess)}$ with $Titrant_2$ C

$cC_{(Back\ titration)} + dA_{(excess)} \rightarrow Products_{\ Titrant_2}$

mmol $reagent_{(Titrant1)}$ taken = mmol $reagent_{(}$net) reacted with analyte + mmol $reagent_{(excess)}$ titrated with $Titrant_2$

Then the ***analyte*** can be determined since mmol reagent added are known, and mmol reagent titrated can be calculated from back titration.

$A_{added} = A_{net} + A_{excess}$

mmol reagent taken = mmol reagent $_{net}$ reacted + mmol reagent back titrated

mmol reagent $_{net}$ reacted = mmol reagent taken – mmol reagent back titrated.

Finally, the number of mmol reagent net reacted with analyte can be related to the number of mmol analyte from the stoichiometry of the reaction between the two substances as normal titration up on the equation.

$aA + bB \rightarrow$ Products

Now net calculations will be as follows:

$aA_{(Titrant_1)} + bB_{(analyte)} \rightarrow$ Products + $A_{(excess)}$

$cC_{titration} + dA_{titrant2} \rightarrow Products_{(excess)}$ (Back titration)

$$[(\text{ml}_A)(M_A)] - \left[(\text{ml}_C)(M_C)\left(\frac{d}{c}\right)\right] = \text{mmoles}_A \text{ Net reacted}$$

$$\text{Net reacted } (\text{mmoles}_A)\left(\frac{b}{a}\right)(\text{form wt}_B) = \text{mg}_B$$

Importance of back titration:

Back-titrations are important especially in some situations like:

1. When the rate of reaction is slow.
2. When the titration reaction doesn't have a good end point.

To add excess of the reagent with a second reagent of known conc.

Ex11: A 0.475gm sample containing $(NH_4)_2SO_4$ was dissolved in water and made alkaline with KOH. the liberated NH_3 was distilled in to exactly 50 ml of 0.1N HCl. the excess HCl was back titrated with 11.1ml of 0.121N NaOH. Calculate the percent NH_3 in $(NH_4)_2SO_4$ as the sample. Mwt NH_3 =17.03 g/mole, Mwt $(NH_4)_2SO_4$ =132.1g.

Sol.:

meq HCl = meg NH_3 + meq NaOH

meq NH_3 = meq HCl – meq NaOH

= (50 * 0.100 – 11.1 * 0.121)

$$\%X = \frac{(Vt)\,(Nt)\,(m.eq\,X)}{Wt\ of\ sample\ containing\ X} X100$$

Thus,

$$\%NH_3 = \frac{(50x\,0.100 - 0.121)\,x\,17.03/1000}{0.475} X100$$

= 131.1 %

The number y meq of $(NH_4)\ SO_4$ the same of the number of milliequivalent of NH_3, thus:

$$\%NH_3 = \frac{(50x\,0.100 - 0.121)x\,132.1/1000}{0.475} X100$$

= 50.8%

The question can be solved by applying the previous law and in two steps:

Wt of X = (Vt) (Nt) (meq wt of X)

= (50 x 0.100 – 11.1 x 0.121) x 17.03/ 1000

= 0.0622

$$\%X = \frac{Wt\ of\ X)}{Wt\ of\ sample\ containing\ X} X100$$

$$\%X = \frac{0.0622}{0.475} X100$$

% NH_3 = 13.1 %

And for X =$(NH_4)_2SO_4$

Wt of X = (Vt) (Nt) (meq wt of X)

= (50 x 0.100 – 11.1 * 0.121) * 132.1/ 2*1000 = 0.2415

$$\%X(NH_4)2SO_4 = \frac{Wt\ of\ X}{Wt\ of\ sample\ containing\ X} X100$$

$$\%X(NH_4)2SO_4 = \frac{0.2415}{0.475} X100 = 50.8\%$$

Questions and Answer

Q1. Some students were set the task of determining the concentration of acetic acid in a particular brand of vinegar. An outline of the method they used is given below.

1. A burette is filled with a standard solution of sodium hydroxide.
2. The vinegar is diluted by a factor of 10 in a volumetric flask. A pipette is used to transfer 20.00 mL of diluted vinegar to a conical flask and a few drops of phenolphthalein indicator is added.
3. The diluted vinegar is titrated with the base. Titrations are repeated until three concordant results are obtained.

The equation for the reaction is

$NaOH(aq) + CH_3COOH(aq) \rightarrow CH_3COONa(aq) + H_2O(l)$

a. The volumetric flask, the burette, the pipette and the conical flask are all rinsed before they are used. Indicate which solution should be used to finally rinse each of these pieces of glassware by ticking your responses in the appropriate boxes below.

Sol.

glassware used	rinse with water	rinse with diluted vinegar solution	rinse with NaOH solution
volumetric flask	✓		
burette			✓
20.00 ml pipette		✓	
conical flask	✓		

b. Why is the vinegar diluted before titrating?

Sol. So as not to use too large a volume of the NaOH solution (or to use and obtain a reasonably sized liter).

c. Explain why titrations are repeated until three concordant results are obtained.

Sol. To minimise the error (or to ensure reliability).

d. One student's results are given below. The data shown in the student's laboratory book was

concentration of NaOH(aq) = 0.11 M

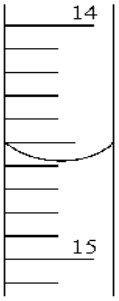
volume of undiluted vinegar = 10.00 Ml total volume of diluted vinegar = 100.00 mL. volume of diluted vinegar used in each titration = 20.00 mL.

Average liter of NaOH = 15.35 mL

Based on these results, calculate the concentration, in mol L^{-1}, of acetic acid in the undiluted vinegar solution.

Sol. Concentration of titrated vinegar = (0.11 x 15.35)/20.00 = 0.0844 M. Since the initial dilution of vinegar is 10, giving the concentration of undiluted vinegar is 0.84 M. The final result needed to be given to exactly two significant figures.

Q2. The diagram below shows a section of a 50.00 mL burette containing a colourless solution.



The reading indicated on the burette is closest to

a. 14.50

b. 14.58

c. 15.42

d. 15.50

Q3. 0.132 g of a pure carboxylic acid (R–COOH) was dissolved in 25.00 mL of water and titrated with 0.120 M NaOH solution. A volume of 14.80 mL was required to reach the endpoint of the titration.

The carboxylic acid could be:

a. HCOOH

b. CH_3COOH

c. C_2H_5COOH

d. C_3H_7COOH

Sol. c. n(NaOH) = $0.120 \times 14.80 \times 10^{-3}$

= 1.78×10^{-3} mol

n(RCOOH) = 1.78×10^{-3} mol

M(RCOOH) = 0.132g/ 1.78×10^{-3} mol = 74.3 g mol^{-1}

M(**C_2H_5COOH**) = 74.0 g mol^{-1}

Q4. A student is to accurately determine the concentration of a solution of sodium hydrogencarbonate in a titration against a standard solution of hydrochloric acid, HC1. The first step in this experiment is to accurately dilute 100.0 mL of a 1.00 M HCl stock solution to a 0.100 M solution using a 1.00 L volumetric flask. However, instead of using distilled water in the dilution, the student mistakenly adds 900.0 mL of 0.0222 M sodium hydroxide, NaOH, solution.

a. Write an equation for the reaction that occurs in the 1.00 L volumetric flask.

$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$ or $H_+(aq) + OH_-(aq) \rightarrow H_2O(l)$

b. Calculate the concentration of the hydrochloric acid in the 1.00 L volumetric flask after the student added the sodium hydroxide solution.

Sol.

n(NaOH) in flask = $0.0222 \times 900.0 \times 10^{-3} = 0.0200$ mol

n(HCl) reacted = 0.0200 mol*

n(HCl) added to flask = $1.00 \times 100.0 \times 10^{-3} = 0.100$ mol

n(HCl) remaining = 0.100 – 0.0200

= 0.080 mol

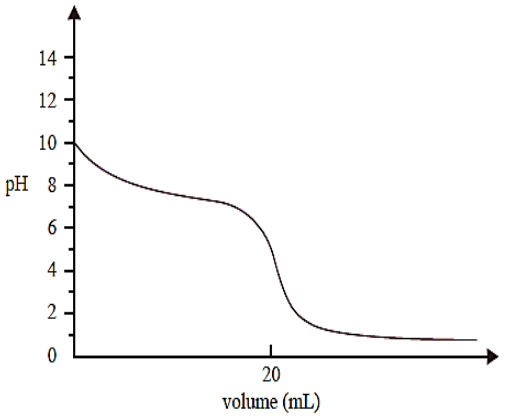
c(HCl) = 0.080* (M)

The student then uses this contaminated hydrochloric acid solution to determine the accurate concentration of the unknown sodium hydrogencarbonate solution.

c. Will the calculated concentration of sodium hydrogencarbonate solution be greater or smaller than the true value?

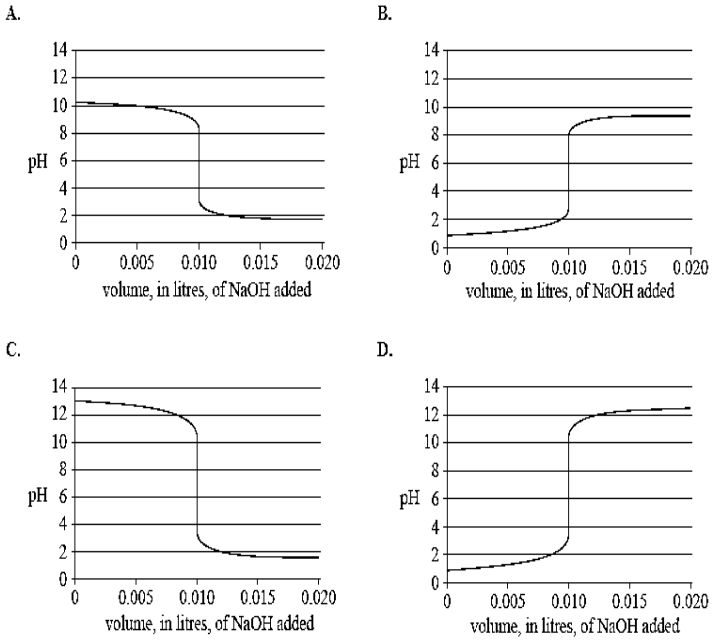
Sol. Greater, since a larger volume of the HCl solution will be required.

5. The following titration curve was obtained by measuring the pH in a reaction flask during an acid-base titration.



The graph represents the change in pH in the reaction flask when
a. a weak acid is added to a strong base.
b. a weak base is added to a strong acid.
c. a strong acid is added to a weak base.
d. a strong base is added to a weak acid.
Sol. c. The starting pH of 10 is indicative of a weak base. The drop in pH to 1 would be due to titration with a strong acid; therefore, a strong acid was added to a weak base.

Q6. Which titration curve best represents the change in pH as 0.100 M NaOH solution is added to a 10.0 mL aliquot of 0.100 M HCl solution?



Sol. d. The solution to be titrated was 0.100 M HCl, so the pH at the start of the titration was 1 as indicated on graphs B and**d.** As 0.100 M NaOH is added beyond the endpoint – that is, after 0.010 L (10 mL) NaOH has been added–the solution becomes increasingly basic and the pH approaches 13 (the pH of 0.100 M NaOH). Hence option D was correct.

After 0.020 L (20 mL) of 0.100 M NaOH has been added, there will be 0.0010 mol OH^- in excess in 30 mL of solution

$\therefore [OH^-] = 0.033$ M

$\therefore$ pH = 12.5

Options A and C were not consistent with a starting solution of 0.100 M HCl.

Q7. A 1.50 mL sample of a sulfuric acid solution from an automobile storage battery is titrated with 1.47 M sodium hydroxide solution to a phenolphthalein endpoint, requiring 23.70 mL. What is the molarity of the sulfuric acid solution?

a. 23.2 M

b. 11.6 M

c. 6.30 M
d. 0.181 M

Q8. Which piece of apparatus can measure a volume of 25.0 mL most precisely?
a. 25 mL beaker
b. 25 mL conical flask
c. 25 mL graduated cylinder
d. 25 mL pipet

Q9. What volume (in mL) of 0.0500 M phosphoric acid is needed to titrate completely 25.0 mL of 0.150 M barium hydroxide solution to a phenolphthalein end point?
$3Ba(OH)_2 + 2H_3PO_4$ r $Ba_3(PO_4)_2 + 6H_2O$
a. 50.0
b. 75.0
c. 100.
d. 150.

Q10. In the determination of the molar mass of a solid acid by titrating it with a standardized base, which procedural error will yield a molar mass that is smaller than the actual value?
a. adding the standardized base to a buret containing drops of water
b. dissolving the weighed solid acid in twice the recommended volume of water
c. using half as many drops of indicator as suggested
d. weighing out half of the recommended mass of solid acid

Q11. What is the difference between the endpoint and equivalence point in a titration?
a. The endpoint is when the pH is exactly 7
b. The equivalence point is when the pH is exactly 7
c. The endpoint and the equivalence point are the same thing.
d. None of these solutions is correct.

CHAPTER FOUR

ACID-BASE EQUILIBRIA

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Introduction

For thousands of years' people have known that vinegar, lemon juice and many other foods taste sour. However, it was not until a few hundred years ago that it was discovered why these things taste sour because they are all acids. The term acid, in fact, comes from the Latin term *acere*, which means "sour".

Acids taste sour, are corrosive to metals, change litmus (a dye extracted from lichens) red, and become less acidic when mixed with bases. Bases feel slippery, change litmus blue, and become less basic when mixed with acids.

Acids react with bases to form salts.

Theory of Acids and Bases

Svante Arrhenius theory: Acids are proton (H^+) sources and bases are hydroxide ion (OH^-) sources.

Svante Arrhenius: An acid is a substance that, when dissolved in water, increases the concentration of hydrogen ions.

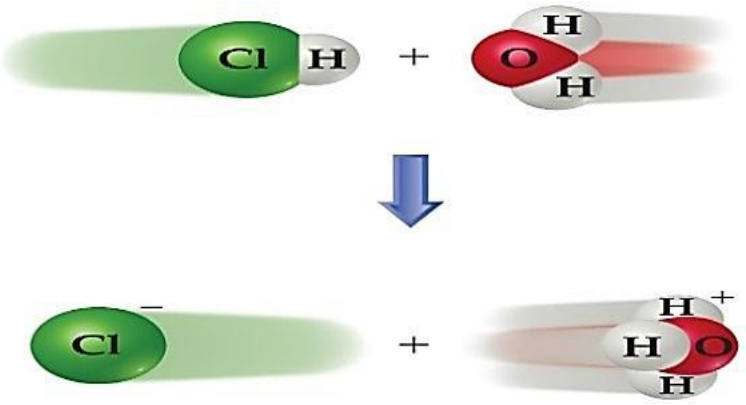
A base is a substance that, when dissolved in water, increases the concentration of hydroxide ions.

E.g. HCl is an acid and NaOH a base

Brønsted-Lowry theory: Acids are proton sources and bases are proton acceptors. A Brønsted–Lowry acid must have at least one removable (acidic) proton (H+) to donate.

A Brønsted–Lowry base must have at least one nonbonding pair of electrons to accept a proton (H+).

E.g. HCl is an acid and NH_3 a base, these form the conjugate base Cl^- and NH_4^+.



Acid is most simply defined as a substance which, when dissolved in water, undergoes dissociation with the formation of hydrogen ions as the only positive ions

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

$$HNO_3 \rightleftharpoons H^+ + NO_3^-$$

And base is a substance that accepts a proton.

So according to this theory, an acid is defined as a proton donor and abase as a proton acceptor.

When sulfuric acid dissolves in water, the acid H_2SO_4 gives up a proton to the base HSO_4^- when hydrogen chloride reacts with ammonia, the acid HCl give, up a proton to the base NH_3 to from the new acid NH_4^+ and the new base Cl^-

$$\underset{\text{Stronger acid}}{H_2SO_4} + \underset{\text{Stronger base}}{H_2O} \rightleftharpoons \underset{\text{weaker acid}}{H_3O^+} + \underset{\text{weaker base}}{HSO_4^-}$$

$$\underset{\text{stronger acid}}{HCl} + \underset{\text{stronger base}}{NH_3} \rightleftharpoons \underset{\text{weaker acid}}{NH_4^+} + \underset{\text{weaker base}}{Cl^-}$$

According to lowry – Bronsted definition, the strength of an acid depends upon its tendency to give up a proton, and the strength of a base depends upon its tendency to accept a proton so H_2SO_4 & HCl are strong a cids since therd to gine up a proton very readily, conversely, bisulfate ion, HSO_4^- and Cl^- must necessarily be weak bases since they have little tendency to hold on to protons, in each of the reactions inst described, the equilibrium faros the formation of the

weaker acid and the weaker base, if we arrange acids in order we must necessarily arrange the corresponding (**Conjugate**) bases in the opposite order.

Acid strength $\begin{matrix} H_2SO_4 \\ HCl \end{matrix} > H_3O^+ > NH_4^+ > H_2O$

Base strength $\begin{matrix} HSO_4^- \\ Cl^- \end{matrix} > H_2O > NH_3 > O\,H^-$

Lewis Theory: According to Lewis definition, a base is a substance that can furnish an electron pair to from a covalent bond, and an acid is a substance that can take up are electron pair to from covalent bond. Thus an acid is an electron –pair a acceptor and a base is an electron – pair donor.

The Lewis acid-base theory explains why BF_3 reacts with ammonia. BF_3 is a trigonal-planar molecule because electrons can be found in only three places in the valence shell of the boron atom. As a result, the boron atom is sp^2 hybridized, which leaves an empty $2p_z$ orbital on the boron atom. BF_3 can therefore act as an electron-pair acceptor, or Lewis acid. It can use the empty $2p_z$ orbital to pick up a pair of nonbonding electrons from a Lewis base to form a covalent bond. BF_3 therefore reacts with Lewis bases such as NH_3 to form acid-base complexes in which all of the atoms have a filled shell of valence electrons, as shown in the figure below.

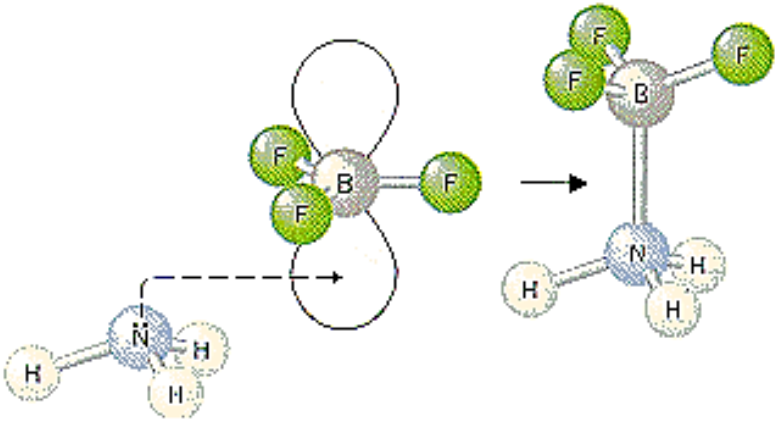


Figure 3-1 Lewis base

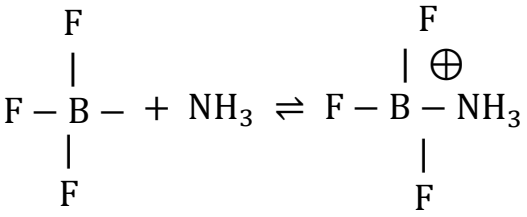
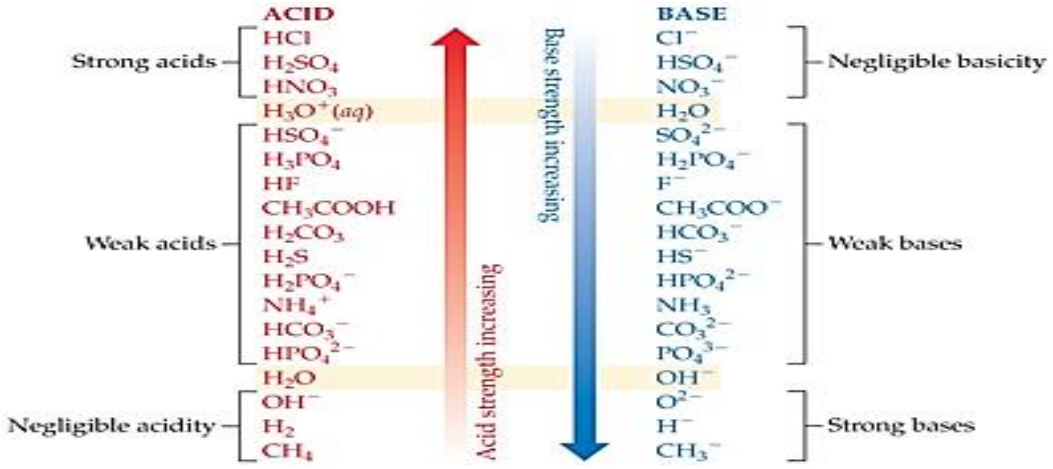


Table 3-1 Relative Strengths of Acids and Bases



Polybasic acids

Poly basic acids dissociates in stages. In sulfuric acid, the first hydrogen atom is almost completely ionized:

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$$

$$\text{or } H_2SO_4 + H_2O \rightleftharpoons H_3O^+ + HSO_4^-$$

The second hydrogen atom is only partially dissociated, except in very dilute solution.

$$HSO_4^- + H_2O \rightleftharpoons H_3O^+ + SO_4^{2-}$$

Phosphoric acid also dissociates in stages:

$$H_3PO_4 \rightleftharpoons H^+ + HPO_4^- \rightleftharpoons H^+ + HPO_4^{2-} \rightleftharpoons H^+ + PO_4^3$$

$$\text{or } H_3PO_4 + H_2O \rightleftharpoons H_3O^+ + H_2PO_4^-$$

$$H_2PO_4^- + H_2O \rightleftharpoons H_3O^+ + HPO_4^{2-}$$

$$HPO_4^{2-} + H_2O \rightleftharpoons H_3O^+ + PO_4^{3-}$$

Acid-Base Equilibria in Water

As we mentioned that acids and bases dissociates when they are dissolved in water and the quantity of the ionized species depends up on the strength of the acid, the strong electrolyte undergoes dissociation completely whereas the weak electrolyte, partially dissociate.

Weak Electrolyte	Strong Electrolyte
CH_3COOH	HCl
NH_3	$HClO_4$
C_6H_5OH	H_2SO_4
$HCOOH$	HNO_3
$C_6H_5NH_2$	$NaOH$
	CH_3COONa

For reaction below,

$$HOAC + H_2O \rightleftharpoons H_3O^+ + O^- AC$$

$$CH_3\overset{O}{\overset{||}{C}}-O- = OAC$$

For the reaction up, the equilibrium constant may be with the following equation:

$$K = \frac{^aH_3O^+ \; a \; OAC^-}{^aHOAC \;\; ^aH_2O}$$

$K = acidity\ constont. a = activity$

So the value of the general equilibrium constant is;

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

Infinity can be considered as the activity a represents the ion concentration of the action and is explained by the following equation:

ai = fi {Ci}

ci = molarity concentration for ion i

fi = Activity coefficient for the ion in the solution

The activity coefficient varies with the total number of ions in the solution.

Ex1: the activity coefficient of a single electrolyte in a dilute solution 10^{-3} M is close to one unit and the activity is approximately equal to molarity. Activity is widely measured by the pH-meter

It is necessary for the activity to remain constant in the dilute solutions and therefore it can be entered in K and then the equation can be rewritten as follows:

$$Ka = \frac{^{a}H_3O\ ^{a}OAC}{^{a}HOAC}$$

Auto Photolysis of Water

Water molecules in pure water interact with one another to form ions. Net effect is the formation of equal amounts of hydronium and hydroxide ions.

$$2\,H_2O \rightarrow H_3O^+ + OH^-$$

And the equilibrium is fixed to it

$$K = \frac{^{a}H_3O^+ + {}^{a}OH^-}{^{a2}H_2O}$$

The activity of water in dilute solutions is stable, and for this,

$$Kw = {}^{a}H_3O^+ + {}^{a}H_3O^-$$

***Kw* = self –ionization constant**

Accounts can be simplified by adding activity parameters, and it using simplified changes, for example H^+ instead of H_3O^+ and express the molar concentration in parentheses.

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

$$HOAC \rightleftharpoons H^+ + OAC^-$$

$$Ka = \frac{[H^+][CAC^-]}{[HOAC]}$$

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

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

$$at\ 25\ C^{\circ}\ Kw = 1 \times 10^{-14}$$

That is, the product of the concentration of hydrogen ions and the hydroxyl ions in the aqueous solution is equal to 1×10^{-14} at room temperature.

The concentration of these two ions is equal in distilled water, because there are no other sources that give OH^- and H^+ except for the dissociation of H_2O.

$at\ 2S^0C$ the conc. of the two species will be equal. So:

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

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

$[H^+] = 1 \times 10^{-7}\ M = [OH^-]$

At the addition of an acid to the water, hydroxyl ion could be calculated if hydrogen ion concentration is known unless the conc, of $[H^+]$ in acid, so little, ie less than $10^{-6}H$

Ex2: Preparing $1 \times 10^{-3}M$ of HCl solution. What is the concentration of hydroxyl ion (OH^-)

$soln$: Because of HCl is astrongt electrolyte so it dissociate completely so the conc, of H^+ will be equal to 1.0×10^{-14}

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

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

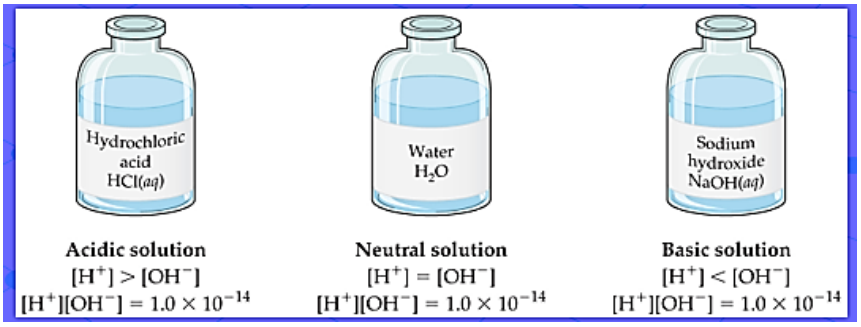


Figure 3-1 types of solution

The pH Scale

pH is a method of reporting hydrogen ion concentration

pH = –log[H+]

Neutral pH is 7.00., Acidic pH is below 7.00., Basic pH is above 7.00.

The concentration of H^+ or OH^- can be changed in aqueous solutions with a wide range from 1M or more to 10^{-4}M or less. It is difficult to build a relationship between the concentration and some of variables, especially if the concentration changes from 10^{-1}M to 10^{-3}M, given that this is the known range in the titration. It is more appropriate to reduce the acidity range by expressing it with a logarithmic relationship where the solution pH can be defined from the relationship: $\text{pH} = -10\text{g}\,[\text{H}^+]$

The reason that the negative relationship exists in most of the concentrations used is less than the IM and therefore it works by giving a positive number of pH value, and pH can be defined more specifically as equal log $^{a}H^+$.

Ex3: Calculate the pH value for HCl solution with concentration equal to $2 \times 10^{-3}\ M$

Sol.: HCl ionizes completely so:

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

$pH = -\log [2.0 \times 10^{-3}] = 3 - 0.30 = 2.70$

For pOH CalC.

$-log\ Kw = -log\ [H^+]\ [OH^-] = -log\ [H^+] - 10g\ [OH^-]$

$pKw = pH + pOH$

$At\ 25\ C^{\circ}$, $14.00 = pH + pOH$

Ex4: calc the pH and pOH for $5.0 \times 10^{-2} M\ Na$

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

$pOH = -log[5.0 \times 10^{-2}] = 1.30$

$pH + 1.30 = 14.00. pH = 12.70$ = pOH=14-2.7=11.3

Ex5: When PH of sol is 9.67 calculate concentration of H^+ in the solution.

sol.: $-log[H+] = 9.67$

$[H^+] = 10^{-9.67} = 2.1 \times 10^{-10} M$NaOH

The concentration of $[H^+]$ in pure H_2O is equal to $10^{-7} M$ so the solutionwill be neutral when $pH = 7$. But when $pH > 7$ the solutionwill be basic and $pH < 7$ solution will be acidic.

pH values in minus means that $[H^+]$ concentration is bigger than IM Scientific facts indicate that the negative pH value is unfamiliar to two reasons;

1- Strong acids can become partially dissociated at high concentrations.

2- The activity that can be neglected in dilute solutions where pH is $-\log^a H^+$

This is measured by pH-meter, when $[H^+]$ is 1.5M and the value of pH may be because tactivity is less than 1.0M That is, at high concentrations, the activity factor can be less than one unit.

Ex6: Calculate pH and pOH of $(3.2 \times 10^{-4} M)$ of $Ba(OH)_2$solution.

Sol.: $[OH^-] = (3.2 \times 10^{-4}) * 2\ Ba\ (OH)_2$

$= 6.4 \times 10^{-4}\ Ba\ (OH)_2$

$pOH = -\log 6.4 \times 10^{-4} \Rightarrow POH = 3.19$

$$pH = 14.00 - 3.19 = 10.81$$

Digression – base 10 Logs

Number	1	2	3	5	7	10
Log_{10}	0.00	0.30	0.48	0.70	0.84	1.00

4=2*2, log 4=.30+.30 = .60

2.5 = 25*10^{-1}= 5*5*10^{-1} log 2.5= .70+.70+(-1) = .40

Weak Acids

Ionization constant of weak acids (Ka)

Weak acids are partially ionized in water, where the ionization constant (ka) is used to calculate the ionized quantity and then to calculate the value of pH, for example, the ionization of acetic acid in water (HOAc).

$$HOAC + H_2O \rightleftharpoons H_3O^+ + OAC^-$$

$HOAC = CH_3COOH$

$OAC = CH_3COO^-$

applyy the $Chemical\ equilibriom$)

Ka the value of the equilibrium constant

$$Ka = \frac{[H_3O^+][OAC^-]}{[H_2O][HoAc]}$$

$$or\ Ka[H_2O] = \frac{[H_3O^+][OAC^-]}{[HoAc]}$$

Therefore, in dilute solutions the concentration of molar water is 55.5 M,

$$Ka[55.5] = \frac{[H_3O^+][OAC^-]}{[HoAc]} = Ka = 1.75\ \times 10^{-5}$$

Therefore, ka is a new ionization called the weak acid ionization constant that all the concentrations of ions and moleculs shown in the equation of the ionization constant and must be in mol/ l.

Hydronium Ion Concentration of Weak Acids

To calculate the value of the hydronium ion concentration, let us assume a weakly acidic aqueous such as (HA):

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

Apply the law of the act of mass:

$$\frac{[H_3O^+][A^-]}{[HA]} = ka$$

$$100\ a = percent\ ionization = \frac{[H_3O^+]}{C} \times 100$$

The value of the ionization constant for ka can be calculated from the degree of dissociation using the equation below:

$$\boldsymbol{Ka = \frac{(M \propto)(M \propto)}{M(1-\propto)}}\ \ldots\ \boldsymbol{(4-1)}$$

$(M \propto) = H_3O^+$

$M(1-\propto)) =$ Concentration of non-ionizing molecules of acid.

Ex7: Calculate the value of ka for acid, if $0.1M$

sol. is ionized to the extent of 1.34% at $25\ C^{\circ}$

Sol.: $ka = \frac{(M \propto)(M \propto)}{M(-\propto)}$

$M = 0.1\ M/L$, $\propto = 1.34\ \% = 0.0134$

$$ka = \frac{(0.1 \times 0.0134)(0.1 \times 0.0134)}{0.1\ (1-0.0134)} = 1.8\ \times 10^{-5}$$

Ex8: Calculate the value of pH and pOH for $1.0 \times 10^{-3} M$ Acetic acid

Sol.: $oHAc \rightleftharpoons H^+ + oAc^-$

$(1.0 \times 10^{-3} - x)\ x\ x$

$[H_3O^+] = [A]$ HA is in pure aqueous solutions of

The partial acid concentration HA = $C - [H_3O^+]$, where C is the original concentration of HA. That's when equilibrium;

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

$C - [H_3O^+] \rightleftharpoons [H_3O^+]\ [H_3O^+]$

$C - [A^-] \rightleftharpoons [A^-]\ [A^-]$

By applying the above equation, we get:

$$\frac{[H_3O^+]2}{C - [H_3O^+]} = Ka = \frac{[A^-]^2}{C - [A^-]} \ \ldots (4-2)$$

$$[H_3O^+] = -\frac{1}{2} ka + \sqrt{\frac{1}{4} K_a^2 - k_a C} \ \ldots (4-3)$$

In the case that the degree of ionization of the guest acid is less than 5%, then the value of $[H_3O^+]$ will be very small compared to C where it can be found, and then the equation (2-3) will be arranged as follows;

$$\frac{[H_3O^+]^2}{C} = ka$$

$[H_3O^+] = \sqrt{k\ a}\ C$ .....(4-4)

$$pH = -log\ [H_3O^+] = -log \sqrt{k_a C} = -\frac{1}{2} log\ k_a - \frac{1}{2} log\ C$$

$$pH = \frac{1}{2} PK_a - \frac{1}{2} logC \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4-5)$$

Degree of Ionization of Weak Acids (a)

In the concept of Laurie-Bronstedt, the acid tendency to lose or donate a proton is a measure of its acidic strength, and it is known as the acidity degree (∝). This degree of equilibrium condition is known as the equation below;

$\propto = \frac{[H_3O^+]}{C}$. C = molar concentration for acid

$$\frac{(x)\ (x)}{(1.0\ \times 10^{-3} - x)} = 1.75\ \times 10^{-5}$$

Ignoring x Compared with C (in the equaled will be $10^{-3}M$) and simplifying will be valid if ka$< 10^{-4}$ $ie\ C = 0.01M$ 0r if ka $< 10^{-3}$ when $C = 0.1\ M$ so

$$\frac{x^2}{1.0\ \times 10^{-3}} = 1.75 \text{ x}10^{-5}$$

$x = 1.32\ \times 10^{-4}M = [H_3O^+]$

$so\ pH = -log 1.32\ \times 10^{-4} = 3.88$

$pOH = 14.00 - 3.88 = 10.22$

The question can be solved directly by applying the previous equation (2-4)

$[H_3O^+] = \sqrt{ka\ C}$

$= \sqrt{1.75 \times 10^{-5} \times 1.0\ \times 10^{-3}} = 1.32\ \times 10^{-4}M$

Ex9: Calculate the hydronium ion concentration, the pH, and the percent ionization of a 0.30 $M\ HCN. ka$ for $HCN\ = 7.2\ \times 10^{-10}$

Sol.: $HCN + H_2O \rightleftharpoons H_3O^+ + CN^-$

$let. x = [H_3O^+]\ .then\ x = [CN^-]$

$and. 0.30 - x = [HCN]$

$$\frac{[H_3O^+]\ [CN^-]}{[HCN]} = ka = 7.2\ \times 10^{-10}$$

$$\frac{(x)\ (x)}{0.30 - x} = 7.2\ \times 10^{-10}$$

x neglected

$$\frac{x^2}{0.3} = 7.2\ \times 10^{-10}$$

$and. x = \sqrt{(0.30)(7.2\ \times 10^{-10})} = 1.47\ \times 10^{-5} = [H_3O^+]$

$pH = -log\ [H_3O^+] = -log 1.47\ \times 10^{-5} = 4.83$

$$\propto = \frac{[H_3O^+]}{[HCN]} = \frac{1.47\ \times 10^{-5}\ M}{0.30\ M}$$

$\propto = 4.9 \times 10^{-5}$

% ionzation $= \propto 100 = (4.9 \times 10^{-5})(100) = 4.9 \times 10^{-3}$

Ionization Constant of weak monoprotic Bases (k_b)

As defined by Bronstedt, the base is any substance that produces the hydroxyl ion in the water medium or any substance that accepts protons from the acid.

Ionization of weak bases can be dealt with as the reaction with weak acids but except that the equilibrium contains a hydroxyl ion (OH) instead of H_3O^+.

Most common week base as Ammonium hydroxide or ammonia are changes. When ammonia is dissolved in water, the equation below is obtained.

$NH_3 + H_2O \rightleftharpoons NH_4OH \rightleftharpoons NH_4^+ + OH^-$

It is known that in the solution of ammonia there is a equilibrium between OH^- and.NH_4^+ and the above equation can be expressed in the equation below as well.

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

Other weak bases may be used in analytical chemistry such as methyl amine CH_3NH_2, Ethylene amine $C_2H_5NH_2$ and other.

Applying the chemical equilibrium law to the above equation, it gets the following:

$$\frac{[NH_4^+][OH^-]}{[NH_3][H_2O]} = k_b$$

$$\frac{[NH_4^+][OH^-]}{[NH_3]} = k_b\,(55.5) = k_b = 1.75 \times 10^{-5}$$

kb: is the ionization constant of the weak base.

Hydronium ion concentration of weak bases

Suppose a weak base aqueous solution such as BOH is ionized as follows:

$BOH \rightleftharpoons B^+ + OH^+$

By applying a constant equilibrium law, we obtain:

$$\frac{[B^+][OH^-]}{[BOH]} = k_b$$

$\frac{[OH^-]^2}{[BOH]} = k_b = \frac{[OH^-]^2}{C}$. where C is the conc, of base in moles per Liter.

$[OH^-] = \sqrt{(k_b)(C)}$ ... (4-6)

where $[OH^-] = \frac{KW}{[H_3O^+]}$

so $\frac{KW}{[H_3O^+]} = \sqrt{(k_b)(C)}$

$and\ [H_3O^+] = \frac{KW}{\sqrt{(k_b)(C)}} \ldots (4-7)$

Degree of Ionization of Weak Bases ($\propto$)

The strength of the base can be defined by the Aarhus concept as the degree of its ionization in the solution to give the hydroxyl ion

$$\propto = \frac{[OH^-]}{molarity\ of\ the\ weak\ base} = \frac{[OH^-]}{C}$$

$$ionization\ ratio = \frac{[OH^-]}{C} \times 100$$

Ex10: when k_b for ammonia is $(1.75 \times 10^{-5}\ at\ 25\ C^{\circ})$.calculat pH and pOH. For $1.0 \times 10^{-3} M$ ammonia solution.

Sol.:

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

$(1.0 \times 10^{-3} - x)\ x\ x$

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

$$\frac{(x)(x)}{1.0 \times 1.0^{-3}} = 1.75 \times 10^{-5}$$

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

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

$pH = 14.00 - 3.88 = 10.12$

Ex11: A 15.8 gm Pyridine $(C6H_5N)$ was dissolved in 200 mL of distilled water, knowing that its ionization constant is 1.6×10^{-9} $calculate$.

a) The concentration of $[OH^-]$ (b) pH (c) deqree of ionization (d) present ionization. Mwt C_6 $H_5N = 79$ gram/ mole

Sol.: $M = \dfrac{wt * 1000}{mwt \times 200}. = \dfrac{15.8 \times 1000}{70 \times 200} = 1M$

$C_6H_5N + H_2O \rightleftharpoons C_6H_5\,NH^+ + OH^-$

$K_b = \dfrac{[C_5H_5N\,H^+][\,OH^-]}{[C_5H_5N\,]}. 1.6 \times 10^{-9} = \dfrac{x^2}{1-x}$ $x = neglected$

a) $x = 1.6 \times 10^{-9}. x = 4 \times 10^{-6}\ mole/\text{L}. [OH^-]$

$pOH = -log[OH^-] = -log[4 \times 10^{-6}] = 4.32$

b) $pH = 14.00 - 4.3 = 9.08$

c) $\propto = \dfrac{[OH^-]}{C} = \dfrac{4 \times 10^{-5}}{1} = 4 \times 10^{-5}$

d) $\propto = \dfrac{[OH^-]}{C} \times 100 = \dfrac{4 \times 10^{-5}}{1} \times 100 = 4 \times 10^{-4}$

Ex12: Calculate the pH of a liter of solution prepared by dissolving $0.1M$ of ammonia. (a) $K_b\,NH_3 = 1.75 \times 10^{-5}$, (b) 0.1 mole of armmonia P1us 0.1 mole $NaOH$

Sol.: $(a)[H_3O^+] = \dfrac{Kw}{\sqrt{(kb)(C)}} = \dfrac{1 \times 10^{-14}}{\sqrt{(1.8 \times 10^{-5})(0.1)}}$

$= \dfrac{1 \times 10^{-14}}{1.34 \times 10^{-4}}$

$[H_3O^+] = 7.45 \times 10^{-12}$

$pH = -log[H_3O^+] = -log[7.45 \times 10^{-12}] = 11.13$

(b) In such a strong solution of $NaOH$, the 0.1 mole of ammonia will practically be all in the molecular from (NH_3) therefore the conc. of OH^- ions furmed from dissociation of amonis will be very low, Thus $[OH^-] = 0.1\ M$

$[H_3O^+] = \dfrac{kw}{[[OH^-]]} = \dfrac{1 \times 10^{-14}}{0.1} = 1 \times 10^{-13}\ M$

$pH = -log\, 1 \times 10^{-13} = 13$

Salt of Weak Acids and Bases

Hydrolysis of salts of weak acids and strong Base

As a rule, a salt of strong base and weak acid is a strong electrolyte, as it is completely ionized in water. The hydrolysis produces a solution which is strongly basic. The anions of this types of salts are monoprotic such as $CN^-.CH_3COO^-$. Diprotic such as $CO_3^{2-}\, or$ triprotic such as PO_4^{3-}

$OAC^- + H_2O \rightleftharpoons HOAC + OH^-$

. The HOAC here is not dissolved, so it does not affect the pH acidity, and this ionization can be considered as aqueous analysis of the salt ion. The sodium acetate below is a weak base (the base conjecated to acetic acid). The ionization constant of the above equation is equal to the salt value constant. Where the weaker the conjecated acid, the conjecated base is stronger, and the salt's association with the proton (from water) is strong to make the ionization direction in the equation toward the right.

$$K_h = K_b = \frac{[HOAc][OH^-]}{[OAC^-]}.K_h = \ hydroysis\ constant$$

K_b value could be calculated from k_a of $HOAC$ by multiplying the upper and lower value of the equation by $[H^+]$

$$K_b = \frac{[HOAc][OH^-][H^+]}{[OAC^-][H^+]}$$

$Kw = [H^+]\,[OH^-]\ k\ w$ equal $[OH^-][H^+]$

$\frac{1}{Ka} =$ rest

$$\therefore Kb = \frac{kw}{k_a} = \frac{1 \times 10^{-14}}{1.75 \times 10^{-5}} = 5.7 \times 10^{-10}$$

This is a method for calculating k_b from k_a for a weak acid derived from salt.

How to Calculate the Concentration of Hydroxyl Ion?

hydronium ion (H_3O^+) and acid solution of salt derived from weak acid and weak base (or weak acid salt).

The multiple product of the value of k_a for any acid and kb of the base conjecated it is always equal to kw.

$k_a * K_b = kw$

Salt of any weak acid HA undergoes ionization in water

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

$$\frac{[HA][OH^-]}{[A^-]} = k_b = \frac{kw}{K_a}$$

pH calculation for this salt (Bronsted base) was held for any weak base. When the salt is ionized it gives equal quantities of $HA^- \times OH^-$. and if the concentration of original A is A^- So

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

$(C - x)\ x\ x$

x value could be ignored for C value and if the ionization is lesser about 10% or 15 % then it will be surely lesser from NH_3 ionization because K_b value will be less with 3×10^6: and OH^- concentration could be calculated using the following eq.

$$\frac{[OH^-][OH^-]}{C} = \frac{kw}{ka}$$

$$\boldsymbol{[H_3O^+] = \sqrt{\frac{kw}{k_a} C}} \ \ldots\ldots\ldots\ldots (\boldsymbol{4-8})$$

Calculates the value of H_3O^+ and changes [OH^-] to [H_3O^+] using a law

$$[OH^-] = \frac{kw}{[H_3O^+]}$$

$$\frac{kw}{[H_3O^+]} = \sqrt{\frac{kw}{k_a} C}$$

$$\boldsymbol{[H_3O^+] = \sqrt{\frac{kw\ k_a}{C}}} \ \ldots\ldots\ldots (\boldsymbol{4-9})$$

$$pH = -log[H_3O^+] = -log\sqrt{\frac{kw\ k_a}{C}}$$

$$pH = -\frac{1}{2}log\ kw - \frac{1}{2}log\ k_a + \frac{1}{2}log\ C$$

$$pH = -\frac{1}{2}log\ 10^{-14} + \frac{1}{2}P\ k_a + \frac{1}{2}log\ C$$

$$\boldsymbol{p\ H = 7 + \frac{1}{2}\ Pk_a + \frac{1}{2}log\ C} \ldots.(\mathbf{4-10})$$

From the calculation of the salt analysis that anion is base can be calculated ionization degree from the equation below;

$$\boldsymbol{Degree\ oJ\ ionization} \propto = \frac{[\boldsymbol{OH^-}]}{\boldsymbol{C}} \ldots.(\mathbf{4-11})$$

$$\boldsymbol{Percent\ hydrolysin} = \frac{[\boldsymbol{OH^-}]}{\boldsymbol{C}} \times \mathbf{100} \ldots(\mathbf{4-12})$$

$$\boldsymbol{K_h = \frac{kw}{ka}} \ldots\ldots\ldots.(\mathbf{4-13})$$

Some examples of these salts

$NaCN.KCN.CH_3COONa.CH_3COOK.HCOONa$

Note/ here in these salts the only source of hydroxyl ion is the aqueous hydrolysis of these salts.

Ex13:

Calculate the pH value for 0.1 M sodium acetate solution.

The first method;

Sol.: $pH = 7 + \frac{1}{2}pka + \frac{1}{2}logC\ .\ k_a = 1.75\ \times 10^{-5}$

$= 7 + \frac{1}{2} \times 4.75 - 0.5$

$= 8.89\ kw = 1 \times 10^{-14}$

= 8.89

The second method;

$$[\mathrm{OH}^-] = \sqrt{\frac{kw}{k_a}C} = \sqrt{\frac{1.0 \times 10^{-14}}{1.75 \times 10^{-5}} * 0.1} = 7.6 \times 10^{-6}M$$

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

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

The third method;

$$[H_3O^+] = \sqrt{\frac{kw\ k_a}{C}} = \sqrt{\frac{1 \times 10^{-14} \times 1.75 \times 10^{-5}}{0.1}} = 1.3 \times 10^{-9} M$$

$$[H_3O^+] = \frac{kw}{[OH^-]} = \frac{1.0 \times 10^{-14}}{7.6 \times 10^{-6}} = 1.3 \times 10^{-9} M$$

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

Ex14: Calculate the, pOH and percent hydrolysis of a o.03M solution of sodium acetate $k_a = 1.75 \times 10^{-5}\ at\ 25\ C^{\circ}$

Sol.: $[H_3O^+] = \sqrt{\frac{kw\ k_a}{C}} = \sqrt{\frac{(1\times10^{-14})(1.85\times10^{-5})}{0.03}} = 2.45 \times 10^{-9} M$

$$pH = -log 2.45 \times 10^{-9} = 8.6$$

$$pOH = 14.00 - 8.60 = 5.4$$

$$Degree\ of\ hydrolysis = \frac{[OH^-]}{C}$$

to calculate $[OH^-]$ at least two methods can be used

Calculate pH and pOH

(a) $[OH^-] = \frac{Kw}{[H_3O^+]} = \frac{1 \times 10^{-14}}{2.45 \times 10^{-9}} = 4.1 \times 10^{-5} M$

$$Degree\ of\ hydrolysis = \frac{4.1 \times 10^{-5}}{0.03} = 1.4 \times 10^{-3}$$

(b) $[H_3O^+] = \sqrt{\frac{kw}{k_a} C} = \sqrt{\frac{1 \times 10^{-14}}{1.75 \times 10^{-5}} \times 0.03} = 4.1 \times 10^{-5} M$

Ex15: Calculate the ionization constant $ka.kh$ for anion of sodium sodium phenoxide C_6H_5ONa with $pOH = 3$ and concentration of 0.01M/L

Sol.: $pOH + pH = 14$

$$pH = 14 - 3$$

$$pH = 11$$

$log\ [H_3O^+] = 11$

$[H_3O^+] = 10^{-11}\ M$

$$[H_3O^+] = \sqrt{\frac{kw\ k_a}{C}} = 10^{-11} = \sqrt{\frac{1 \times 10^{-14} \times k_a}{0.01}}$$

$k_a = 1 \times 10^{-10}$

$$kh = \frac{kw}{ka} = \frac{1 \times 10^{-14}}{1 \times 10^{-10}} = 1 \times 10^{-4}$$

Note: The hydrolysis constant kh is inversely proportional to dissociation constant of the weak acid.

$kh = 1 \times 10^{-14} > K_a CH_3\ OH = 1 \times 10^{-10}$

***Ex*16:** A 0.04M solution of KNO_2 with $kh = 2.5 \times 10^{11}$ calculate the pH of the solution and its nature? (How)

Salts of Weak Diprotic Acid

These salts include sodium and potassium salts of oxalic acids $H_2C_2O_3$ carbonic acid, sulfurose acid, and aqueous sulfuric acid($HSO_3^{2-}.(SO_3^{2-})$), These salts reacte with two parts of water. As an example, Na_2SO_3 gives two anions in the solution.

$$Na_2\ SO_3 \rightarrow 2Na^+ + SO_3^{2-}$$

Suffer two stage of hydrolysis; SO_3^{2-}The ion

$$SO_3^{2-} + H_2O \rightleftharpoons HSO_3^- + OH^-$$

$$HSO_3^- + H_2O \rightleftharpoons H_2SO_3 + OH^-$$

(K_h) hydrolysis constant

$$\frac{[HSO_3^-][OH^-]}{[SO_3^{2-}]} = \frac{kw}{ka_2} = \frac{1 \times 10^{-14}}{6.2 \times 10^{-8}} = 1.6 \times 10^{-7} = kh_1$$

$$\frac{[H_2SO_3][OH^-]}{[HSO_3^-]} = \frac{kw}{ka_1} = \frac{1 \times 10^{-14}}{1.7 \times 10^{-2}} = 5.9 \times 10^{-13} = kh_2$$

$kh_1 > kh_2$ as

The second step of the analysis is neglected and derives an amount

$[H_3O^+]$ ⊥Ka_2

$$[H_3O^+] = \sqrt{\frac{kw\ ka_2}{C}} \quad \ldots (4-14)$$

Ex17. Calculate the pH and percent hydrolysis of a 0.3 M Na_2CO_3 solution of which 25ml were diluted with water to give 100 ml.

Sol.:

M_2 =the concentration of Na_2CO_3 solution after dilutoion

$(V_1)\ (M_1) = (V_2)(M_2)$

$$(25mL)(0.3\ m\ mole/\ ml\ = (10\ mL)(M_2)\ .M_2 = 0.075\ mole$$

$$[H_3O^+] = \sqrt{\frac{kw\ ka_2}{C}} = \sqrt{\frac{(1 \times 10^{-14})(5.6\ \times 10^{-11})}{0.075}}$$

$$[H_3O^+] = 2.74\ \times 10^{-12} M$$

$$pH = -log[H_3O^+] = -log 2.74\ \times 10^{-12} = 11.56$$

Since the solution is basic then,

$$Percent\ hydrolysis = \frac{[OH^-]}{C} \times 100 = \frac{kw\ [H_3O^+]}{C} \times 100$$

$$= \frac{(1 \times 10^{-14})(2.74\ \times 10^{-12})}{0.075} \times 100$$

$$= 4.91$$

Hydrolysis of Salt of Strong Acids and Weak Bases

The salts derived from weak bases and strong acids behave like a strong electrolyte, so they are completely hydrolysis. The cations of this type of salts are the conjugated acid of the strong base, which are proton donations. Acid cations can be unhydrated cations for each of;

$C_5H_6N^+ < C_6H_5NH_3^+ < NH_4^+$

Hydrated cation: Al $(H_2O)_6^{3+}.Cr\ (H_2O)_6^{3+}.Fe\ (H_2O)_6^{3+}.Zn(H_2O)_6^{2+}$

Hydrolysis of Unhydrated Cations

Taking the example of $NH_4Cl.$ which is composed of aprotic chloride anion and the proton donor NH_4^+ Cation. In water solution the amrnium ion donates a proton to a water mole. molecule. The hydrolysis reaction, therefore, is

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

Weak base salts are the pronstedt acids that ionize in water

$$BH^+ + H_2O \rightleftharpoons B + H_3O^+$$

$$Kh = ka = \frac{[B][H_3O^+]}{[BH^+]}$$

$ka = \frac{[B]\,[H_3O^+]\,[OH^-]}{[BH^+]\,[OH^-]}$ OH^- × multepling numerater and denominator

$ka = \frac{kw}{kb}$ $for\ NH_4^-$ $ka = \frac{1.0 \times 10^{-14}}{1.75 \times 10^{-5}} = 5.7 \times 10^{-10}$

Calculate the Concentration of Hydronium Ion

When the salt of a weak base is ionized it gives equal quantities of Bx and H_3O^+ SO

$$BH^+ + H_2O \rightleftharpoons B + H_3O^+$$

C x x

C H^+ H^+

$$\frac{[H^+]\,[H^+]}{C} = \frac{kw}{kb}$$

$$[\boldsymbol{H^+}] = \sqrt{\frac{\boldsymbol{kw}}{\boldsymbol{kb}}\boldsymbol{C}} \ \ldots(\mathbf{4-15})$$

Ex18. calculate pH for 0.25 M of NH_4Cl

Sol.: $H^+ = \sqrt{\frac{1.0 \times 10^{-14}}{1.75 \times 10^{-5}}} \times 0.25 = 1.2 \times 10^{-5} M$

$pH = -log(1.2 \times 10^{-5}) = 4.42$

Ex15: Calculated the pH of $0.1M$ solution of Phenylammonium chloride, $C_6H_5NHCl.Kb$ for $C_6H_5NH_2 = 3.8 \times 10^{-10}$, what will be the degree of hydrolysis if the concentration of this salt is 0.01M

Sol.: $C_6H_5NH_3Cl \rightarrow C_6H_5NH_3^+ + Cl^-$

$C_6H_5NH_3^+ + H_2O \rightleftharpoons C_6H_5NH_2 + H_3O^+$

$$[H_3O] = \sqrt{\frac{kw}{kb}C} = \sqrt{\frac{1 \times 10^{-14}}{3.8 \times 10^{-10}} \times 0.1}$$

$$[H_3O] = \sqrt{2.6 \times 10^{-6}} = 1.6 \times 10^{-3} M$$

$$pH = -log\ 1.6 \times 10^{-3} = 2.8$$

When the conc. of the salt is 0.01 M, then $C = 0.01\ M$

Substitutes in the equation above;

$$[H_3O] = \sqrt{\frac{1 \times 10^{-14}}{3.8 \times 10^{-10}} \times 0.01} = 5.1 \times 10^{-4} M$$

$$Degree\ hydrolysis = \frac{[H_3O^+]}{C} = \frac{5.1 \times 10^{-4} M}{0.01 M} = 0.051$$

Ex19: A 35 gm of NH_4Cl was dissolved in 500 mL of water. Calculate $[H^+]$. $[OH^-]$. pH. pOH. of the **sol**. $k_b NH_3 = 7.5 \times 10^{-5}$

$$soln: mwt\ NH_4Cl = 53.5\ g\ m/\ mole$$

$$M = \frac{wt \times 1000}{Mwt \times Vml} = \frac{35.5 \times 1000}{35.5 \times 500} = 0.5\ M/L$$

$$[H^+] = \sqrt{\frac{kw}{kb}C} = \sqrt{\frac{1 \times 10^{-14}}{1.75 \times 10^{-5}} \times 0.2} = 10^{-5}\ m/l$$

$$pH = -log[H^+] = -log\ [10^{-5}] = 5$$

$$[OH^-] = \frac{kw}{[H^+]} = \frac{1 \times 10^{-14}}{1 \times 10^{-5}} = 1 \times 10^{-9}$$

$$pOH = 9$$

$[OH^-] < [H^+]$ The solution is acidic because

$1 \times 10^{-9} < 1 \times 10^{-5}$

Buffer Solutions

It's the solution which resists the change in pH when it added to a solution in the lesser amount of acid or base or in solution dilution. A buffer solution is one which maintains its pH fairly constant even upon the addition of small amounts of acid or base. There are two types of buffer solution. 1. Acidic Buffer 2. Basic Buffer

Acidic Buffer: A weak acid together with a salt of the same acid with a strong base. These are called Acidic Buffer, For Example. CH_3COOH CH_3COONa.

Basic Buffers: A weak base and its salt with a strong acid. These are called Basic Buffers, For Example, NH_4OH+NH_4CL

Let us illustrate buffer action by taking example of a common buffer system consisting of solution of acetic acid and sodium acetate.

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

$CH_3COONa \rightleftharpoons Na^+ + CH_3COO^-$

Since the salt is comletely ionized,it provides the common ion $CH3COO^-$ in excess.

A buffer solution maintains the pH by neutralizing small amounts of added acid or base. An acid must be present to react with any OH^- added, and a base must be present to react with any H_3O^+ added.

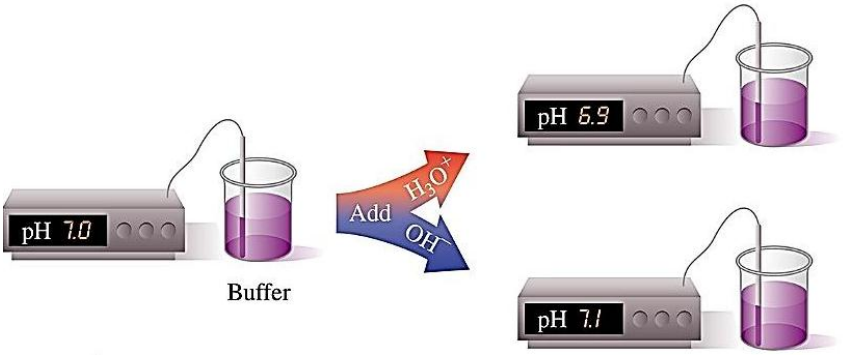


Figure 3- 3 range of buffur solution

Weak acid and its salt buffer solution:

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

Taking minus logarithm of the both sides of the equation:

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

$$pH = pk_a - log \frac{[HOAC]}{[OAC^-]}$$

Henderson – Hasselbach Equation

An above equation is useful in calculation pH of weak a cid in the presence of its salt.

Equation of weak acid generally could be written as below

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

$$\boldsymbol{pH = pK_a + log\frac{[salt]}{[acid]}} \ldots (\mathbf{2-16})$$

$[salt]$ = Molarity of the salt, $[acid]$ = molarity of the acid

Ex20: Calculate the pH of a solution prepared by adding 10 ml of 0.1M of a ceticacid $to\ 20\ ml\ of\ 0.1M$ sodium a acetate.

Sol.: $M_1 \times V_1 = M_2 \times V_2$

for HOAC

$0.1\ \text{mmoles/ml} \times 10\ \text{ml} = M_{HOAC} \times 30\ \text{ml}$

$M_{HOAC} = 0.033\ \text{mmoles/ml}$

For acetate (OAc^-)

$0.10\ \text{mmoles/ ml} \times 20\ \text{ml} = MoAC^- \times 30\text{ml}$

$M_{OAC^-} = 0.067\ \text{mmoles/ ml}$

Some of HoAC dissociates into $H^+ + OAC^-$ and the concentration at equilibrium concentration will be the added quantity $0.033M$ substrated from it the dissociated amount.

When the concertation of OAC^- is the added quantity $0.067M$

Plus the amount oJ dissociated HOAC. So:

$$pH = -\log(1.7\,5 \times 10^{-5}) + \log\frac{0.067\ \text{mmole/ml}}{0.033\ \text{mmoles /ml}}$$

$$= 4.76 + \log 2.0$$

$$= 5.06$$

A norther way for solution:

Calculation may by summarized as log value

(m moles salt/ ml) (m moles acid/ml) ration can be ignored and substituted by (m moles salt)/ (m moles acid) ratio.

$M\ moles_{HOAC} = 0.10\ \text{m moles}\ |m| \times 10\text{ml} = 1.0\ \text{m moles}$

$M\ moles_{OAC^-} = 0.10\ \text{m moles}\ |m| \times 20\text{ml} = 2.0\ \text{m moles}$

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

Benefit of Buffers

1- They resist changes in pH from the addition of an acid or a base.

2- In the body, they absorb H_3O^+ or OH^- from foods and cellular processes to maintain pH.

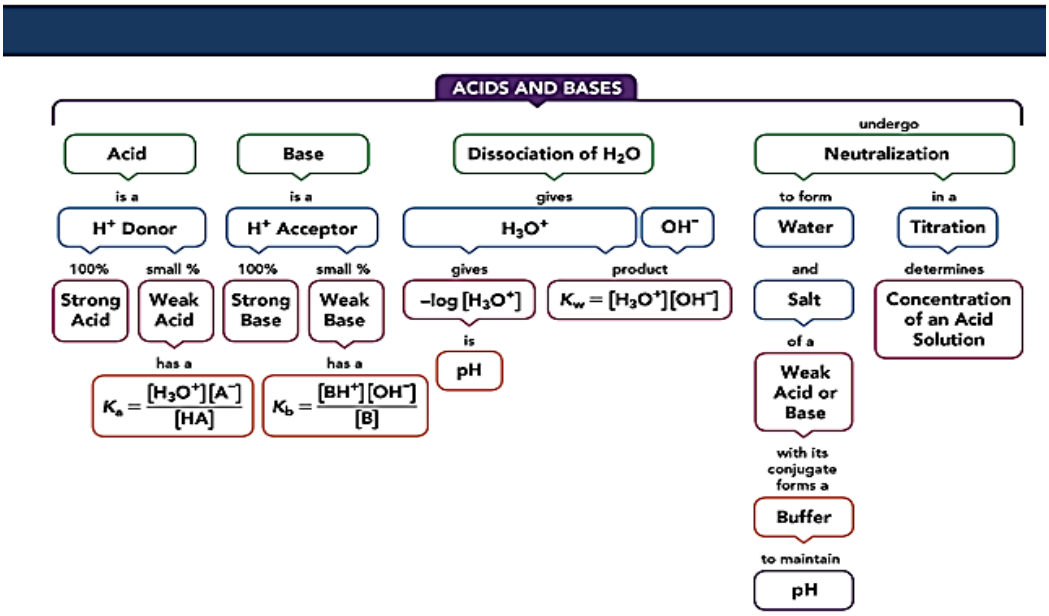
3- they are important in the proper functioning of cells and blood.

4- they maintain a pH close to 7.4 in blood.

A change in the pH of the blood affects the uptake of oxygen and cellular processes**.**

Table 3-3 equilibrium of acid and base

Concept Map



Questions and Answer

Q1. Considered the following equilibrium expression:

$$K = \frac{[L][M]^4}{[J]^6[K]}$$

The equation of the forward reaction for this equilibrium expression is:

a. $6J + K \rightleftharpoons L + 4M$

b. $L + M_4 \rightleftharpoons J_6 - K$

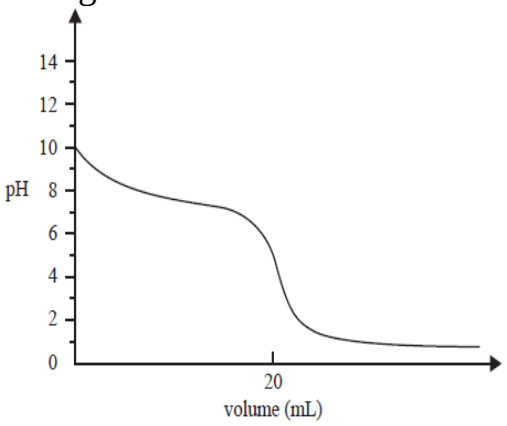
c. $J_6 - K \rightleftharpoons L + M_4$

d. $L + 4M \rightleftharpoons 6J + K$

Q2. What is the pH of a solution made by diluting 1.00 mL of 0.10 M HCl with enough distilled water to make 1.00 L of solution?

a. 1.0
b. 2.0
c. 3.0
d. 4.0
e. 7.0

Q3. The following titration curve was obtained by measuring the pH in a reaction flask during an acid-base titration.



Q4. The graph represents the change in pH in the reaction flask when
a. a weak acid is added to a strong base.
b. a weak base is added to a strong acid.
c. a strong acid is added to a weak base.
d. a strong base is added to a weak acid.

Sol. The starting pH of 10 is indicative of a weak base. The drop in pH to 1 would be due to titration with a strong acid; therefore, a strong acid was added to a weak base.

Q5. 1g of each of the following substances is dissolved in 1 L of water. In which one would the pH of the resultant solution be closest to 7?
a. H_2SO_4
b. NH_3
c. $NaHSO_4$
d. NaCl

Q6. In pure water at 5oC the hydroxide ion concentration is measured to be 4.0×10^{-8} M.
The Kw and pH of pure water at this temperature will be, respectively,
a. 1.0×10^{-14} and 7.0
b. 1.0×10^{-1}4 and 6.6
c. 1.6×10^{-15} and 7.0
d. 1.6×10^{-15} and 7.4
Sol. Many still find this difficult. The high frequency of the incorrect response B is attributed to students believing that Kw is always 10-14 whatever the temperature. The important point to see here is that $[H_+]$ and $[OH_-]$ in pure water must always be the same, whatever the temperature.

Q7. At 25ºC, the pH of 0.0050 M Ba(OH)2 is:
a. 2.0
b. 2.3
c. 11.7
d. 12.0
Sol. d. $Ba(OH)_2(aq) \rightarrow Ba^{2+}(aq) + 2OH^-(aq)$
$[OH^-] = 2 \times [Ba(OH)_2] = 2 \times 0.0050 = 0.010$ M
$[H_3O^+] = 10^{-14}/ 0.010 = 10^{-12}$ M
$pH = -\log10(10_{-12}) = 12$

Q8. Equal masses of each of the following substances are dissolved in separate samples of water to give 500 mL of solution.
Which substance would produce the solution with the lowest pH?
a. NH_3
b. HCl
c. HNO_3
d. $HClO_4$
Sol. b. HCl(aq), HNO_3(aq) and $HClO_4$(aq) are all strong monoprotic acids. For equal masses the acid with the lowest molar mass will have the highest n(acid) and hence produce the highest n(H^+), highest [H^+] and lowest pH:
M(HCl) = 36.5 g mol^{-1}
M(HNO_3) = 63 g mol^{-1}
M($HClO_4$) = 100.5 g mol^{-1}
So HCl will produce the solution with lowest pH.

Q9. Methanoic acid HCOOH is a weak acid present in the sting of some ants. It ionises in water according to:
HCOOH(aq) $HCOO^-$(aq) + H^+(aq) Ka = 1.8×10^{-4} at 25°C
a. Explain the meaning of the terms 'weak acid' and 'strong acid'.
Sol. Weak acid– only partially ionises (donates few H^+ ions/protons) in water.
Strong acid – completely ionises (donates many H^+ ions/protons) in water.
b. Write the expression for the K^a of methanoic acid.
Sol.

$$K_a = \frac{[HCOO^-][H^+]}{[HCOOH]}$$

c. Assuming a small degree of dissociation, calculate the concentrations of H^+(aq) and $HCOO^-$(aq) in 0.10 M methanoic acid at 25°C.
Sol. [HCOOH] = 0.10 M; [H+] = [$HCOO^-$]
1.8x10-4 = [H+]2/ 0.10 → [H^+]2 = 1.8x10-4 x 0.10

$[H^+] = \sqrt{(1.8x10^{-5})} = 4.2x10^{-3}$ M

$[HCOO^-] = 4.2x10^{-3}$ M

Q10. For the reaction: H2O(l) $H^+(aq) + OH^-(aq)$, Kw = 10^{-14} at 25ºC, 55.9 kJ mol–1 of heat is evolved when one mole of $H^+(aq)$ reacts with one mole of $OH^-(aq)$.

At 80ºC, the Kw and pH for pure water is:

	K_w	pH
A.	greater than 10^{-14}	less than 7
B.	greater than 10^{-14}	greater than 7
C.	less than 10^{-14}	less than 7
D.	less than 10^{-14}	greater than 7

Sol. a. The reaction $H^+(aq) + OH^-(aq) \rightarrow H_2O$ is exothermic. So the equilibrium $H_2O(l)$ $H^+(aq) + OH^-(aq)$ is endothermic

At 25°C; Kw = 10^{-14}, pH = 7

At 80°C the position of equilibrium will lie further to the right, so $[H^+]$ and [OH-] will be greater.

Hence Kw{=$[H^+][OH^-]$} will be>10^{-14} and pH{=-log10$[H^+]$} will be<7

Q11. The Ka of hydrofluoric acid, HF, is 6.8×10^{-4}.

The pH of a 0.10 M solution of HF in water is closest to

a. 1

b. 2

c. 3

d. 4

Sol. b. HF(aq) $H^+(aq) + F^-(aq)$

Ka = $[H^+][F^-]/ [HF]$

Since HF is a weak acid $[H^+]e = [F^-]e$ and [HF]e = 0.10

$6.8x^{10-4} = [H^+]2/ 0.10 \rightarrow [H+]2 = 0.10 \times 6.8x10^{-4}$

$[H^+] = \sqrt{(6.8x10^{-5})} = 8.2 \times ^{10-3}$

pH = -log10$(8.2x10^{-3}) = 2.1\times10^{-3}$

CHAPTER FIVE

CHOICE OF INDICATOR OF ACID-BASE TITRATION

CHAPTER FIVE
Choice of indicator of acid-base titration

Introduction

Acid - Base indicators (also known as pH indicators) are substances which change color with pH. They are usually weak acids or bases, which when dissolved in water dissociate slightly and form ions.

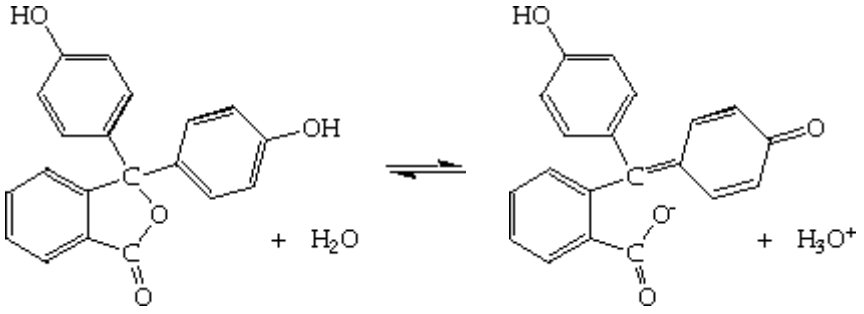
Consider an indicator which is a weak acid, with the formula HIn. At equilibrium, the following equilibrium equation is established with its conjugate base:

$$HIn\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + In^-\ (aq)$$

acid (colour A) — conjugate base (colour B)

The acid and its conjugate base have different colors. At low pH values the concentration of H_3O^+ is high and so the equilibrium position lies to the left. The equilibrium solution has the color A. At high pH values, the concentration of H_3O^+ is low, the equilibrium position thus lies to the right and the equilibrium solution has color B.

Phenolphthalein is an example of an indicator which establishes this type of equilibrium in aqueous **Sol.:**



colorless (Acid) pink (Base)

Under acidic conditions the equilibrium forward to the left and the concentration of anions are so low and that pink color cannot be observed. However, under alkaline conditions the equilibrium is on the right and the anion concentration is sufficient for pink.

Equilibrium Law of Indicator

We can apply equilibrium law to indicator equilibrium in general for a weak acid indicator:

$$K_{In} = \left(\frac{[H_3O^+][In^-]}{[HIn]} \right)_{eq}$$

The indicator color changes from A to B or reveres at the convert point.

At this point:

$$[HIn] = [In^-]$$

So from equation:

$$K_{In} = [H_3O^+]$$

The pH of the solution at its turning point is called the pK_{In} and is the pH at which half of the indicator is in its acid form and the other half in the form of its conjugate base.

The change in the pH of the solution during the titration can be drawn as a titration curve, which shows the acid change in the pH by the change in the quantity of the acid or the base added, and the titration curve can be determined in two ways:

1. Mathematical method: in which the pH is calculated with the added amounts of acid or base.

2- The practical method: in which the pH is measured practically using the pH-meter device. The process is summred up by immersing the two electrodes of the device (idicator electrode and reference electrode) in the solution and read the pH value against the different added volumes. The end point occurs when a significant change in the pH value.

The Titration Curve

There are four types of acid-base titration; each has a characteristic curve.

strong acid (HC*l*) v. strong base (NaOH)
weak acid (CH_3COOH) v. strong alkali (NaOH)
strong acid (HC*l*) v. weak base (NH_3)
weak acid (CH_3COOH) v. weak base (NH_3)

Titration of Strong Acid With Strong Base

The titrant and analyte materials are completely ionized in the solution of a strong acid l as in the hydrochloric acid against sodium hydroxide.

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

H^+ is taken with OH^- to form H_2O, while the other ions (Na^+, Cl^-) remain constant and the neutral result is the conversion of HCl into a neutral NaCl solution.

The following figure shows titration curve of a 50 ml HCl (0.1M) with 0.1 M NaOH.

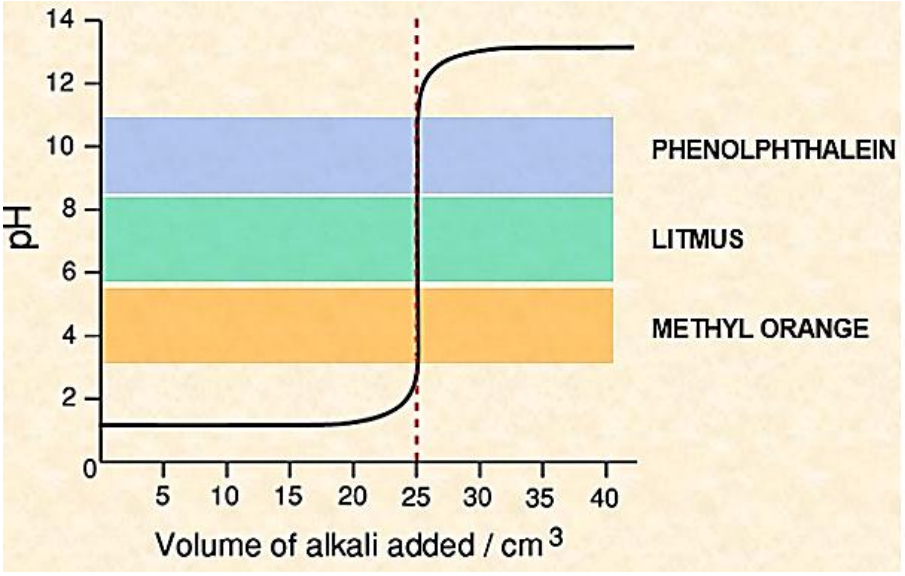


Figure 5-1 effect of pH on indicator

Note: any of indicators listed will be suitable, they all change in "vertical" portion.

Ex1. The pH of the solution at 50 ml the beginning of the titration is 1.0 and a portion of H^+ is removed during the titration process of the solution to form H_2O. Therefore, the concentration of H^+ decreases gradually.

1- pH of the acid solution before the addition of NaOH;

$[H_3O^+] - 0.1$

$pH = - \log (0.1) = 1$

2- after addition of 10 ml of 0.1 N NaOH

$$[H^+] = \frac{50 * 0.1 \text{ x } -10 \text{ x } 0.1}{60},$$

$$[H^+] = \frac{4}{60} = 6.6 \text{ x } 10^{-2}, \quad pH = -\log 6.6 \text{ x } 10^{-2} = 1.18$$

The concentration $[H^+]$ is gradually removed quickly by the progressive addition of NaOH, to its equivalent point.

3- After addition 25 ml of NaOH.

$$[H+] = \frac{50 \text{ x } 0.1 - 25 \text{ x } 0.1 \; 2.5}{75} = \frac{2.5}{75} = 0.033$$

pH = -log 0.033 =1.45

Upon completion of the reaction, the solution will be neutral (NaCl) where the solution pH is 7.0

4- After addition of 50 ml of NaOH

No of meq of aCid = 50 x 0.1 =5

No of meq of Base =50 x 0.1 =5

pH = 7

pKW = pH + pOH

14 = 7 + 7

5- after adding 50.01 ml of NaOH (after end point)

$$\mathbf{(OH^-) = \frac{50.01 \text{ x } 0.1 - 50 \text{ x } 0.1}{100.01} = 1x10^{-5}}$$

pOH = - log (OH) =- log (1x 10^{-5}) =5

pH = 14 – 5 = 9

6- after adding 60 ml of NaOH

$$\mathbf{(OH^-) = \frac{60 \text{ x } 0.1 - 50 \text{ x } 0.1}{110} = \frac{1}{110}}$$

pOH = -log 1/110 = 2.04

pH = 14 – 2.04 = 11.96

Titration of Weak Acid With Strong Base

The titration of a weak acid with a strong base involves the direct transfer of protons from the weak acid to the hydroxide ion. The reaction of the weak acid, acetic acid, with a strong base, NaOH, can be seen below. In the reaction the acid and base react in a one to one ratio.

$CH_3COOH\ aq) + OH^-(aq) \rightarrow CH_3COO^{-1}(aq) + H_2O(L)$

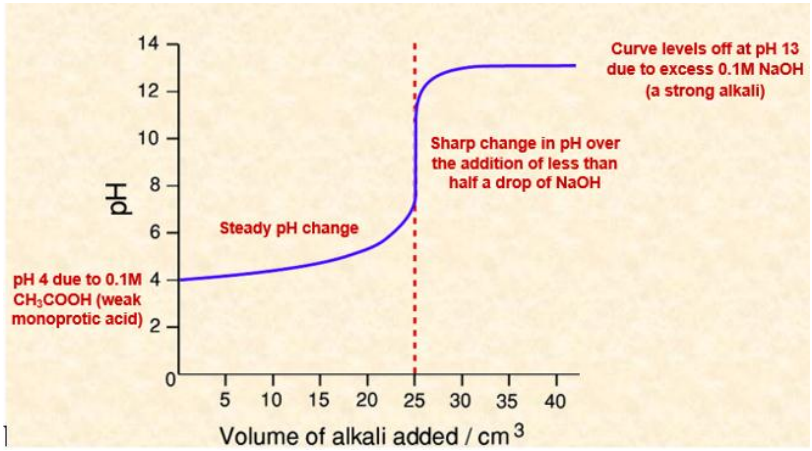


Figure 5-2 The titration of a weak acid with strong base.

Ex2. Calculated the pH value of titrant acetic acid (50ml) versus sodium hydroxide.

$HOAC + Na^+ + 0H^- \rightarrow Na + OAC^- + H_2O$

1- at start (acid only is exist in the conical flask) $Ka = 1.75 \times 10^{-5}$

$Ka = x^2/(0.1)$, $x = \sqrt{0.1 \times 1.75 \times 10 - 5}$

$pH = -\log 0.1 \times 1.320.1 \times 10^{-3}$

$pH = 2.88$

it is calculated the pH value for the acid before titration

2- after adding 10 ml of NaOH

No of mmole of salt

$pH = pKa + \log (salt)/(H^+)$ ... **(5-1)**

$$salt = \frac{No.\ of\ mmole\ of\ salt}{Vt\ (ml)} \quad = 10x\ 0.1/60 = 1/60$$

$$(HA) = \frac{(50 \times 0.1) - (10 \times 0.1)}{60} = \frac{4}{60}$$

pH = ka + log[salt] = -log 1.75x 10^{-5} + log 25 x 10^{-2} =4.15

Here at the beginning of the titration, an indicator is converted from HOAC to NaOAC, then the buffer solution is fixed and its pH values range slowly at the stage of the titration process with a change in the ratio of (HOAC) and (OAC).

3- after adding 25ml of NaOH (midd point)

pH =pKa because pH = pKa + log salt/acid

= -log 1.75 x 10^{-5} =4.75

4 – at equivalence point (addition of 50 ml (NaOAC)

Where there will be a NaOH solution at equivalent point where the protsted base which is hydrolyzed and pH at the equivalent point is base.

pH is dependent on NaOAC concentration as the equation:

$[H_3O^+] = \sqrt{KaKw/[c]}$

$$\frac{(OH^-)(OH^-)}{CA^-} = \frac{Kw}{Ka}$$

pH =1/2 (log C + pKa + pKw)

= 1/2 (log 0.05 – log 1.75 x 10^{-5} – log 1 x 10^{-14}) = 8.73

5- after adding 50.05 ml of NaOH =

50.05 x 0.1 – 50 x 0.1 = 0.005= $\frac{[OH-]}{[C-]}$

$[OH^-]$ = 0.005/ 109.05 = 4.998 x 10^{-3}M

pOH = 4.3 , pH = 9.7

When the base concentration increases after theequivalent point, the ionization of the base OAC- decreases to a quantity that may be neglected.

$OAH^- + H_2O \leftrightarrow HOAC + OH^-$

6- after adding (60 ml 0f NaOH)

No of moles of excess NaOH = 60 x 0.1 -50 x 0.1 =1

(OH) = 1/110 pOH = -log 1/110 = 2.04 → pH= 14-2.04 =11.46

Thus the ratio of the buffer solution depends on the HOAC and OAC- the concentration.

Titration of Weak Base With Strong Acid

Chemists are typically interested in calculating volume and acidity data for the following critical points: at the starting point before any titrant is added, at the midpoint, at a point before the equivalence point (excluding the initial condition), at the equivalence point, and past the equivalence point.

The titration state of the weak base is similar to the strong acid with the situation above, but the titration curves are opposite to the curves of the weak acid with the strong base. A 50 ml titration curve of 0.1 M NH_3 with 0.1M HCl can be illustrated in the figure below.

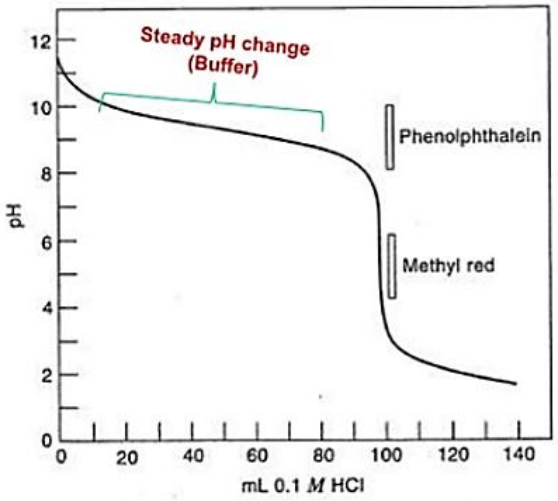


Figure 5-3 range of idicator

Ex3. Calculate pH solution of titrant hydrochloric acid (0.1M) versus 50 ml of ammonia(0.1M).

The neutralization reaction can be illustrated by the following equation

$NH_3 + H^+ + Cl^- \rightarrow NH_4^+ + Cl^-$

1- At the start of the titration 0.1M NH_3 is present in the reaction vessel and the pH is calculated as following;

$Kb = \frac{X2}{NH3}$, $X = \sqrt{1.75 \times 10^{-5}} \times 0.1 = [OH^-] = 0.4 \times 10^{-3}$, pOH=2.3

pH= 14-POH =11.7

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

When adding 10ml HCl of the burette to the reaction vessel, part of NH_3 is converted to NH_4^+ depending on the above equation, where the buffer solution is formed NH_3/ NH_4^+.

mmole of NH_3= 50 x 0.1 = 5, mmole $[H^+]$ =10 x 0.1 =1

mmole of excess NH_3 =5 - 1 = 4

$$pOH = pKb + \frac{[salt]}{[base]}$$

$$pOH = pka + + \frac{[1/60]}{[4/60]}$$, pOH =4.7 + 4.15, pH=8.9

3- after adding 25 ml of HCl (mid-point)

It will be pOH = pKb because;

$$pOH = pKb + \frac{[salt]}{[base]}$$

$$pOH = \frac{2.5/75}{}$$ pOH = 4.7 +log 1, pOH =4.7

pH = 14 – 4.7 = 9.3 at $[NH_3] = [NH_4]$

4) at equivalence point (addition of 50ml HCl)

At its equivalent point, NH_4Cl is formed as a weak bronsted acid which is hydrolyzed to give an acidic solution. In addition, the value of pH depends on the concentration or decrease the value of pH as the concentration increases.

$$[H^+] = \sqrt{\frac{Kw}{Kb} NH_4^+}$$ [c] = (50 x 0.1)/100 = 0.05

$$[H^+] = \sqrt{\frac{1x10-14}{1.75x10-5}}$$ x 0.05, pH = 5.27

the excess of [H +] is decreases the ionization after the equivalent point and pH suffers from the concentration of H^+ was added.

5) After adding (60 ml of HCl)

= (60 x 0.1) – (50 x 0.1) =1 excess m mole of HCl

$[H^+]$ =0.005/100.05, $4.998x10^{-5}$, pH =4.3

6) after addition (60ml of HCl)

No of moles HCl= 60 x 0.1 – 50x0.1=1

$[H^+]$ = 1/110, pH=2.4

After the equivalent point, the titration curve arises with the strong base titration, and since the constant value of Kb of ammonia is equal

to Ka of acetic acid, it becomes a titration of ammonia with strong acid. It is a mirror image of the curve of acetic acid titration with a strong base.

Titration of Diprotic Acid With Strong Base

0.1 N H_2CO_3 and 0.1 N NaOH

Ex4. You can find acidic function values at any point of titration with a strong base using the following steps:

$H_2A \leftrightarrow H^+ + HA^-$

$HA^- \leftrightarrow H^+ + A^{-2}$

1- Before addition of base, $Ka1 = \frac{X^2}{[H_2A - X]} = \frac{X^2}{[H_2A]}$

pH = -log X

2- When strong base is added before 1st equivalence point

$$pH = pKa_1 + \log \frac{\mathbf{[NaHA]}}{\mathbf{[H_2A]}}$$

3- at first eq. point

a) m mole of base added

b) m mole of weak acid

$$\mathbf{pH = \frac{pKa1 + pKa2}{2}} \quad \ldots (5\text{-}2)$$

4- $HA^- \leftrightarrow H^+ + A^{-2}$

During titration of 2nd acidic hydrogen, but before 2nd eq. point

a) Determine moles of $[A^{-2}]$

b) Determine moles of [HA] remained

$$pH = pKa_2 + \log \frac{[A^{-2}]}{[HA^-]\ rem}$$

5- at second eq. point all acid becomes salt

$$[OH^{-1}] = [A^{-2}] \frac{Kw}{Ka_2}$$

$$MA^{-2} = \frac{\text{Mole } A^{-2}}{\text{V solution}}$$

6- after 2nd eq. point

a) Determine excess of m moles of OH^-

b) Determine $[OH^-] = \frac{\textbf{no.of moles OH−}}{\textbf{V total}}$

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

EX5: 25ml of 0.1 N from malic acid ($H_2C_4H_2O_4$) titration with 0.1 N(NaOH). find pH at (0, 5ml, 20ml), first eq. point 25.5 ml, 40 ml, 50 ml, 60 ml, if $Ka_1 = 1.5 \times 10^{-2,}$ $Ka_2 = 2.6 \times 10^{-7}$

Sol.:

$H_2C_4H_2O_4 \leftrightarrow HC_4H_2O_4^- + H^-$

$$1)\ Ka_1 = \frac{[X^2]}{[H_2C_4H_2O_4]}$$

$X = 1.5 \times 10^{-2} \times 0.1$

$X = 0.03$

$pH = -\log [H^-] = -\log [0.053]$

$pH = 1.4$

2) after adding 5ml NaOH

a) meq of $H_2C_4HO_4 = 0.1 \times 25 = 2.5$

b) meq of $OH^- = 0.1 \times 5 = 0.5$

c) meq of $H_2C_4HO_4$ remained $= 2.5 - 0.5 = 2$

$pH = PKa_1 + \log [salt]/[base]$

$pH = 1.8 + \log \frac{\textbf{0.5/3}}{\textbf{2/30}} = 1.22$

3- after adding 20 ml

Meq of $H_2C_4H_2O_4 = 2.5$

Meq of $OH^- = 20 \times 0.1 = 2$

c) meq of $H_2C_4H_2O_4$ remained = 2.5 – 2=0.5

pH = PKa_1 + log [salt]/[HA] = 1.8 =log $\frac{\mathbf{2/45}}{\mathbf{0.5/45}}$ = 0.6, pH =2.4

4- **at first equivalence point**

$$pH = \frac{pK_1}{2} + \frac{pK_2}{2} + \frac{1.8+6.6}{2} = \frac{8.4}{2} = 4.2$$

$H_2C_4H_2O_4 \leftrightarrow 2H^+ + C_4H_2O_4^{-2}$

(5) after adding 25.5ml

a) meq of $H_2C_4HO_4$ =2.5

b) meq of OH = 25.5 x 0.1 =2.55

c) meq of OH_{excess} =2.55 -2.5 =0.05

d) meq of $H_2C_4HO_4$ remained = 2.5 – 0.05 = 2.45

pH = pKa_1 + log [salt]/[HA] = 6.6 +log $\frac{\mathbf{0.05/50.5}}{\mathbf{2.45/50.5}}$

pH =4.9

(6) After addition of 40ml

a) Meq of $H_2C_4HO_4$ =2.5

b) Meq of OH =40*0.1 =4

c) Meq of OH_{excess} = 4-2.5 =1.5

Meq of $HC_4H_2O_{remained}$ = 2.5 – 1.5 =1

pH = pKa_1 + log [salt]/ [$H_2C_4HO_4$] =6.6 +log $\frac{\mathbf{1.5/6.5}}{\mathbf{1/65}}$ =6.8

(7) after adding 50ml

a) meq of $H_2C_4HO_4$ =2.5

b) meq of OH_{excess} = 5 - 2.5 =2.5

$OH^- = \frac{\mathbf{KW}}{\mathbf{Ka_2}}$ x salt

$OH^- = \frac{\mathbf{2.6 \times 10^{-14}}}{\mathbf{2.6 \times 10^{-7}}} \mathbf{X0.6}$

$OH^- = 0.2 \times 10^{-8}$

$OH^- = 0.4 \times 10^{-4}$, POH =4.4

pH = 9.6

(8) after addition of 60 ml.

Meq of HC_4H_2O =2.5

Meq of OH =60 x 0.1 = 6

Meq of OH_{excess} = 6 - 2.5 = 3.5

$[OH^-]$ =3.5/85 = 0.4, pOH = 1.4
pH =12.6

A Summary of The Important Curves

The way you normally carry out a titration involves adding the acid to the alkali. Here are reduced versions of the graphs described above so that you can see them all together

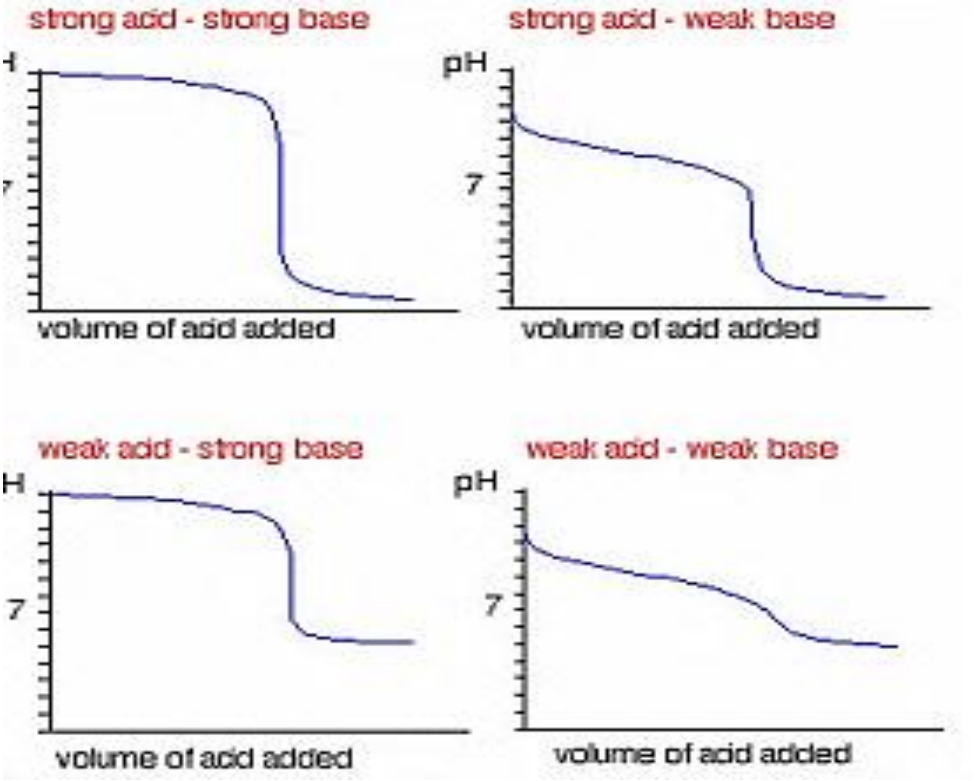


Figure 5-4 type of titration acid-base

The pH Range of Indictors

Indictors does not change color sharply at one particular pH, they change over a narrow range of pH.

Table 5-1 change color of indicator

Must have an easily observed colour change.

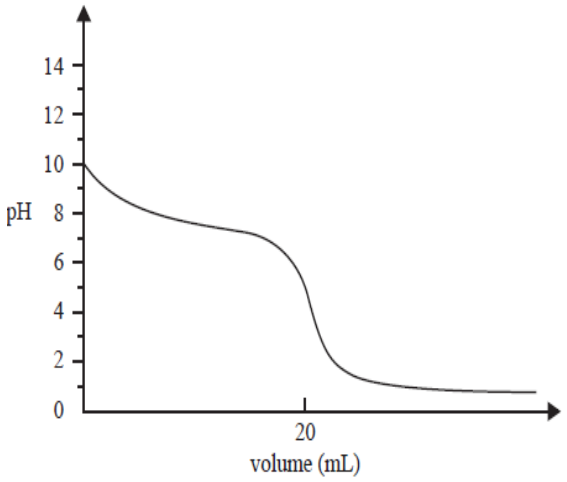
Must change immediately in the required pH range over the addition of 'half' a drop of reagent.

COLOUR CHANGES OF SOME COMMON INDICATORS

pH	1	2	3	4	5	6	7	8	9	10	11	12	13	14
METHYL ORANGE			CHANGE											
LITMUS							CHANGE							
PHENOLPHTHALEIN								CHANGE						

Questions and Answer

Q1. The following titration curve was obtained by measuring the pH in a reaction flask during an acid-base titration.

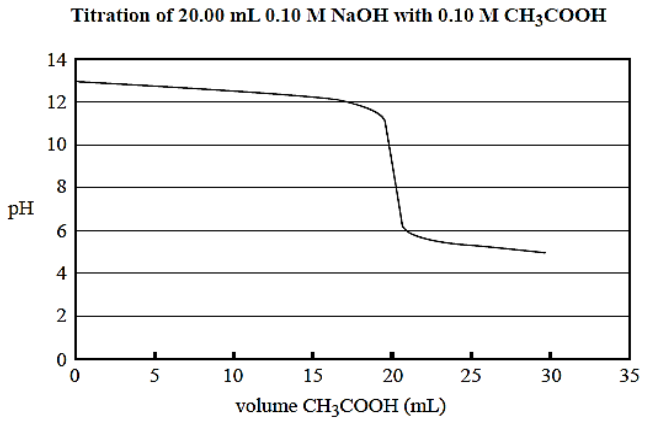


Which one of the following is a suitable indicator for use in this titration?

a. phenol red
b. thymol blue
c. phenolphthalein
d. bromophenol blue

Sol. The titration curve suggests that the endpoint is around pH 4. Of the indicators listed, only bromophenol blue (3.0–4.6) would be suitable for identifying the endpoint.

Q2. The graph below shows the change in pH of a reaction solution during a titration of 0.10 M NaOH with 0.10 M CH_3COOH.



A suitable indicator for the titration and the color change observed is

indicator color change observed

a. methyl red yellow to red

b. methyl red red to yellow

c. phenolphthalein colorless to red

d. phenolphthalein red to colorless

Sol. d. The titration curve shows that the endpoint for the titration occurs in the pH range 6 to 11. Table 11 of the data book shows that phenolphthalein changes color in the pH range 8.3–10.0, while methyl red changes color in the pH range 4.2–6.3. Therefore, phenolphthalein is the better option.

Since the acid is being added to the base, the pH will drop as the endpoint is passed through and hence phenolphthalein will change from red to colorless

Q3. 0.132 g of a pure carboxylic acid (R–COOH) was dissolved in 25.00 mL of water and titrated with 0.120 M NaOH solution. A

volume of 14.80 mL was required to reach the endpoint of the titration.

Which of the following best represents the pH of the solution at the equivalence point and the name of a suitable Indicator for this titration?

pH at the equivalence point suitable indicator

a. less than 7 phenolphthalein

b. less than 7 bromophenol blue

c. greater than 7 phenolphthalein

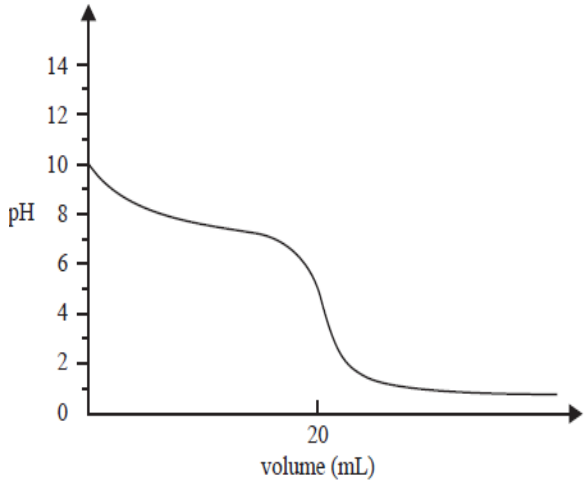
d. greater than 7 bromophenol blue

Sol. c. At the equivalence point all of the RCOOH will have reacted with NaOH(aq) according to:

$RCOOH(aq) + OH^-(aq) \rightarrow RCOO^-(aq) + H_2O(l)$.

The pH at the equivalence point is due to $RCOO^-(aq)$ which as the conjugate base of the carboxylic acid is a weak base, hence the solution has **pH>7**. During the titration the pH of the solution increases and to accurately identify the endpoint, as close as possible to the equivalence point, the indicator must change colour once the pH becomes greater than 7. Phenolphthalein fits these criteria.

Q4. The following titration curve was obtained by measuring the pH in a reaction flask during an acid-base titration.



Which one of the following is a suitable indicator for use in this titration?

a. phenol red
b. thymol blue
c. phenolphthalein
d. bromophenol blue

Sol. d. The titration curve suggests that the endpoint isaround pH 4. of the indicators listed, onlybromophenol blue (3.0–4.6) would be suitable for identifying the endpoint.

Q5. A standard HCl solution is titrated to a pink phenolphthalein endpoint by adding a NaOH solution while stirring. If a solution becomes pink throughout but loses its color upon standing for a short time, what should be done to restore the color?

a. Add more phenolphthalein indicator.
b. Add an additional drop of NaOH solution.
c. Add an additional drop of HCl solution.
d. Stir more vigorously

Q6. Which pair of solutions forms a buffer solution when equal volumes of each are mixed?

a. 0.20 M HCl and 0.20 M NaOH
b. 0.40 M $HC_2H_3O_2$ and 0.20 M NaOH
c. 0.20 M HCl and 0.20 M NH_3
d. 0.40 M HCl an 0.20 M NH_3

Q7. 0.132 g of a pure carboxylic acid (R–COOH) was dissolved in 25.00 mL of water and titrated with 0.120 M NaOH solution. A volume of 14.80 mL was required to reach the endpoint of the titration.

Which of the following best represents the pH of the solution at the equivalence point and the name of a suitable Indicator for this titration?

pH at the equivalence point suitable indicator;

a. less than 7 phenolphthalein

b. less than 7 bromophenol blue
c. greater than 7 phenolphthalein
d. greater than 7 bromophenol blue
Sol. c. At the equivalence point all of the RCOOH will have reacted with NaOH(aq) according to:
$RCOOH(aq) + OH^-(aq) \rightarrow RCOO^-(aq) + H_2O(l)$.
The pH at the equivalence point is due to $RCOO^-(aq)$ which as the conjugate base of the carboxylic acid is a weak base, hence the solution has **pH > 7**. During the titration the pH of the solution increases and to accurately identify the endpoint, as close as possible to the equivalence point, the indicator must change colour once the pH becomes greater than 7. Phenolphthalein fits these criteria.

Q8. A standard HCl solution is titrated to a pink phenolphthalein endpoint by adding a NaOH solution while stirring. If a solution becomes pink throughout but loses its color upon standing for a short time, what should be done to restore the color?
a. Add more phenolphthalein indicator.
b. Add an additional drop of NaOH solution.
c. Add an additional drop of HCl solution.

CHAPTER SIX
Complex Formation Titrations

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Complex Formation Titrations

Introduction

The complexes titration is among the oldest volumetric methods, including iodide correction with mercury, which was first discovered in the year 1834.

$Hg^{+2} + 4I^{-} \leftrightarrow HgI_4^{-2}$

1- Titration with inorganic complexing reagent,

Found, Liebig, for the first time in 1851, the method for estimating sovereignty based on the formation of the dicyanoargenate Ag $Ag(CN)_2^{-}$. The table below shows some reagents for the formation of nonchelating complexes and their uses.

Table 6-1 reagents for the formation of nonchelating complexes.

Titrant	Anlyat	Notes
$Hg(NO_3)_2$	$Br^{-}.Cl^{-}.SCN^{-}.CN^{-}$	The resultes are the mercury complexes neutral, using different idrcators.
$AgNO_3$	CN^{-}	*The the result is $Ag(CN)_2^{-}$, the reagent is I^{-} titrante until the onset of turbid appearance of AgI*
KCN	$Cu^{+2}.Hg^{+2}.Ni^{+2}$	The reagent is AgI was titrante until the onset of the turbid AgI formation, the results $Cu(CN)_4^{-2}.Hg(CN)_2$ Using different indicators

2- Titration with aminopolycarboxylic acid

Complex Formation Titrations EDTA-ethylenediamine tetracetic acid:

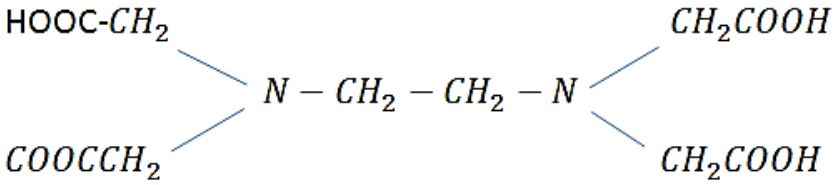
1- Most widely used chelator in Analytical Chemistry.

2- Forms chelates with metal ions (1:1).

3- Many are stable – serves as a basis for volumetric analysis.

4- polyprotic weak acid.

There are a number of tertiary amines that contain a carboxyl group that are stable complexes with a number of metal ions.
The EDTA reagent has the following structure;



EDTA the reagent most widely used as multible carboxylic amino acid and it is a weak acid that Decomposes in four steps, as follows:

$$H_4Y^- + H_2O \leftrightarrow H_3O^+ + H_3Y^-. K = 1.0 \times 10^{-2} = \frac{[H3O^+)(H_3Y^-]}{[H_4Y^-]}$$

$$H_3Y^- + H_2O \leftrightarrow H_3O^+ + H_2Y^{-2}. K = 2.6 \times 10^{-3} = \frac{[H_3O^+)(H_2Y^{-2}]}{[H_3Y^-]}$$

$$H_2Y^{-2} + H_2O \leftrightarrow H_3O^+ + HY^{-3}. K = 6.9 \times 10^{-7} = \frac{[H_3O^+)(HY^{-3}]}{[H_2Y^{-2}]}$$

$$HY^{-3} + H_2O \leftrightarrow H_3O^+ + Y^{-4}. K = 5.5 \times 10^{-11} = \frac{[H_3O^+][Y^{-4}]}{[HY^{-3}]}$$

Composition of EDTA Solutions a Function of pH

The EDTA dissolves into the aqueous solution of the acid, giving four types of ions, so the relative amount of each in the solution depends on pH.
The most appropriate methods to illustrate this relationship is plot the values for different types as indicating pH.

$$\alpha_0 = \frac{[H_4y]}{[C_T]}. \alpha_1 = \frac{[H_3y-]}{[C_T]}. \alpha_2 = \frac{[H_2y^{-2}]}{[C_T]}. \alpha_3 = \frac{[Hy^{-3}]}{[C_T]} \quad .$$

$$\alpha_4 = \frac{[y^{-4}]}{[C_T]}$$

The α values represent the total concentration portions of each type in solution.

$$\alpha_0 + \alpha_1 + \alpha_2 + \alpha_3 + \alpha_4 = 1$$

Considering that C_T = the sum of the concentrations of different species in a equilibrium function.

$C_T = [H_4y] + [H_3y-] + [H_2y^{-2}] + [Hy^{-3}] + [y^{-4}]$

Complexes of EDTA with Metal Ions

EDTA is dissented as titrant with important properties because it combines with metal ions at a 1:1 ratio regardless of its positive ion charge. These reactions can be represented in the acidic medium solution at the following equations at pH = 5.

$M^{+2} + H_2Y^{-2} \leftrightarrow My^{-2} + 2H^+$

$M^{+3} + H_2Y^{-2} \leftrightarrow My- + 2H^+$

$M^{+4} + H_2Y^{-2} \leftrightarrow My + 2H^+$

$M^{+n} + HY^{-3} \leftrightarrow My^{(n-4)} + H^+$

The EDTA is being soluble complexes of high stability and reacte significantly with all positive ions except nitrates. Fixed complexes that are essential in volumetric analysis.

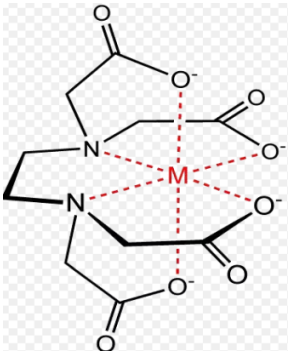


Figure 6-1 structure of M-EDTA

The stability of the M-EDTA complexes depends on the nature of the metal ion and pH of the solution; the hydrogen ions compete with the metal ions to reacte with the active sites ligand for the formation of a stable complex. In general, the stability of the complexes increases with the height of the pH solution, as the following reaction:

$M^{+n} + Y^{-4} \leftrightarrow (MY)^{(n-4)}$

$K_{ST} = \frac{[(MY)^{(n-4)}]}{[M^{+n}][Y^{-4}]}$ *stability constant of chleting complex..*

EDTA is mainly used as a titration solution in volumetric analysis.

Titration Curve

Ex1. To obtain the titration curve, the ion concentrations to be analyzed before and after the equivalent point must be found and a graph should be drawn between the P^M values (such as p^{Cd}) and the valium of titration solution.

Like a strong acid/strong base titration, there are three points on the titration curve of a metal with EDTA: before, at equivalent point, and after the equivalence point. We'll consider a titration where we have 50.0 mL of 0.040 M Ca^{2+} (buffered at pH=10) with 0.080 M EDTA.

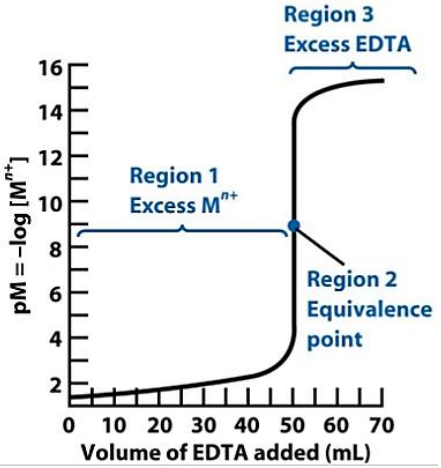


Figure 6-2 titration drawn between the P^M values and the volume of EDTA

Ex1. 5o ml of 0.1M of Mg solution was titrated with 0.1M solution of EDTA. Calculate pMg before and after equivalent the point. K_{sT} Mg − EDTA $= 5 \times 10^3$.

Preequivalent point = before equivalent point.

$pMg = -10g[Mg^{+2}]$

$pMg = -10g[0.1]=1.0$

at 10 ml addition of EDTA

$$[Mg^{+2}] = \frac{(50 \times 0.1) - (10 \times 0.1)}{60} = 0.067 ml/l$$

pMg=-10g(0.067)=1.2

at equivalent point

At its equivalent point, the concentration of Mg^{+2} is equivalent to the concentration of Y^{-4}.

$[Mg^{+2}] = [Y^{-4}] = [EDTA] = Y$

$$[MgY^{-2}] = \frac{0.1 \text{ x } 50}{100} = 0.05$$

Since the value of the stability constant is high 5×10^3, it is expected that the number of moles of Mg^{2+} and Y^{-4}) which are disassociated (x) after formation the complex is very few and the number of moles for Mg^{2+} can be calculated.

m mole Mg^{2+}= 50 x 0.1/100= 0.05

stability constant can be expressed;

$KMgY^{2-}= [Mg^{2+}]/ [Mg^{2+}][Y^{4-}]$

$5 \text{ x } 10^3 = 0.05/x,x, \quad x^2 = 0.05/5 \text{ x } 10^3 = 1x10^{-5}$

$pMg= -\log 1x10^{-5}= 5.0$

Post-equivalent point at 60 ml EDTA

The number moles of MgY^{2-} in the total volume 110 that comes from the disassociation of the complex is;

$50\times 0.1/110+x$

And the number of millimoles of Y^{4-} in the total volume of the solution 110, which is disassociate from the complex is;

$x- 10\times 0.1/110$

The value of x will be negleevt because very small.

m mole $MgY^{2-}= 50\times \frac{0.1}{110} = 0.045$

m mole $Y^{4-}= 10\times \frac{0.1}{110} = 0.009$

$$5 \times 10^3 = \frac{0.045}{[Mg2] \times 0.009}.$$

$[Mg^{2+}]= 1\times10^{-8}$

$pMg= -\log [1\times10^{-8}]= 8.0$

Derivative of EDTA Titration Curve

Effect pH on Titration Curve;

By choosing the EDTA metal equlibrium, the formation range of the complex depends on the medium pH. Therefore, titration involving positive ions such as $Ca^{2+}.Mg^{+2}$ will be weak complexes that need a basic medium. As for the titration that include positive ions, such as zn^{2+}, the complexes are more stable in moderate acidic solutions.

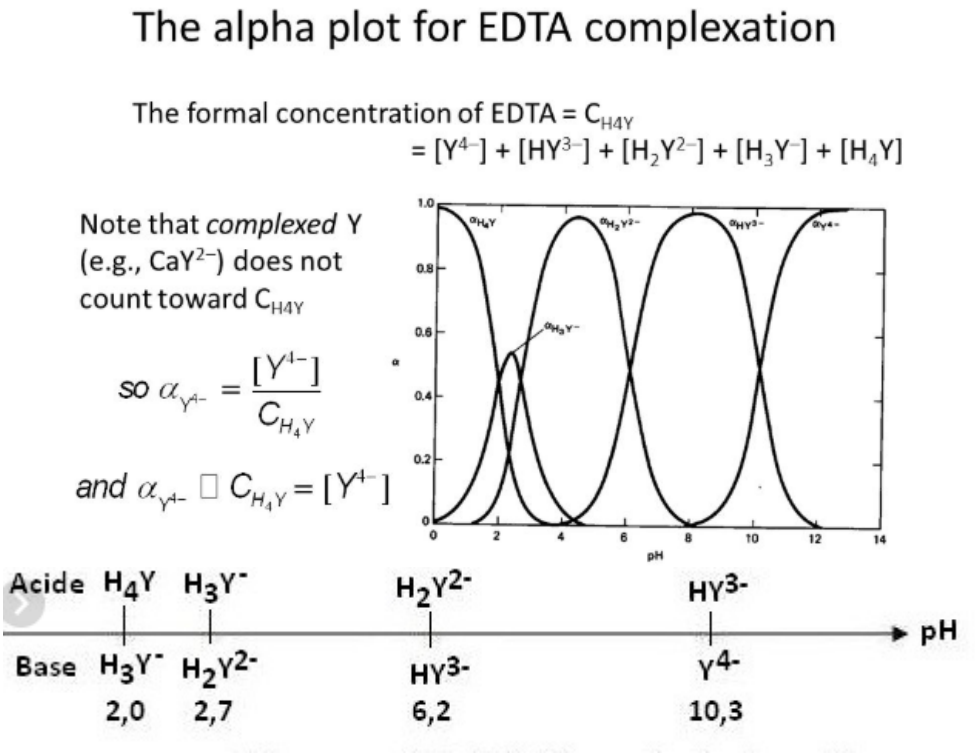


Figure 6-3 pH of EDTA species

The α_4 value can be used to derive EDTA titration curves for solutions containing buffer solutions.

$$\alpha_4 = \frac{[y^{-4}]}{[C_T]}$$

In this equation, C_T represents the total unreacted concentration of EDTA:

$$C_T = [Y^{-4}] + [HY^{-3}] + [H_2y^{-2}] + [H_3Y^{-}] + [H_4Y]$$

Where α_4 represents the total portion of the Y^- unreacted reagent of (y^- 4) α_4 depend on pH and four dissociation constants of EDTA, which are $K_4.K_3.K_2.K$

$$\alpha_4 = K_1.K_2.K_3.K_4/\,[H^+]^4 + K_1[H^+]^3 + K_1K_2[H^+]^2 + K_1K_2K_3[H^+] + K_1K_2K_3K_4$$

Arrange $\alpha_4$to

$$K'MY = \alpha_4\, KMY = \frac{MY^{(n-4)^+}}{[M^{n+}]C_T} \ldots (2\text{-}4)$$

Ex2: 5oml of (0.01M) Ca^{2+} titrated with 0.01M EDTA in a solution buffered to a pH=10 if $K_{CaY^{-2}} = 5.0 \times 10^{10}.\alpha_4 = 0.35.\, at\ pH = 10$

Sol. calculation of conditioned constant

$$KCaY = KCa \times \alpha_4 = 5.0 \times 10^{10} \times 0.3 = 1.75 \times 10^{10}$$

1) at start

$$P^{Ca} = -10gCa = -10g0.01 = 2$$

2) at per-equivalance point, at 25ml of EDTA

$$[Ca^{+2}] = \frac{50\times0.01-25\times0.01}{75} + c_T = 3.33 \times 10^{-3}$$

$$P^{Ca} = -10g3.33 \times 10^{-3} = 2.48$$

3) at equivalance point

$$[Ca^{+2}] = c_T$$

$$K' = \frac{CaY^{-2}}{[Ca^{+2}][c_T]} = \frac{CaY^{-2}}{[Ca^{+2}]^2}$$

$$[CaY^{-2}] = \frac{50\times0.01}{100} = \frac{0.50}{100} = 0.005$$

$$[Ca^{+2}] = \frac{0.005}{1.75 \times 10^{10}} = 5.35 \times 10^{-13}$$

$$[Ca^{+2}] = 5.35 \times 10^{-7}$$

PCa =-10gCa =6.27

$$K = \frac{CaY^{-2}}{[Ca^{+2}][c_T]}$$

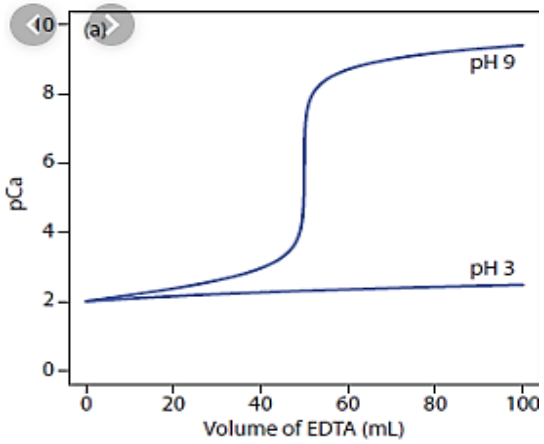
4) post equivalence point (60ml of EDTA)

$$[CaY^{-2}] = \frac{50 \times 0.01}{116} = 4.54 \times 10^{-3} - [Ca^{+2}] \cong 4.55 \times 10^{-3}$$

$$c_T = [Y^{-2}] = \frac{10 \times 0.01}{110} = 9.1 \times 10^{-4} + [Ca^{+2}] \cong 9.2 \times 10^{-4}$$

$$1.75 \times 10^{10} = \frac{4.54 \times 10^{-3}}{[Ca^{+2}]9.1 \times 10^{-4}} = [Ca^{+2}] = 2.85 \times 10^{-10}$$

pCa=9.54



Ex3. Calculate PCa when 0, 10, 20 and 130ml of 0.3N of EDTA was added to 60ml of 0.6N $[Ca^{+2}]$ at pH=10, $\alpha_4 = 0.35$ Kf=1.5×10^{10}

Sol.: 1) at start PCa =-10g$[Ca^{+2}]$=-10g 0.6 =0.22

2) at 100 ml of EDTA

Meq of Ca =0.6×60 =36

Meq of EDTA = 100×0.3 =30

$[Ca^{+2}]$=36-30=6 → $[Ca^{+2}]$=$\frac{6}{160} = 0.04$

pCa =-10g =0.04=1.4

3) at 120ml of EDTA

Meq of $[Ca^{+2}]$=0.6×60=36

Meq of EDTA = 120×0.3 =36

;. This is equivalance point

$$K' = \frac{[CaY^{-2}]}{[Ca^{+2}][c_T]} = [Ca^{+2}] = [c_T] = K' = \frac{[CaY^{-2}]}{[[Ca^{+2}]^2}$$

$$[CaY^{-2}] = \frac{36}{180} = 0.2$$

K=$K_f \alpha_4 = 1.5 \times 10^{10} \times 0.32 = 5.25 \times 10^{+9}$

$$[Ca^{+2}] = \sqrt{\frac{0.2}{5.25 \times 10^{9}}}$$

$= 6.1 \times 10^{-6} = Pca = 5.2$

After adding 130 ml from EDTA

Meq of Ca =36

Meq of EDTA =130 × 0.3

$EDTA_{res} = 39 - 36 = 3 \rightarrow C_t = \frac{3}{190} = 0.012$

$[CaY] = \frac{36}{140} = 0.189$

$$K = \frac{[Ca]Y}{[Ca]Ct} = 5.25 \times 10^{-9}$$

Determination of End Point in EDTA Titration

EDTA can form four or six coordination bonds with a metal ion. Total hardness is due to the presence of bicarbonates, chlorides and sulphates of calcium and magnesium ions. The total hardness of water is estimated by titrating the water sample against EDTA using Eriochrome Black-T (EBT) indicator.

In the case of Mg^{2+} titrate with EDTA solution, we add a little EBT indicator to the solution before starting the titration, producing a complex burgundy color ion depending on the following reaction:

Mg^{2+}- $HIn^{2-} \leftrightarrow H^{+}$-$MgIn^{-}$

Therefore, the solution takes a red color at titrante this solution with the EDTA (HY^{3-}) which will then react with all the free Mg^{2+} as the following chemical equation;

Mg^{2+}- $HY^{3-} \leftrightarrow MgY^{2--}$-$H^{+}$

That's because MgY^{2-} is more stable than $MgIn^{-}$

$MgIn^{-} + HY^{3-} \leftrightarrow MgY^{2--} + HIn^{2-}$

Blue color Red color

Titration Method of EDTA

Direct titration: analyte is titrated with standard EDTA with solution buffered at a pH where $K_f^{'}$ is large.

Back titration: known excess of EDTA is added to analyte. Excess EDTA is titrated with 2nd metal ion.

25.0 mL of an unknown Ni^{2+} solution was treated with 25.00 mL of 0.05283 M Na_2EDTA. The pH of the solution was buffered to 5.5 and

then back-titrated with 17.61 mL of 0.02299 M Zn^{2+}. What was the unknown Ni^{2+} M?

$$Zn^{2+} + Y^{4-} \leftrightarrow ZnY^{2-}$$

$$\text{mol EDTA} = (25.00\,\text{mL})(0.05283\,\text{M}) = 1.32\,\text{mmol EDTA}$$

$$\text{mol } Zn^{2+} = (17.61\,\text{mL})(0.02299\,\text{M}) = 0.4049\,\text{mmol } Zn^{2+}$$

$$Ni^{2+} + Y^{4-} \leftrightarrow NiY^{2-}$$

$$\text{mol } Ni^{2+} = 1.321\,\text{mmol EDTA} - 0.4049\,\text{mmol } Zn^{2+} = 0.916\,\text{mmol}$$

$$\text{M } Ni^{2+} = (0.916\,\text{mmol})/(25.00\,\text{mL}) = 0.0366\,\text{M}$$

Questions and Answer

1. How many times does EDTA bind in a coordination complex?

Sol. EDTA is a hexadentate ligand, which means that it binds six times. It binds twice at the nitrogens and four at the oxygens.

2. List in order of most to least thermodynamically stable as a ligand: ONO, en (ethylenediamine), EDTA.

Sol. EDTA (which binds six times), en (which binds two times), ONO (which binds one time)

3. What are the most common forms of EDTA?

Sol. EDTA is used most commonly as salts and in a dry form.

4. Why is EDTA so overused? Why is this problem?

Sol. EDTA is a great chelating agent, allowing multiple bindings in a coordination complex. This gives it the ability to displace other undesirable ligands due to entropy and thermodynamics, and is thus used in laboratories, factories, and in medicine. The problem with its overuse is that it degrades into a toxin. By having excess of this, more toxins is created and left in the environment.

5. What does Professor Larsen commonly refer to EDTA as?

Sol. "The Kraken" because it is the ultimate ligand (it binds six times, which is a very large amount for ligand binding).

CHAPTER SEVEN
Solubility of Precipitates

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Solubility of Precipitates

Introduction

Most of the steps of qualitative analysis depend on the formation of distinctive deposits or on preventing the formation of deposits by adding substances that block the interaction of ions involved in their formation or dissolving the formed deposits. The formation or dissolution of the deposits is obeying to chemical balance parameters in terms of dynamics. In generally, it is compounds which are unable to dissolve in liquid solutions.

Solubility Rules

The following simplified rules are useful in describe on the solubility of the following positive ions compounds in water due to their importance in qualitative analysis and include ions: silver, lead, mercury, zinc, zinc, nickel, zinc, manganese, ferrous, ferric, chromic, aluminum, barium, strontium Calcium, Magnesium, Ammonium, Potassium, Sodium (25 Ions). Solubility is defined as the amount of a given substance that can be dissolved in a certain amount of solvent.

The solubility of compounds is based on a number of rules. At this stage it is important to be aware and exposed to these:

1- All compounds containing Na^+, NH_4^+, K^+ or NO^-_3 will dissolve in water (soluble).

2- Compounds containing Cl^-, Br^- and I^- ions are SOLUBLE except if they have (Ag^+, Pb^{2+} or Hg^{2+} ions).

3- Compounds containing SO_4^{-2} are SOLUBLE except (Ba^{+2}, Pb^{+2} and Ca^{2+}).

4- Compounds containing CO_3^{-2} and PO_4^{-3} are INSOLUBLE except with Na^+, NH_4^+ or K^+.

5- Compounds containing OH^- are insoluble unless with Na^+, NH_4^+ or K^+.

Solubility Product Principle

As a result of some experiments, it was found that the molar concentration of ions of each electrolyte salt would result in water

solubility (its solubility is less than 50 mg/ l It shall be a fixed amount with a stable temperature, and this symbol shall be denoted by Ks, and it shall be called a solubility product.

To clarify the importance of this, i.e. this constant, we take a saturated solution of scarce soluble barium sulfate and add a small amount of barium chloride solution to it, some of the barium sulfate is deposited and at the same time it is observed that the solution remains saturated.

practically, it was found that the decrease in the amount of sulfate ions dissolved in the solution is proportional to the increase in the concentration of barium ions, and this can be formulated mathematically;

$[Ba^{+2}] \times [SO_4^{-2}] = constant$

This type of relationship is valid for all scarce saturated solutions which are soluble in water such as copper sulfide and silver chloride.

$[Ag^{+}] \times [Cl^{-}] = K_s$

$[Cu^{+2}] \times [S^{-2}] = K_s$

Its constant value Ks varies with salt. In the case of electrolyte salts of more than two ions, such as magnesium hydroxide Mg $(OH)_2$ which is containing two ions of hydroxyl and one magnesium ion, The decrease in the concentration of magnesium ions occurs when adding hydroxyl ions at a double rate, that is:

$[Mg^{+}] \times [OH^{-}]^2 = K_s$

As a general formula, the value of the salt product is A_mB_n

$[A^{+n}]^m \times [B^{-m}]^n = K_s$

The rule of solubility product is formulated as follows:

The value of the solubility product for the scarce saturated solution of the electrolytic compound is soluble in water equal to value of multiple for molar concentrations of ions with each limit raised to a power equal to the number of ions at constant temperature.

For the AB saturated dielectric solution, this ionizes to:

$AB \leftrightarrow A^{+} + B^{-}$ ... **(7-1)**

Solution solid

$[A^{+}][B^{-}] = K_{sp}$

In the case of the electrolyteA_pB_q is ionize to:

$A_pB_q \leftrightarrow PA^p + PB^q$... **(7-2)**
solid solution
$Ksp = [A^{q+}]^p[B^{p-}]^q$

The Practical Application of the Solubility Product

When the electrolyte AB ionize to A and B as in equation then*:*
$Ksp = [A^{q+}]^p[B^{p-}]^q$
The solubility product can be used to organize ideal conditions for the formation of the solubility of the precipitate. This includes Such as temperature, hydrogen ion, concentration strength, reagent concentration, salt concentration and nature of the solvente.

Ex1: set up expressions for the solubility product constants of the following: AgCl
$AgCl \leftrightarrow Ag^+ + Cl^-$
$Ksp = [Ag^+][Cl^-]$
X × X =X^2 where x is the concentration of the salt in moles
Examples include calculating the Ksp value of solubility;

Ex2 it was found that solubility for $BaSO_4$ is 1.14×10^{-5}M calculate the value of Ksp?
Sol.:
$BaSO_4 \leftrightarrow Ba^{+2} + SO_4^{-2}$
$Ksp = [Ba^{2+}][SO_4^{-2}]$
$[Ba^{2+}] = 1.14 \times 10^{-5}.[SO^{-2}] = 1.14 \times 10^{-5}$
$Ksp = [1.14 \times 10^{-5}][1.14 \times 10^{-5}] = 1.30 \times 10^{-10}(M)^2$

Ex3. Calculate the Ksp of silver carbonate Ag_2CO_3 whose molar solubility $1.1 \times 10^{-4} mole|liter$ at room temperature?
Sol.:
$Ag_2CO_3 \leftrightarrow 2Ag^+ + CO_3^{-2}$
$Ksp = [Ag^+]^2[CO_3^{-2}]$
$Ag_2CO_3 \leftrightarrow 2Ag^+ + CO_3^{-2}$
$[Ag^+]^2 = 2(1.1 \times 10^{-4}M) = 2.2 \times 10^{-4} = [Ag^+]$
$[CO_3^{-2}] = 1.1 \times 10^{-4}M$
$Ksp = [Ag^+]^2[CO_3^{-2}]$

$Ksp = [2.2 \times 10^{-4}]^2[1.1 \times 10^{-4}]$
$Ksp = 5.3 \times 10^{-14}$

Ex4. The solubility of silver phosphate is 6.5×10^{-3}g|L calculating its solubility product? (Mwt ofAg_3PO_4 = 418.7)
Sol.:
$\frac{6.5\times10^{-3}\text{g|L}}{418.7\ \text{g|mole}} = 1.6 \times 10^{-5}$mole|L, the molarity of the saturate of solution
$Ag_3PO_4 \leftrightarrow 3Ag^+ + {PO_4}^{-3}$
1.6×10^{-5} (3) 1.6×10^{-5} 1.6×10^{-5}

Thus $[Ag^+]$=*(3)* $1.6 \times 10^{-5} = 4.8 \times 10^{-5}\ M$
$\left[{PO_4}^{-3}\right] = 1.6 \times 10^{-5} M$
$Ksp = [Ag^+]^3\left[{PO_4}^{-3}\right] = [4.8 \times 10^{-5}]^3[1.6 \times 10^{-5}]$
$Ksp = 1.8 \times 10^{-18} the\ solubility\ product\ of\ Ag_3PO_4$

Ex5. Calculate the solubility in g/L for $Pb(OH)_2$ knowing its Ksp=2.5×10^{-16}?
Sol.:
$Pb(OH)_2(s) \leftrightarrow Pb^{+2} + 2OH^-$
$Ksp = [Pb^{+2}]\ [OH^-]^2 = 2.5 \times 10^{-16}$
$[Pb^{+2}] = s$
Depending on the equation
$[OH^-]^2 = 2s$
$[S][2S]^2 = 2.5 \times 10^{-16}$
$4S^3 = 2.5 \times 10^{-16}$
$S = 3.97 \times 10^{-16} M\ Pb(OH)_2$
S × Mwt g/mole
$3.97 M|L \times 10^{-16} \times 241.2\ g|mole = 9.6 \times 10^{-4} g|L$

Ex6. How many milligrams of $Ba(IO_3)_2$can be dissolved in water at 25C? Ksp. 1.27×10^{-9}, Mwt=487 g/mole.
Sol.: $Ba(IO_3)_2 \leftrightarrow Ba^{+2} + 2IO_3^-$
$[Ba^{+2}] = S, [IO_3^-] = 2S$

$Ksp = [S][2S]^2 = 4S^3$

$1.27 \times 10^{-9} = 4S^3$

$S = 6.8 \times 10^{-4} M$

$$S \times M.wt = \frac{6.8 \times 10^{-4} \times 487 \times 150}{1000} = 5 \times 10^{-2} g/150ml$$

Ex7. What is the minimum silver ion concentration required to the preparation of $AgBrO_3$ from 0.01 M of $KBrO_3$

Sol.:

$Ksp = AgBrO_3 = 6 \times 10^{-5} AgNO_3$

$AgNO_3 \leftrightarrow Ag^+ + NO_3^-$

$KBrO_3 \leftrightarrow K + BrO_3^-$

$BrO_3^- + Ag^+ \leftrightarrow AgBrO_3$

$Ksp = [BrO_3][Ag]$

$6 \times 10^{-5} = [0.01][Ag]$

$$[Ag^+] = \frac{6 \times 10^{-5}}{0.01} = 6 \times 10^{-3} \text{mol/L}$$

Ex8. (A) Calculate the solubility in gm|100ml of lead phosphate ($Pb_3((PO_4)_2$, If its solubility product is 1.5×10^{-32}?

(b) How many grams of lead and phosphate ions are present in a liter of the saturated lead phosphate?

M.wt $Pb_3(PO_4)_2$ = 811.6

Sol. (a) let X = the molar concentration of lead phosphate solution.

$Pb_3(PO_4)_2 \leftrightarrow 3Pb^{+2} + 2PO_4^{-3}$

(X) (3X) (2X)

$[Pb^{+2}]$= 3X and $[PO_4^{-3}]$= 2X

$Ksp = [Pb^{+2}]^3[PO_4^{-3}]^2 = [3X]^3[2X]^2 = 1.5 \times 10^{-32}$

$$X = \sqrt[5]{\frac{1.5 \times 10^{-32}}{108}} = 1.7 \times 10^{-7} \text{M}$$

Number of grams per liter = (Molarity) (Mwt)

$No.of\ g/L = (1.7 \times 10^{-7} mole|l)(811.6\ g|mole) = 1.4 \times 10^{-4} g|L$

$$\frac{1.4 \times 10^{-4}}{10} = 1.4 \times 10^{-5} g|100\ ml$$

Solubility of Precipitation in the Presence of Common Ion

EX9: calculate the solubility of $BaSO_4$ in 0.1M solution of Na_2SO_4.

Sol.: if solubility of $BaSO_4$ is x ml, so each mole of the solid dissolved gives x mole/L of $Ba^{+2}$and x mole/L of SO_4.

$[Ba^{+2}] = X. [SO_4] = X + 0.1$

$[Ba^{+2}][SO_4] = 1 \times 10^{-10}$

$X(X + 0.1) = 1 \times 10^{-10}$

As Conc of SO_4 in $BaSO_4$ solution. in water is 1×10^{-5}

So SO_4 resullted from dissolving $BaSO_4$ is less than thus value

So $(X+0.1) \cong 0.1$

$X=\frac{1\times10^{-10}}{0.1} =$

$X= 1 \times 10^{-9}M$

So solubility of $BaSO_4$ in 0.1 M $Na_2SO_4 = 1 \times 10^{-9}$m|L

And in its solubility in water = 1×10^{-5}m|L

Ex10. Calculate the solubility of CaF_2 in:

$CaF_2 \leftrightarrow Ca^{+2} + 2F^-$

(a)H_2O

(b)0.2 M solution $Ca(NO_3)_2$

(c) 0.2 M solution NaF

Knowing that Ksp $(CaF_2) = 4 \times 10^{-11}$

Sol.:

(a) $4\ x^3 = 4\ x\ 10^{-11}$

$X^3 = 1\ x10^{-11} \quad = \sqrt[3]{\frac{Ksp}{4}} = \sqrt[3]{\frac{4\times10^{-11}}{4}} = 2.2\times10^{-4}$

$X = 2.2\ x10^{-4} = 0.00022$ m/L

(b)$[F^-] = 2X$

$[Ca^{+2}] = 0.2 + x$

$[F^-]^2[Ca^{+2}] = Ksp$

$[2x]^2[0.2 + x] = 4 \times 10^{-11}$

$(2X)^2(0.2) = 4 \times 10^{-11}$

$0.8X^2 = 4 \times 10^{-11}$

$X^2 = 5 \times\ 10^{-11}$

$X = 7.1 \times 10^{-6} m|L$

(C) Final solution is 1×10^{-9}

Ex11. Saturated solution of $Zn(OH)_2$ with pH.

1) calculate its solubility

2)Ksp

3) Solubility in solution containing barium hydroxide $Ba(OH)_2$ with pH=13

4) Discuss the difference in solubility.

Sol.:

1) pOH =14 – pH = 14 – 11 = 3 pOH =$-10g\ [OH^-]$

$[OH^-] = 10^{-3}\ M|L$

$Zn(OH)_2 \leftrightarrow Zn^+ + 2OH^-$

(X) (2X)

$2X = 1 \times 10^{-3}\ ;.x = 0.5 \times 10^{-3} M/L$

2) Ksp = $[x][2x]^2 = 1 \times 10^{-6}(4 \times x^2)$

$Ksp = 0.5 \times 10^{-9}$

3) POH =14 – 13= 1

$;.[OH^-] = 0.1M$

$Zn(OH)_2 \leftrightarrow Zn^+ + 2OH^-$

2X

$Ba(OH)_2 \leftrightarrow Ba^+ + 2OH^-$

0.1

$Ksp = [Zn^+][OH^-]^2$

$0.5 \times 10^{-9} = (X)(2X + 0.1)^2$

$0.5 \times 10^{-9} = (X)(0.1)^2$

$x = 0.5 \times 10^{-7} M/L$

Ex12. what is the mass of $Mg(OH)_2$/ number of grams dissolved in 1 liter containing OH^- ions with concentration equal to 0.01 M with Ksp of $Mg(OH)_2$=1.2 $X10^{-7}$

Mwt = 58 g|mole

Sol.:

$Mg(OH)_2 \leftrightarrow Mg^{+2} + 2OH^-$

X 2X

OH

0.1

Ksp = $[Mg^{+2}][OH^-]^2$

$1.2\ X10^{-7} = (X)(0.01 + 2X)^2$

$1.2\ X10^{-11} = 1 \times 10^{-4}$

;. X =$1.2\ X10^{-7}$M/L

$No = \frac{wt}{Mwt}$ $wt = No.\ of\ mole \times Mwt$

$1.2 \times 10^{-7} \times 58 = 69.6 \times\ 10^{-7} gm/L$

Ex31. calculate the solubility of $Ba(IO_3)_2$ in the solution that results when 200ml of 0.01 M$Ba(NO_3)_2$ are mixed with 100 ml of 0.1 M $NaIO_3$.

Sol.: mmole Ba = 200ml X 0.01 mmole/ml =2.00

mmole IO_3 =100 X 0.1 mmole/ml =10.00

if formation of $Ba(IO_3)_2$ is complete

mmole excess IO_3= 10.0 – 2(2.0) =6.00

thus:

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

Ksp= $[Ba^{2+}][IO_3^-]^2$

$[IO_3^-]= \frac{6.00mmole}{300ml} = 0.02\ M$

As in the previous example

Molar solubility of $Ba(IO_3)_2 = [Ba^{+2}]$,

however

$[IO_3^-]= 0.020 + 2[Ba^{+2}]$

When $2[Ba^{+2}]$ represents the iodate $contributed$ by the sparingly soluble $Ba(IO_3)_2$

$[IO_3^-] \approx 0.0200$

The solubility of $Ba(IO_3)_2 = [Ba^{+2}] = \frac{Ksp}{[IO_3]}$

$= \frac{1.57 \times 10^{-9}}{(10.0200)^2} = 3.93 \times 10^{-6} mole|L$

Solubility Applications of Precipitation Process:

1- Precipitation

The solubility product is useful for clarifying the completeness and predictability of precipitation reactions. When the value of the product of multiplying the foundations for the concentrations of any two types of ions in the solution exceeds the value of the corresponding solubility product The positive ion and the negative ion are participate as a result of their union until it becomes the product of the concentration of these two types of ions remaining in the solution equal to the value of solubility.

General rule: precipitation occurs when the ionic product exceeds (it is a product of concentration and not a equilibrium constant) Soluble product. The precipitation continues until the ionic product is equal to the soluble product, that is:

[X][X] > Ksp

This precipitation can be predicted by some experiments and calculations.

Ex14. if 20 ml of 0.01 M $AgNO_3$ was added to 80ml of 0.05 M K_2CrO_4. Show the possibility of formation of a precipitate Ksp. $AgCrO_4$ = 1.7 x 10^{-12}

Sol.: at 0.01 M of $AgNO_3$

Ag^+= 0.01

If 20 ml of this solution is diluted to 100 ml so conc.of

$Ag^+ = 0.01 \times \frac{20}{100} = 0.002M$

In 0.05M of $AgCrO_4$

$[CrO_4^{-2}]$= 0.05x80/100=0.04M

$[CrO_4^{-2}] =][Ag]^2 = (4 \times 10^{-2}) \times (2 \times 10^{-3})^2 =$ ionic product

$= 1.6 \times 10^{-7}$

Solublity product < ionic product, It will get precipitation.

2- Solution of precipitation

Example// Dissolve the AgCl precipitate by adding ammonia where before the equilibrium;

$$AgCl \leftrightarrow Ag^+ + Cl^- \; Ksp = 1 \times 10^{-10} \ldots\ldots (1)$$

Where the addition of ammonia is a constant complex reacte with Ag

$$Ag^+ + 2NH_3 \leftrightarrow Ag(NH_3)_2$$

To avoid the defect, an equivalent amount of AgCl dissolve with present an increase of NH_4OH.

3- Prevention of precipitation

To prevent the precipitation of the soluble salt, it is necessary to add a little substance that helps to reduce the concentration of one of the ions, so that the scarce soluble salt cannot be reache to value of solubility product.

Ex15. How many grams of ammonium nitrate must be added to 50 ml of 0.5 M ammonium hydroxide to prevent the precipitance of magnesium hydroxide when the solution is added to 50ml of 0.1 M magnesium chloride solution?

Sol.: When 50 ml of 0.5 M $(NH_4)OH. containing$ of ammonium $the\ necessary\ weight$ nitrate, are added to the 50ml of 0.1 M magnesium chloride the final volume of the resulting solution will be 100 ml

$$\frac{of\ (50ml)(0.5M)}{100ml} = 0.25M. the\ concentration\ of\ (NH_4)OH$$

= 0.25M =C_b

$$\frac{of\ (50ml)(0.5M)}{100ml} = 0.05M, the\ concentration\ MgCl_2$$

= 0.05M = $[Mg^+]$

The solubility product expression for $Mg(OH)_2\ is\ [Mg^{+2}][OH^-]^2 = Ksp = 3.2 \times 10^{-11}$

Solubility for $[Mg^{+2}]$ in the above expression, (0.05) $[OH^-]^2 = 3.2 \times 10^{-11}$

$$[OH^-] = 2.6 \times 10^{-5}M$$

When ammonium nitrate is added to $(NH_4)OH$ a buffer solution is obtained, the OH concentration of which is given by the equation

$$[OH^-] = K_b \frac{C_b}{C_s}$$

Substituting for [OH] . $K_b$and $C_b$the salt concentration Cs can then be calculated;

$2.6 \times 10^{-5} = 1.8 \times 10^{-5} 0.25/Cs.$

$Cs = 0.17M.$

$$the\ conc\ NH_4 = (0.17mole|L)\frac{(80g|mole)}{10}$$

$= 1.36.(NH_4)OH$

any weight of NH_4NO_3> 1.36 g prevent the precipitation of $Mg(OH)^2$

$for\ 50ml\ solution\ of\ 0.1\ M\ \ MgCl_2$

Factors that affect solubility:

1- Temperature - Solubility generally increases with temperature.

2- Common ion effect - Common ions reduce solubility

3- pH of solution - pH affects the solubility of ionic compounds.

4- Formation of complex ion. The formation of complex ion increases solubility

5- Nature of precipitation- It is known that some substances are more soluble in water than others, and the reason for this difference is due to the variation in the crystalline energy of each of them.

5- Volume of precipitation particles- Solubility increases the solubility product as the particle radius decrease.

6- Effect of the solvent- The solubility of the organic compounds in the solvents is affected by two factors (a) the polarity of the solvent (b) the dielectric constant,

Effect of Hydronium Ion on Solubility of Salts

Slightly soluble salts of strong acids are in general in soluble strong acid, whereas those of most weak acids are readily soluble difficulty soluble. Difficultly soluble sulfides vary widely in their solubilities in nonoxidizing acids such as hydrochloric acid. some sulfides dissolve easily in dilute acid. Other dissolve only in concentrated acid, yet, some are insoluble even in concentrated HCl.

if a salt of a weak acid H_2A reperesented by the formuln MA and dissolves in a strong acid,it will do so according to the reaction.

$MA + H_3O^+ \leftrightarrow M^{+2} + H_2A + 2H_2O$

The solubility product expression of salt is $[Mg^{+2}][A^{-2}]$=Ksp…….(5-1)

For a weak dibasic acid the over all dissociation constant expression

$$\frac{[H_3O^+]^2[A^{-2}]}{[H_2A]} = K_a \dots\dots\dots (5-2)$$

Combining the two expression (1+2) in one give (3)

$$[Mg^{+2}][A^{-2}] = \frac{Ksp}{Ka} \dots\dots\dots (5-3)$$

$$\frac{[H_3O^+]^2[A^{-2}]}{[H_2A]}$$

Simplifying equation (3) leads to

$$\frac{[\mathrm{M}^{+2}][H_2A]}{[H_3O^+]^2} = \frac{Ksp}{Ka} \dots\dots. (5-4)$$

For slightly soluble salt such as those of the sulfide

$$\frac{[\mathrm{M}^{+2}][H_2A]}{[H_3O^+]^2} = \frac{Ksp}{6.8 \times 10^{-23}} \dots. (5-5)$$

For slightly soluble carbonate salts

$$\frac{[\mathrm{M}^{+2}][H_2CO_3]}{[H_3O^+]^2} = \frac{Ksp}{2.4 \times 10^{-17}} \dots\dots. (5-6)$$

For slightly soluble oxalate salts

$$\frac{[\mathrm{M}^{+2}][H_2C_2O_4]}{[H_3O^+]^3} = \frac{Ksp}{3.3 \times 10^{-6}} \dots\dots. (5-7)$$

Ex16. Calculate the molar solubility of CaC_2O_4 at solution with $[H_3O^+$ concentration equal to $1.0 \times 10^{-4}M$. Knowing that the Ksp of this matter is 1.9 X10^{-9}.

Sol.:

$CaC_2O_{4(s)} \leftrightarrow Ca^{+2} + C_2O_4^{-2}$

$C_2O_4^{-2} + H_3O^+ \leftrightarrow HC_2O_4^{-2} + H_2O$

$HC_2O_4^{-2} + H_3O^+ \leftrightarrow H_2C_2O_4^{-2} + H_2O$

S =[Ca^{+2}]

Solubility [Ca] mole/L = $[H_2C_2O_4] + [HC_2O_4^-] + [C_2O_4^{-2}]$

Ksp = [Ca^{+2}] $[C_2O_4^{-2}] = 1.9$ X10^{-9}.

Ionization constant(I) of $H_2C_2O_4^{-2}$ in $K_1 = 6.5 \times 10^{-2}. K_2 = 6.1 \times 10^{-5}$

So

$$K_2 = \frac{[H_3O^+][C_2O_4^{-2}]}{[H_2C_2O_4]} = 6.1 \times 10^{-5}$$

$$K_1 = \frac{[H_3O^+][HC_2O_4^-]}{[H_2C_2O_4]} = 6.5 \times 10^{-2}$$

$$I = [C_2O_4^{-2}] + [HC_2O_4^-] + [H_2C_2O_4].[H_3O^+] = 1.0 \times 10^{-4}$$

$$\frac{[C_2O_4^{-2}][1.0 \times 10^{-4}]}{[HC_2O_4^-]} = 6.1 \times 10^{-5}.[H_3O^+] = 1.0 \times 10^{-4}$$

$$[HC_2O_4^-] = \frac{1.0 \times 10^{-4}}{6.1 \times 10^{-5}} \times [C_2O_4^{-2}] = 1.64 \times [C_2O_4^{-2}]$$

$$\frac{[1.0 \times 10^{-4}][1.64 \times [C_2O_4^{-2}]]}{[H_2C_2O_4]} = 6.5 \times 10^{-2}$$

$$[H_2C_2O_4] = \frac{[1.0 \times 10^{-4}][1.64 \times [C_2O_4^{-2}]]}{6.5 \times 10^{-2}} = 0.0025 \times [C_2O_4^{-2}]$$

$$[Ca^{+2}] = [C_2O_4^{-2}] + 1.64 \times [C_2O_4^{-2}] + 0.0025 \times [C_2O_4^{-2}]$$
$$= 2.64 \times [C_2O_4^{-2}]$$

$$[C_2O_4^{-2}] = \frac{[Ca^{+2}]}{2.64}$$

As for when this value is substute in the equation

$$1.9 \times 10^{-9} = [Ca^{+2}] \times \frac{[Ca^{+2}]}{2.64}$$

$$[Ca^{+2}]^2 = 5.02 \times 10^{-9}, [Ca^{+2}] = 7.1 \times 10^{-5} mole\ |liter$$

Ex17. What must be the concentration of HCl that dissolve 0.1M of NiS

(Ksp=1.4 X10^{-24}) in a liter solution? will concentrated HCl bcable to dissolve 0.1mole of Cds (Ksp=3.6X10^{-29}) ؟

Sol.:when 0.1mole of NiS dissolves in a liter of solution, 0.1mole of H_2S and 0.1 mole of Ni^{+2} ions will be formed.

$NiS + 2H_2O \leftrightarrow Ni^{+2} + H_2S + 2H_2O$

upon substitution of these values into equation (5) the H_3O+ conc. can be the calculated

$$\frac{[Ni^{+2}][H_2S]}{[H_3O^+]^2} = \frac{1.4\ X10^{-24}}{6.8 \times 10^{-23}} = \frac{(0.1)(0.1)}{[H_3O^+]^2}$$

$$[H_3O^+]^2 = \frac{6.8 \times 10^{-25}}{1.4 \times 10^{-24}} = 4.85 \times 10^{-1}$$

0.7M is the minimum value of the H_3O^+conc. that can dissolve 0.1M Nis the hydronium ion concentration into equation (5)

$$CdS + 2H_3O^+ \leftrightarrow Cd^{+2} + H_2S + 2H_2O$$

0.1mol 0.1 mol 0.1mol

$$\frac{[Cd^{+2}][H_2S]}{[H_3O^+]^2} = \frac{6.3 \times 10^{-29}}{6.8 \times 10^{-23}} = \frac{(0.1)(0.1)}{[H_3O^+]^2}$$

$$[H_3O^+]^2 = \frac{6.8 \times 10^{-25}}{6.3 \times 10^{-29}} = 10793.7.\ [H_3O^+] = 103.9M$$

concentrated HCI is 12M, therefore CdS is very insoluble in HCl since it is impossible to obtain a concentration of 103,9 molar HCl.

Solubility of Metal Hydroxide in Water

Ex18. A solution is 0.2M in each Al^{+3} and Ni^{+2}.at what pH value reach metal hydroxide begins to precipitate

Sol.: Although the trivalent cations of (Al^{3+}.Cr^{3+}, and $Fe_2O_3.H_2O$). the hydroxide formula is used for the purpose of simplicity

$$\text{Ksp of } Al(OH)_3 = [Al^{+3}][OH^-]^3 = 2.2 \times 10^{-32}$$

$$\text{Ksp of } Ni(OH)_2 = [Ni^{+2}][OH^-]^2 = 2.0 \times 10^{-14}$$

$$[Al^{+3}][OH^-]^3 = 2.2 \times 10^{-32}$$

$$[Ni^{+2}][OH^-]^2 = 2.0 \times 10^{-14}$$

$$(0.2)\ [OH^-]^3 = 2.2 \times 10^{-32}$$

$$(0.2)\ [OH^-]^2 = 2.0 \times 10^{-14}$$

$$[OH^-]^3 = 11 \times 10^{-32} = [OH^-]^2 = 1 \times 10^{-13}$$

$$-10g[OH^-]^3 = 32 - 1.0414$$

3pOH =30.96

pOH=10.32, pH= 3.68

$$-10g\ [OH^-]^2 = 13$$

2pOH=13

pOH=6.5, pH=7.5

Separation of Ions by Control of the Concentration of the Precipitation Reagent

When an ion reacts with another ion to form a precipitate of different solubility, the substance that is less soluble will be deposited using a lower concentration of the precipitation reagent, but if there is a clear difference in the solubility capabilities, then the first ion can be removed quantitatively from the solution without precipibate the second ion.

Separation of Sulfides

For the purpose of separating sulfides, the solutions are usually saturated by constantly introducing bubbles of H_2S through the solutions, so that the concentration of the reagent in the solution is constant at during the precipitation process. Since H_2S is a very weak acid, the molar concentration will be close to its solubility in water Therefore, the concentration of H_2S in the solution can be considered during any precipitation process is 0.1M at practic process.

$H_2S \cong 0.1$ mole|liter

Subsitude these in the decomposition equation H_2S

$$H_2S + H_2O \leftrightarrow 2H_3O^+ + S^{-2}$$

$$K_1K_2 = \frac{[H_2O^+]^2[S^{-2}]}{[H_2S]} = 6.8 \times 10^{-23}$$

$$= \frac{[H_2O^+]^3[S^{-2}]}{0.10} = 6.8 \times 10^{-23}$$

$$[S^{-2}] = \frac{6.8 \times 10^{-24}}{[H_2O^+]^2}$$

Ex19. Find the condition in which Pb^{+2}/ can be quantitatively separated by precipitately with H_2S for 0.1M solution. for each cation, knowing that

$$PbS_{(s)} \leftrightarrow Pb^{+2} + S^{-2}. [Pb^{+2}][S^{-2}] = 7 \times 10^{-28}$$

$$Ti_2S_{(s)} \leftrightarrow 2Ti^{+} + S^{-2}. [Ti^{+}]^2[S^{-2}] = 1 \times 10^{-22}$$

Sol.: PbS precipitation when concentration of $H_2S > Ti_2S$

$(0.1)^2[s^{2-}]=1x10^{-22}$

$[s^{2-}]= 1x10^{-20}$

So for separation sulfide concentration between $1x10^{-20}$ and Concentration $[H_3o^+]$ needed to decrease s^{2-}using following equation:

$[s^{2-}]=6.8x10^{-24}/[H_3o^+]$

$[H_3o^+]^2= 6.8x10^{-24}/1x10^{-20}$

$[H_3o^+]= 0.1$

$[H_3o^+]^2= 6.8x10^{-24}/1x10^{-20}$

$[H_3o^+]= 0.03M$

Separation by Complex-Ion Formation

The separation of certain ions is influenced in analytical chemistry by the use of the equilibrium between the ion and its the complexs.

Ex20.calculate the number of AgBr grams which will dissolve in 1L of ammonia (NH_4OH).if the result solution is 2.0M ammonia. Mwt =188 g/mole

Sol.:

$$[Ag^+][Br^-] = Ksp = 5.0 \times 10^{-13}$$

$$\frac{[Ag^+][NH_3]^2}{[Ag(NH_3)_2]} = K = 6.8 \times 10^{-8}$$

$$[Ag(NH_3)_2] = [Br^-]\text{of AgBr}$$

$$\frac{5.0 \times 10^{-13}}{x} = [Ag^+]$$

$$\frac{(5.0 \times 10^{-13}|x)(2.0)^2}{X} = 6.8 \times 10^{-8}$$

To solve the last equation

$X = 5.4\ X\ 10^{-3}M$

$5.4\ X\ 10^{-3} \times 188 = 1.0\ gm$

Ex21. A solution of 0.1 M Cu^{+2}, 0.1 M Cd^{+2} were reacted with KCN & (NH_4OH) to from $Cu(CN)_3^{-2}.Cd(CN)_4^{-2}$ containing 0.02 M of CN ions. if H_2S gas bubble through the solution to give 0.01M of S^{2-}, that Cu_2S and/or CdS could be precipitate under such conditions.

Sol.:

$$\frac{[Cu^{+}][CN^{-}]^{3}}{[Cu(CN)_{3}^{-2}]} = 5.0 \times 10^{-28}$$

$$\frac{[Cu^{+}][0.020]^{3}}{[0.10]} = 5.0 \times 10^{-28}$$

$$[Cu^{+}] = 6.2 \times 10^{-24}$$

$$[Cu^{+}]^{2}[S^{-2}] = (6.2 \times 10^{-24})^{2}(0.01)$$

$$= 3.8 \times 10^{-49}$$

$$\text{Ksp } Cu_2S = 1.0 \times 10^{-46} > 3.8 \times 10^{-49}$$

$$\frac{[Cd^{+2}][CN^{-}]^{4}}{Cd(CN)_{4}^{-2}} = 1.4 \times 10^{-17}$$

$$\frac{[Cd^{+2}][0.020]^{4}}{0.10} = 1.4 \times 10^{-7}$$

So

$$[Cd^{+2}] = 8.7 \times 10^{-12}$$

$$[Cd^{+2}][S^{-}] = (8.7 \times 10^{-12})(0.01)$$

$$= 8.7 \times 10^{-14}$$

$$\text{Ksp CdS is } 3.8 \times 10^{-29} < 8.7 \times 10^{-14}$$

It will precipitate CdS within these conditions because the ionic soluble product is greater than Ksp value.

Precipitation Titration

Methods of Precipitation Titration:

1- Mohr ‘s method:

It involves formation of colored precipitate at the end point.

2- Villard's method:

It involves formation of soluble colored complex at the end point.

3- Fagan’s method- It involves adsorption of a colored indicator on the precipitate at the end point.

Fields of use:

Titration is a widely applied analytical technique. Some areas where titration is used are given below:

Agriculture, Oil Industry, Chemical industry, Pharmaceuticals, Food Industry.

Advantages of titration: There are several reasons why titration is used in laboratories worldwide:

1) Titration is an established analytical technique.
2) It is fast.
3) It is a very accurate and precise technique.
4) Titration offers a good price/performance ratio as compared to more sophisticated techniques.
5) It can be used by low-skilled and low- trained operators.
6) No need for highly specialized chemical knowledge.

Precipitating titratios are those that involve reactions that lead to the formation of a precipitate or a little soluble salt. The use of precipitation reactions in volumetric analysis is easier than in gravimetric analysis.

Precipitation Curve

Ex22. A 50 ml of 0.1 NaCl was titrated against 0.1 M $AgNO_3$. The values of pCl after addition of 0.00, 10, 49.95, 50.00, 52.60 ml of $AgNO_3$. $Ksp = 1.82 \times 10^{-10}$

Sol.:

1) At 0.00 ml of Ag

pCl = -10g [Cl] = -10g 0.1 = 1.0

2) At 10ml $AgNO_3$

$$[Cl^-] = \frac{50 \times 0.1 - 10 \times 0.1}{60} + [Ag^+]$$

$[Ag^+]$ is too low, it can be neglected with respect to the chloride concentration, so therefore;

$$[Cl^-] = 6.7 \times 10^{-2}$$

$$\therefore pCl = -10g 6.7 \times 10^{-2} = 1.17$$

3) At addition of 49.95 ml of $AgNO_3$

$$[Cl^-] = \frac{50 \times 0.1 - 49.95 \times 0.1}{99.95ml} + [Ag^+]$$

$$[Cl^-] = 5 \times 10^{-5}$$

$$pCl = -10g\, 5 \times 10^{-5} = 4.3$$

4) At equivalence point =50.00 ml of $AgNO_3$

$Ksp = [Ag][Cl].[Ag] = [Cl] = \sqrt{Ksp}$

$pCl = -10g\ 1.35 \times 10^{-5} = 4.87$

5) After addition of 52.50 ml of $AgNO_3$

$$[Ag^+] = \frac{52.5 \times 0.1 - 50 \times 0.1}{102.5} + [Cl^-]$$

Since the value of $[Cl^-]$ is very low, it can be neglected, so therefor

$[Ag^+] = 2.4 \times 10^{-3}$

$Ksp = [Ag][Cl]$

$1.52 \times 10^{-10} = 2.4 \times 10^{-3}[Cl^-]$

$[Cl^-] = 7.6 \times 10^{-8}$

$pCl = 7.6 \times 10^{-8} = 7.12$

Ex23. 32.10 ml of silver nitrate solution was required to titrate 0.3504 of pure sodium chloride, what is the normality of the solution and the weight of sodium chloride equivalent to 1ml of the solution

Sol.: no. of meq of $AgNO_3$ = no. of meq of Nacl

$$(V_{AgNO_3}) \times (N_{AgNO_3}) = \frac{\text{wt of NaCl}}{0.05845 mg/meq}$$

$$(32.10ml)(N) = \frac{0.3504mg}{0.05845mg}$$

$N = 0.1868\ meq/ml$

$0.3504g|32.10ml = 0.010916\ g\backslash ml$

Vollhard Method

Ex21. it has been found from experiment that the average observer ear. just detected the red color of $Fe(SCN)^{+2}$ When its concentration is $6.4x10^{-6}M$. in the titration of 50.0ml of 0.050M AgI was 0.100M KSCN, what concentration of Fe^{3+} should be need to be used reduce the titration error to zero.

Sol.: at equivalent point

$[Ag^+] = [SCN^-][Fe(SCN^-)2$

Since the concentration of the complex to be $6.4 \times 10^{-6}M$ at equivlent point

$[Ag^+] = [SCN^-] - 6.4 \times 10^{-6}$

Or $\frac{Ksp}{[[SCN^-]]} = \frac{1.1\times10^{-12}}{[[SCN^-]]} = [SCN^-] + 6.4 \times 10^{-6}$

Which rearranges to

$[[SCN^-]] + 6.4 \times 10^{-6}[SCN^-] - 1.1 \times 10^{-12} = 0$

Solving the

$[[SCN^-]] = 1.7 \times 10^{-7}$

The formation constant for $FeSCN^{+2}$ is

$$\frac{[Fe(SCN)2]}{[Fe3][[SCN^-]]} = Kf = 1.4 \times 10^{-2}$$

$$\frac{[6.4 \times 10^{-6}]}{[Fe3+][1.7 \times 10^{-7}]} = Kf = 1.4 \times 10^{-2}$$

$[Fe^{3+}]=0.27$

Questions and Answer

Q1. A saturated soluation of which compound has the lowest $[Ca^{2+}]$:

	K_{sp}
CaF_2	4.0×10^{-11}
$CaCO_3$	8.7×10^{-9}
$Ca(OH)_2$	8.0×10^{-6}
$CaSO_4$	2.4×10^{-5}

(A) CaF_2 (B) $CaCO_3$ (C) $Ca(OH)_2$ (D) $CaSO_4$

Sol. b.

Q195. What is the conjugate base of HSO_4^-?

a. H+

b. H_2SO_4

c. OH^-

d. $SO4^{-2}$

Q2. What's the concentration of Ag+ ion in a saturated silver chloride solution? Ksp = 1.56 x 10^{-10}.

a. 1.25 x 10^{-5} M

b. 4.90 M

c. 3.39 x 10^{-4} M

d. none of these

CHAPTER EIGHT
Oxidation-Reduction

CHAPTER EIGHT
OXIDATION-REDUCTION

Introduction

Chemical reactions in which the oxidation states or oxidation numbers of the atoms are reformed is known as oxidation- reduction reaction. These reactions are also known as redox reactions, which is short form for reduction-oxidation reaction. Oxidation is the process of losing of electrons throughout a reaction by a molecule an atom or an ion. Oxidation arises when the oxidation state of a molecule, atom or ion is higher. The contrast process is known as reduction, which happens when the electrons are gained or when oxidation state of an atom, molecule, or ion lowers. An example for redox reaction is as:

$2\ Al + 3\ Br_2 \rightarrow Al_2Br_6$

In this reaction Bromine is been oxidized and Aluminum is being reduced

Oxidation-reduction reactions are also known as redox reactions. Redox reactions describe all chemical reactions in which there is a net change in atomic charge. It is a class of reactions that include:

1- Formation of a compound from its elements.
2- All combustion reactions.
3- Reactions that generate electricity.
4- Reactions that produce cellular energy.

Oxidation-Reduction Reactions is Defined;

Oxidation-reduction ("redox") reactions involve the transfer of electrons from one substance to another.

Oxidized substances lose electrons and reduced substances gain electrons.

An oxidation-reduction reaction
provides us with energy from food.
provides electrical energy in batteries.
occurs when iron rusts.

$$4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s)$$

Transfers electrons from one reactant to another.

Loses electrons in oxidation. (LEO) or (OIL)

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-} \text{ (loss of electrons)}$$

Gains electrons in reduction.

$$Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s) \text{ (gain of electrons)}$$

Balancing Oxidation-Reduction Equations

Balancing Redox Equations

There are two methods used to balance redox reactions:

1)the oxidation number change method

2)the half reaction method

These methods are based on the fact that the total number of electrons gained in reduction must equal the total number of electrons lost in oxidation.

Redox reactions are often quite complicated and difficult to balance. For this reason, you'll learn a step-by-step method for balancing these types of reactions, when they occur in acidic or in basic solutions.

Oxidation Number Change Method

Balance the following: $Fe_2O_3 + CO \rightarrow Fe + CO_2$

1) Assign ON to all atoms

$$\overset{+3\ -2}{Fe_2O_3} + \overset{+2\ -2}{CO} \longrightarrow \overset{0}{Fe} + \overset{+4\ -2}{CO_2}$$

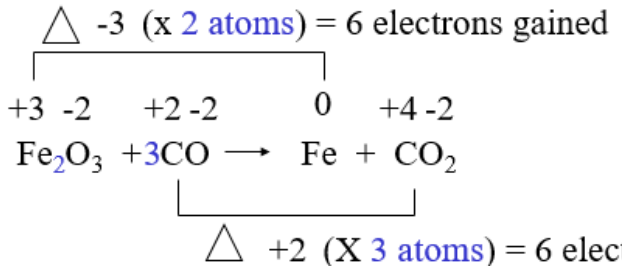
2) Identify which atoms are oxidized and which are reduced

$$\overset{+3\ -2}{Fe_2O_3} + \overset{+2\ -2}{CO} \longrightarrow \overset{0}{Fe} + \overset{+4\ -2}{CO_2}$$

△ -3 (Fe reduced)

△ +2 (C oxidized)

3) Make the total increase in oxidation number equal the total decrease in oxidation number by using appropriate coefficients on the reactant side only.



4) Finally check to be sure that the equation is balanced both for atoms and charge.

$Fe_2O_3 + CO \rightarrow Fe + CO_2$

Balancing Equations with the Half-Reaction Method

1) First split the original equation into two half-reactions, one "reduction" and the other "oxidation".

In each half-reaction, follow these steps:

2) Balance all elements except "H" and "O".

3) Balance the "O's" by adding water, H_2O.

4) Balance the "H's" by adding hydrogen ions, H^+.

If your rxn is taking place in an acidic solution, skip to step 8

If your rxn is taking place in a basic solution proceed to step 5

5) Adjust for basic conditions by adding to both sides the same # of OH^- ions as the number of H^+ ions already present

6) Simplify the equation by combining H^+ and OH^- that appear on the same side of the equation into water molecules.

7) Cancel any water molecules present on both sides of the equation

8) Balance the charges by adding electrons

9) Recombine the ½ reactions into a complete balanced equation

EX: acidic solution

$$Fe^{2+} + Cr_2O_7^{2-} \rightarrow Fe^{3+} + Cr^{3+}$$

$$6(\ Fe^{2+} \rightarrow Fe^{3+} + 1e^-\ )$$

$$1(\ 6\,e^- + 14\,H^+ + Cr_2O_7^{2-} \rightarrow 2\,Cr^{3+} + 7\,H2O\ )$$

$$Cr_2O_7^{2-} + 6\,Fe^{2+} + 14\,H^+ \rightarrow 2\,Cr^{3+} + 6\,Fe^{3+} + 7\,H_2O$$

Basic Solutions

Follow the same steps as for acidic solutions, and add the following s Add OH- to both sides to equal the H+

$5H_2SO_3 + 2MnO_4^- \rightarrow 2Mn^{2+} + 3H_2O + 5SO_4^{2-} + 4H^+$

$4\ OH^- \rightarrow 4OH^-$

Combine the H^+ and OH^- to make water.

$4\ OH^- + 5H_2SO_3 + 2MnO_4^- \rightarrow 2Mn^{2+} + 3H_2O + 5SO_4^{2-} + 4H_2O$

Cancel the H_2O if they are on both sides.

$4\ OH^- + 5H_2SO_3 + 2MnO_4^- \rightarrow 2Mn^{2+} + 7H_2O + 5SO_4^{2-}$

Benefiting From Oxidation and Reduction Reactions

Applications of Redox Reaction

Redox reactions have numerous industrial and everyday applications. A few of these applications of redox reactions are listed below.

Applications of Redox Reaction in Electrochemistry;

The battery used for generating DC current uses redox reaction to produce electrical energy.

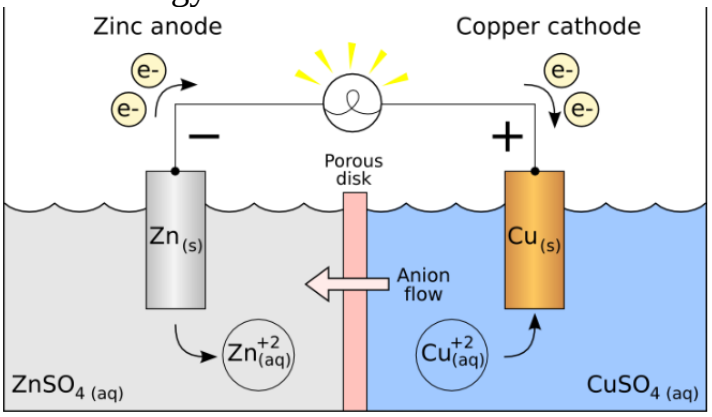


Figure 8-1 Redox reactions in cell

Batteries or electrochemical cells used in our day-to-day life are also based on redox reactions. For example, storage cells are used in vehicles to supply all the electrical needs of the vehicles.

Redox Reaction in Combustion

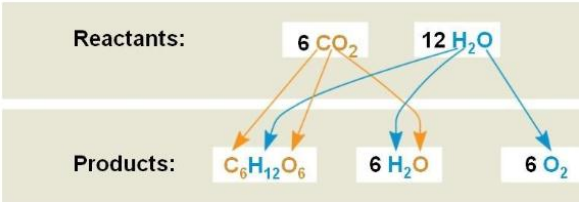
Combustion is a type of oxidation-reduction reaction and hence it is a redox reaction. An explosion is a fast form of combustion and hence

explosion can be treated as a redox reaction. Even the space shuttle uses redox reactions. The combination of ammonium perchlorate and powdered aluminum inside the rocket boosters gives rise to an oxidation-reduction reaction.

Applications in Photosynthesis

Green plants convert water and carbon dioxide into carbohydrates and this process is defined as photosynthesis. The reaction is given as

$6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$



$6\ CO_2 + 12\ H_2O + \text{Light energy} \rightarrow C_6H_{12}O_6 + 6\ O_2 + 6\ H_2O$

Real Life Uses of Redox Reaction

Production of some important chemicals is also based on electrolysis which in turn is based on redox reactions. Many chemicals like caustic soda, chlorine, etc. are produced using redox reactions.

Oxidation-Reduction reactions also find their application in sanitizing water and bleaching materials.

The surfaces of many metals can be protected from corrosion by connecting them to sacrificial anodes which undergoes corrosion instead. A common example of this technique is the galvanization of steel.

The industrial production of cleaning products involves the oxidation process.

Nitric acid, a component of many fertilizers, is produced from the oxidation reaction of ammonia.

Electroplating is a process that uses redox reactions to apply a thin coating of a material on an object. Electroplating is used in the production of gold-plated jewelry.

Many metals are separated from their ores with the help of redox reactions. One such example is the smelting of metal sulfides in the presence of reducing agents.

There are two types of electrochemical cells

1. The galvanic cell
2. The electrolytic cell

The figure below represents a simple galvanic cell.

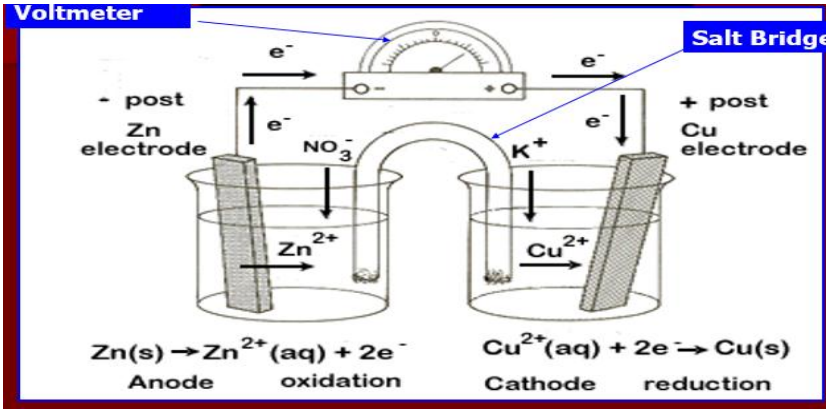


Figure 8-2 reactions in each half of a cell.

Oxidation Reaction

As the zinc loses two electrons, the number of oxidants increases from zero in Zn to +2 in Zn^{+2}.

Reduction Reaction

As the copper ion acquires the electrons lost by the zinc, the oxidation number decreases from +2 in Cu^{+2} to Cu.

$Cu^{+2} + 2e^{-} \rightarrow Cu^{0}$

$Zn^{0} \rightarrow Zn^{+2} + 2e$

Anode – The electrode where oxidation occurs

Cathode – The electrode where reduction occurs.

Salt Bridge – prevents buildup of ions on one side of the cell and balances the charge.

No more electricity can flow when the anode disappears.

Formal Concentration (F)

If the concentration refers to original chemical formula in solution, the molar concentration is sometimes called *formal concentration*. For example, if a sodium carbonate solution (Na_2CO_3) has a formal concentration of $c(Na_2CO_3)$=1 mol/L, the molar concentrations are $c(Na^+)$=2 mol/L and $c(CO_3^{2-})$=1 mol/L because the salt dissociates into these ions.

Ex1. Calculate the half-cell potential at pt electrode containing. $1.0 \times 10^{-4} F$ of (Fe(III)). And $1.0 \times 10^{-2} F$. Fe(II) in 1F HCI.

Sol.:

$$Fe^{+3} + 1e^- \rightarrow Fe^{+2}$$

$$E = E^o_{Fe^{+3}/Fe^{+2}} + \frac{0.059}{1} 10g \frac{(Fe^{+3})}{(Fe^{+2})}$$

$$E = +0.700V + \frac{0.059}{1} 10g \frac{0.0001}{0.01}$$

$$E = +0.700V - 0.118V = +0.582V$$

Ex2. Calculate half cell potential at pt electrode containing $1 \times 10^{-3} F$ Ce(I),1.0×10^{-2} *Ce(IV) at 1 FHCl.*

$$Ce^{+4} + 1e^- \rightarrow Ce^{+3}$$

$$E = E^o_{Ce^{+4}/Ce^{+3}} + \frac{0.059}{1} 10g \frac{(Ce^{+4})}{(Ce^{+3})}$$

$$= 1.28V + \frac{0.059}{1} 10g \frac{(0.01)}{(0.001)}$$

=1.339V

Ex3. Calculate half-cell potential at pt electrode containing 1×10^{-3}F Ce(II),1.0×10^{-2}F Ce(IV)) at 1F HCl.

$Pt|Fe^{+2}(0.01F).Fe^{+3}(0.0001F).HCl(1F)|$
$||Ce^{+4}(0.01F).Ce^{+3}(0.001F).HCl(1F)|Pt$

Sol.: $Fe^{+3} + Ce^{+4} \rightarrow Fe^{+2} + Ce^{+3}$

$$E = E^o_{Ce^{+4}/Ce^{+3}} - E^o_{Fe^{+3}/Fe^{+2}}$$

$$E = E^{o}_{Ce^{+4}/Ce^{+3}} + \frac{0.059}{1}10g\frac{(Ce^{+4})}{(Ce^{+3})} - E_{\frac{Fe^{+3}}{Fe^{+2}}} - \frac{0.059}{1}10g\frac{(Fe^{+3})}{(Fe^{+2})}$$

$$E = 1.28V + \frac{0.059}{1}10g\frac{(0.01)}{(0.001)} - 0.700V - \frac{0.059}{1}10g\frac{(0.0001)}{(0.01)}$$

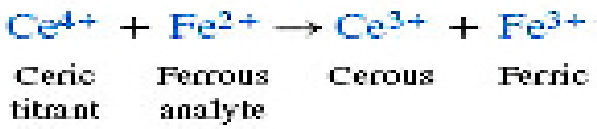
$$E_{cell} = 1.28V + \frac{0.059}{1} - 0.700V - 0.118 = 0.521\text{V}$$

Titration Curve of Oxidation-Reduction

A redox titration is based on an oxidation-reduction reaction between analyte and titrant.

The redox titration curve shows the shift in the concentration of the substance to be analyzed by the titration function. Since the voltage has to do with the concentration through the Nernst equation. So the redox curve is a curve that draws between the voltage and the titrant millimples (oxidizing or reducing agent).

Consider the titration of iron(II) with standard cerium(IV), monitored potentiometrically with Pt and calomel electrodes.



An appropriate way to illustrate these calculations is to use the Fe (II) -Ce (iv) reaction as an example. When Fe (ii) is titrate with Ce (IV) in 1F of sulfuric acid the equilibrium constant is as follows:

$$1\text{ogK} = 16.9\text{n}(\text{E}^{0}_{\frac{Ce^{+4}/Ce^{+3}}{1}} - \text{E}^{o}_{\frac{Fe^{+3}/Fe^{+2}}{1}})$$

$$1\text{ogK} = 16.9 \times 1 \times (1.44\text{V} - 0.68\text{V})$$

$$\text{K} = 10^{12.94} = 8.71 \times 10^{12}$$

There are three distinct regions in the titration of iron (II) with standard cerium(IV), monitored potentiometrically with Pt and calomel electrodes:

a) Before the equivalence point, where the potential at Pt is dominated by the analyte redox pair.10^{12}

b) At the equivalence point, where the potential at the indicator electrode is the average of their conditional potential.
c) After the equivalence point, where the potential was determined by the titratant redox pair.

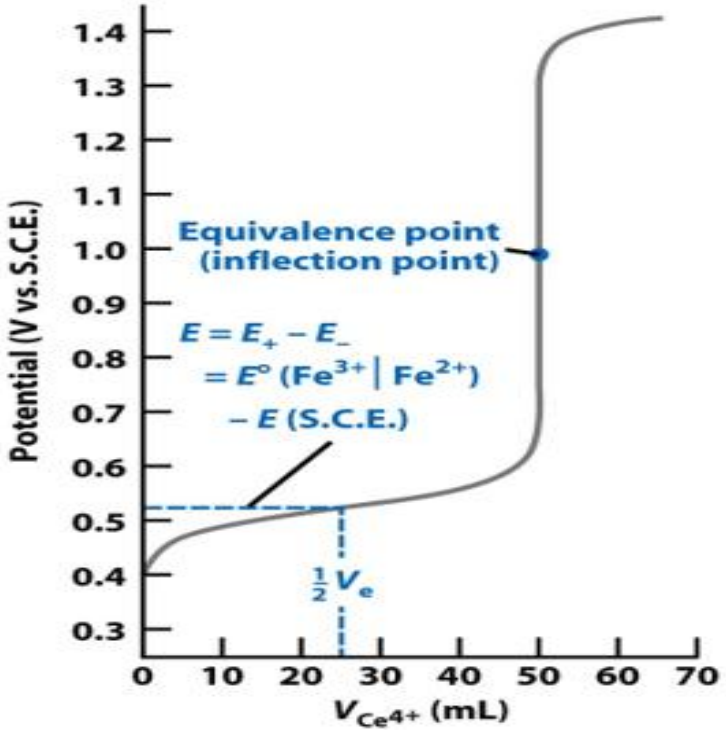


Figure 8-3 titration curve of oxidation-reduction

Initial Potential

Initially the solution consists of Fe (ii) only. There may be a very small amount of Fe^{+3} as a result of air oxidation, so calculating the initial voltage here has no real meaning.

Potential During Titration

Reaction occurs when adding the titrant Ce^{+4} to form an equivalent amount of Fe (ii) and Ce (iii). The potential at the indicator electrode (Eie) when the system reaches equilibrium is as follows.

$$E_{ie} = E^{0}_{Fe^{+3}/Fe^{+2}} + 10g\frac{(Fe^{+3})}{(Fe^{+2})} = E^{o}_{Ce^{+4}/Ce^{+3}} + 10g\frac{(Ce^{+4})}{(Ce^{+3})}$$

When adding 10ml of titrant the calculations are as follows:

at the begining $= 40\text{ml} \times 0.1\text{F} = 4.0\text{mmole } Fe^{+2}$

the added $= 10\text{ml} \times 0.1 = 1.0\text{mmole } Ce^{+4}$

the remaining $50\text{ml} \times 3\text{mmole } Fe^{+2}$

$(Fe^{+2}) = \frac{3.0\text{mmole}}{50\text{ml}}$ =0.06m

$(Fe^{+3}) = \frac{1.0\text{mmole}}{50\text{ml}}$ =0,02m

The potential is at the equivalent point of the two halves of the cell

$$E_{Eq} = E^{0}_{Fe^{+3}/Fe^{+2}} + \frac{0.059}{1} + 10g\frac{(Fe^{+3})}{(Fe^{+2})}$$

$$E_{Eq} = 0.68 + \frac{0.059}{1} + 10g\frac{0.02}{0.06} = 0.652V$$

Equivalent Point Potential

When adding 20 ml of Ce^{4+}, the calculations are as follows;

at the begining $= 40\text{ml} \times 0.1\text{F} = 4.0\text{mmole } Fe^{+2}$

the added $= 20\text{ml} \times 0.1\text{F} = 2.0\text{mmole } Ce^{+4}$

the formed $60.0 = 20\text{mmole } Fe^{+3}$

The potential is at the equivalent point of the two halves of the cell;

$$E_{Eq} = E^{0}_{Ce^{+4}/Ce^{+3}} + \frac{0.059}{1} + 10g\frac{(Ce^{+4})}{(Ce^{+3})}$$

Whereas Eq = equivalent point

$$E_{Eq} = E^{0}_{Fe^{+3}/Fe^{+2}} + \frac{0.059}{1} + 10g\frac{(Fe^{+3})}{(Fe^{+2})}$$

The equation can be as follows;

$$2Eq = E^{f}_{Ce^{+4}/Ce^{+3}} + E^{f}_{Fe^{+3}/Fe^{+2}} + \frac{0.059}{1} + 10g\frac{(Ce^{+4})}{(Ce^{+3})} + \frac{0.059}{1} + 10g\frac{(Ce^{+3})}{(Ce^{+4})}$$

The equation can be simplified as follows;

$$2Eq = E^{0}_{Ce^{+4}/Ce^{+3}} + E^{0}_{Fe^{+3}/Fe^{+2}}$$

$$E_{Eq} = \frac{E^{0}_{Ce^{+4}/Ce^{+3}} + E^{0}_{Fe^{+3}/Fe^{+2}}}{2} = \frac{1.44V + 0.63}{2} = 1.06V$$

After end point

When adding an increase from the titrant Ce^{4+} the molar concentration of Fe^{3+} is greater than the concentration of Fe^{2+}.

the added $= 50ml \times 0.1F = 5.0mmole\ Ce^{+4}$

at the begining $= 40ml \times 0.1F = 4.0mmole\ Fe^{+2}$

the excess $90ml = 1.0mmole\ Ce^{+4}$

Thus in molar units;

$$[Ce^{+4}] = \frac{1.0mmoles}{90ml} = 0.0111M$$

$$[Ce^{+3}] = \frac{4.0mmoles}{90ml} = 0.044M$$

$$E_{Eq} = E^{o}_{Ce^{+4}/Ce^{+3}} + \frac{0.059}{1} + 10g\frac{(Ce^{+4})}{(Ce^{+3})}$$

$$E_{Eq} = E^{o}_{Ce^{+4}/Ce^{+3}} + \frac{0.059}{1} + 10g\frac{(0.0111)}{(0.444)} = 1.40V$$

When adding 80ml of Ce^{4+}

$(Ce^{+3}) = (Ce^{+4})$

$$E_{Eq} = E^{o}_{Ce^{+4}/Ce^{+3}} + \frac{0.059}{1} + 10g\frac{(Ce^{+4})}{(Ce^{+3})}$$

=1.44V

Redox methods are used for analysis in which the concentration is at least $10^{-4} - 10^{-3}$

Examples of titrant curves;

1. $Ce^{+4} + Fe^{+2} \xrightarrow{1F\ HClO_4} Ce^{+3} + Fe^{+3}$
2. $Ce^{+4} + Fe^{+2} \xrightarrow{1F\ HNO_3} Ce^{+3} + Fe^{+3}$
3. $MnO_4^- + 5Fe^{+2} + 8H^+ \xrightarrow{H^+=1M} Mn^{+2} + 5Fe^{+3} + 4H_2O$
4. $Ce^{+4} + Fe^{+2} \xrightarrow{1F\ H_2SO_4} Ce^{+3} + Fe^{+3}$
5. $2Ce^{+4} + AsO_2^- + H_2O \rightarrow 2Ce^{+3} + AsO_3^- + 2H^+$

Ex4. Calcium oxalate (CaC_2O_4) is precipitated from a 0.308g sample of stone containing 41.75 percent CaO.the precipitate is rerated with excess sulfuric acid (H_2SO_4) and titrated whit a potassium permanganate soluation,42.52ml being required. Calculate the molarity of the permanganate solution.

Sol.:

$Ca^{+2} + C_2O_4^{-2} + H_2O \rightarrow CaC_2O_4 + H_2O$

Calcium oxalate may be treated with H_2SO_4 and the resulting CaC_2O_4 is treated with standard $KMnO_4$, or the formed $CaSO_4$is weighed after expelling the excess acid.

$CaC_2O_4 + H_2SO_4 \rightarrow CaSO_4 + H_2C_2O_4$

$5H_2C_2O_4 + 2KMnO_4 + 6H^+ \rightarrow 2Mn^{+2} + 2K^+ + 10CO_2 + 8H_2O$

Calcium oxalate may also be converted into calcium oxalate by igniting

$CaC_2O_4 \xrightarrow{200C} CaO + CO + CO_2$

From the above equation it is evident that one mole of CaO is equivalent to one mole of CaC_2O_4 a reducte is $^1/_2$ of its molecular weight due to 2 electrons loss when $C_2O_4^{-2}$ is oxidized to Co_2 and H_2O

$CaO \Leftrightarrow Ca_2C_2O_4 \Leftrightarrow H_2CaC_2O_4 \Leftrightarrow 2e$

It is clear that the equivalent weight of each compound.

No. of meq of $KMnO_4$ =no.of meq of CaO

weight of CaO = (0.3608g)(41.75/100)=0.1505g

$$(42.52\text{ml})(N) = \frac{0.1505\text{g}}{\left(\frac{56.08}{2000}\right)}$$

$$N = 0.1263\text{g} - \text{meq} = 0.12631.\,N$$

(since a solution containing 1mole of $KMnO_4$ per liter is 1 molar or 50normal (eq.w of $KMnO_4$ is 1/5 mole, the a solution with a molarity of will have a normality of 5.thus

N=5M, and M=N/5.therefore, $M = \frac{0.1263}{5} = 0.2256$ mola

Ex5. (a) The calcium in 0.9082g of a substance is determined by precipitating CaC_2O_4 and igniting the latter to CaO weighing 0.5888g. Calculate the percentage present in terms of elementary calcium.

(b) If the calcium oxate precipitate has been converted $CaSO_4$ before weighing, what weight would have been

(c) if the calcium had been determined volumetrically by treating the calcium oxalate CaC_2O_4 with H_2SO_4 and titrating with 0.1000 M $KMnO_4$ Solution, how many ml of the permanganate would have been used?

Sol.:

(a) The factor for converting CaO to Ca $\frac{Ca}{CaO} = \frac{40.08}{56.08}$ thus,

$\frac{40.08}{56.08} \times 100 = 46.34\%$ Ca in the substanca

$CaC_2O_4 + 2H^+ \rightarrow H_2C_2O_4$

$5H_2C_2O_4 + 2KMnO_4 + 6H \rightarrow 2Mn^{+2} + 2K^+ + 10CO_2$

(b) $CaC_2O_4 == Ca == CaC_2O_4$, therefore,

$0.5888g \times \frac{CaSO_4}{CaO} = 0.5888g \times \frac{136.1}{56.08} = 1.430$ g of$CaSO_4$

(c) with respect to obtained

$(0.5000\ meq)(V) = \frac{\text{Ca obtained}}{\frac{56.08}{2000}}$ meq.

$(0.5000\ meq)(V) = \frac{5.888}{0.02804}.meq$

=42.01 ml

Determination of Sodium Oxalate in the Solution

EX6: A sample of unknown sodium oxalate was deried at 105-110C^0 for one hour and sample was cooled and three sample of it was weighed (0.6g each).postulating that purity of oxalate is 20%.the sample were titrated with same procedure adopted for $KMnO_4$ standardization. Calculate the percent of $Na_2C_2O_4$ in the sample.

Sol.:

$$V_{KMnO_4} \times N_{KMnO_4} = \frac{Na_2C_2O_4\ (wt)}{eq.\,Wt} \times 1000$$

$$eq.\,wt = \frac{134}{2} = 67$$

$$\%Na_2C_2O_4 = \frac{wt\ Na_2C_2O_4}{wt\ of\ sample}$$

Ex7. A 5.400gm of sample containing iron (Fe) was dissolved in a 500 ml volumetric flask.ten ml (10ml) of this solution was transformed to aconical flask and then titrated against stan dard solution of $KMnO_4$ 0.1N. the titrated consumed 10.5ml of $KMnO_4$.calculate the percent purity of the iron in the sample

Sol.:

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

$$\%Fe = \frac{V_{KMnO_4} \times N_{KMnO_4} \times 0.05585 \times \frac{500}{10}}{wt\ of\ the\ sample} \times 100$$

$$\frac{0.1 \times 10.5 \times 0.05585 \times 50}{5.400} \times 100$$

$$= 54\%$$

Note = At wt of Fe =55.85 g/mole, Eqwt/1000 $=\frac{55.85}{1000} = 0.05585$

Ex8. The weight of the combined oxides of iron and aluminum $Fe_2O_3AL_2O_3$

From (2.500)mg sample of limestone is (0.2119)gm. the iron alone is determined volumetrically by dissolving another (2.500)mg sample, reducing the iron and titrating with 0.1N $Na_2Cr_2O_7$,7.38 ml being used. Calculate (Fe+Al) content of limestone, expressing the former in terms of FeO and the latter in terms ofAL_2O_3.

Sol.: both Fe_2O_3 and AL_2O_3 are water insoluble oxides, but they can be brought easily into solution .with HCl.

$Fe_2O_3 + 6H_3O^+ \rightarrow 2Fe^{+3} + 9H_2O$

$Al_2O_3 + 6H_3O^+ \rightarrow 3Al^{+3} + 9H_2O$

In order to determine iron volumetrically the ferric ions (Fe^{+3}) have to be reduced to the ferrous ions prior to … with the standard oxidizing agent solation.

The reduction of (Fe^{+3}) to(Fe^{+2}) can be done by four different methods.

The ferrous iron is oxidized by the dichromate ion according the following equation;

$$6Fe^{+2} + Cr_2O_7^{-2} + 9H_3O^+ \rightarrow 6Fe^{+2} + 2Cr^{+3} + 21H_2O$$

To calculate the percentage for each to iron and aluminum in terms of FeO and Al_2O_3 respectively.

$$N_{K_2Cr_2O_7} \times V_{K_2Cr_2O_7} = \frac{\text{FeO wt}}{\text{FeO eq. wt}}$$

$$0.1000\ \text{meq} \times (7.38\ \text{ml}) = \frac{\text{FeO obtained}}{\left(\frac{71.85}{1000}\right)\frac{\text{meq}}{\text{g}}}$$

FeO obtained =(0.1000)(7.38)(0.07185)g=0.0530gram

Thus, FeO=$\frac{0.0530\ \text{g}}{2.5000\ \text{g}} \times 100 = 2.12\%$ of FeO in the lirneston

The convert 0.0530g of FeO toFe_2O_3, Multiply by factor $\frac{Fe_2O_3}{FeO}$.

There Fure:

$$\frac{(0.0530\text{g})(159.7)}{} = 0.1178\text{g of } Fe_2O_3 \text{ in the sample}$$

0.2119-0.1178 =0.0530g of Al_2O_3 in the sample

$$\frac{0.0530\text{g}}{2.5000} \times 100 = 2.12\%\ Al_2O_3 \text{ in the l irnestone sample}$$

Determination of Organic Compounds by Reduced Titrants

Iodide ion is useful in analyzing organic peroxides and estimating a multi-bonding group such as acetylene and aromatic compounds of non-saturated acids groups. Generally, Ni, Pt is used as a copper estimating agent in a dissolved saline.

Titrate Thiosulfate Solution with Potassium Iodate Solution

Ex9. Calculate the normality of athiosulfate solution if, 37,34 ml is needed to titrate the iodine released by 0.1835gm of KIO_3 when mixed with an excess of KI and acid

Sol.:

$IO_3^- + 6H^+ + 6H_3O^+ \rightarrow 3I_2 + I^- + 9H_2O$

$2S_2O_3^{-2} + I_2 \rightarrow S_4O_6^{-2} + 2I^- \ldots$

No.of g-meq of reluctant =on of g-meq of oxidant

No.of meq of $Na_2S_2O_3$ =no.of meq of KIO_3

37.34ml(N) $\frac{0.1835\ g}{(37.34)(0.04017}$ g.$\frac{meq}{ml} = 0.1378g.\frac{meq}{ml}$

When N is the normality of thiosulfate **sol**, and 241.02 is the Mwt. Of potassium iodate.

$N = \frac{0.1835g}{(37.34)(0.04017)}$meq/ml = 0.1378 meq/ml

There is another way of standardizing sodium thiosulfate solution iodometrically using copper as primary standard. pure Copper (Cu) is taken as primary standared only when the thiosulfate solution is used for the determination of Copper.at certain condition Copper ions can quantitive oxidize iodide ions to iodine and the liberated iodine(I_2) is then titrated with thiosulfate (reducing agent)solution

Determination of Cuper by Iodometric Method

Ex10. if 21.32ml of 0.0937 N thiosulfate solution is needed to titrate the iodine released by the Copper in a 0.615g sample of Copper orn, Calculate the percent of Copper is the sample

Sol.: the oxidation-reduction reactions are

$2Cu^{+2} + 4I^- \rightarrow Cu_2I_2 + I_2 \ldots (1)$

$2S_2O_3^{-2} + I_2 \rightarrow S_4O_6^{-2} + 2I^- \ldots (2)$

It can be seen from eq. (1) above, that the change in oxidation state of Copper is 1, therefore, the equivalent Cu is the same as its atomic weight (63.54).

No.of meq of $Na_2S_2O_3$= no. of meq of I_2 =no.of g-meq

Lef × = meq of Cu in the one sample.

(21.32)().0937) meq/ml= $\frac{x}{\frac{63.54}{1000}}$g-meq

X= (21.32ml)(0.0937)(0.06354)=0.1269g of Cu in the orn.

$\frac{0.126g}{0.615g} \times 100 = 20.60$ Cu in the orn sample.

Redox Indicator

Redox = Reduction + Oxidation

Reduction = Addition of electron

$M^{z+} + n\ e^- \rightarrow M^{(z-n)+}$

Ex11: $Ce^{4+} + 1\ e^- \rightarrow Ce^{3+}$

Oxidation = Removal of electron

$M^{z+} - n\ e^- \rightarrow M^{(z+n)+}$

Ex12: $Fe^{2+} - 1\ e^- \rightarrow Fe^{3+}$

Redox titration involves the titration reaction where transfer of electron between the reactant (titrand) and titrant takes place.

Certain organic compounds are capable to undergo oxidation-reduction reactions and the color of the oxidized form of indicator in solution is significantly different than that of reduced form.

So, Colour of the indicator in the solution will depend on the ratio of

$$\frac{[\ In_{(Red)}\ ]}{[\ In_{(ox)}\ ]}$$

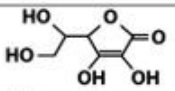
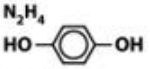
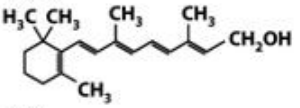
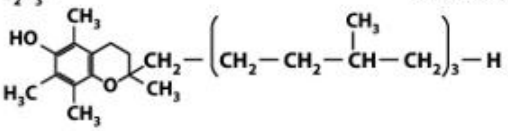
as colour is depend on potential E_{In} Because when E_{In} changes, the ratio of the reduced form of indicator to the oxidized form of indicator will change.

Table 8-1 oxidizing and reducing agent (A and B)

A-

	Color		
Indicator	Oxidized	Reduced	$E°$
Phenosafranine	Red	Colorless	0.28
Indigo tetrasulfonate	Blue	Colorless	0.36
Methylene blue	Blue	Colorless	0.53
Diphenylamine	Violet	Colorless	0.75
4′-Ethoxy-2,4-diaminoazobenzene	Yellow	Red	0.76
Diphenylamine sulfonic acid	Red-violet	Colorless	0.85
Diphenylbenzidine sulfonic acid	Violet	Colorless	0.87
Tris(2,2′-bipyridine)iron	Pale blue	Red	1.120
Tris(1,10-phenanthroline)iron (ferroin)	Pale blue	Red	1.147
Tris(5-nitro-1,10-phenanthroline)iron	Pale blue	Red-violet	1.25
Tris(2,2′-bipyridine)ruthenium	Pale blue	Yellow	1.29

B-

Oxidants		Reductants	
BiO_3^-	Bismuthate		Ascorbic acid (vitamin C
BrO_3^-	Bromate	BH_4^-	Borohydride
Br_2	Bromine	Cr^{2+}	Chromous
Ce^{4+}	Ceric	$S_2O_4^{2-}$	Dithionite
	Chloramine T	Fe^{2+}	Ferrous
Cl_2	Chlorine	N_2H_4	Hydrazine
ClO_2	Chlorine dioxide		Hydroquinone
$Cr_2O_7^{2-}$	Dichromate	NH_2OH	Hydroxylamine
FeO_4^{2-}	Ferrate(VI)	H_3PO_2	Hypophosphorous acid
H_2O_2	Hydrogen peroxide		Retinol (vitamin A)
$Fe^{2+} + H_2O_2$	Fenton reagent[3]	Sn^{2+}	Stannous
OCl^-	Hypochlorite	SO_3^{2-}	Sulfite
IO_3^-	Iodate	SO_2	Sulfur dioxide
I_2	Iodine	$S_2O_3^{2-}$	Thiosulfate
$Pb(acetate)_4$	Lead(IV) acetate		α-Tocopherol (vitamin E
HNO_3	Nitric acid		
O	Atomic oxygen		
O_2	Dioxygen (oxygen)		
O_3	Ozone		
$HClO_4$	Perchloric acid		
IO_4^-	Periodate		
MnO_4^-	Permanganate		
$S_2O_8^{2-}$	Peroxydisulfate		

Questions and Answer

Q1. The amount of iron in a newly developed, heat-resistant aluminum alloy is to be determined.

An 80.50 g sample of alloy is dissolved in concentrated hydrochloric acid and the iron atoms are converted to $Fe^{2+}(aq)$ ions.

This solution is accurately transferred to a 250.0 mL volumetric flask and made up to the mark. 20.00 mL aliquots of this solution are then titrated against a standard 0.0400 M potassium permanganate solution.

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

Four titrations were carried out and the volumes of potassium permanganate solution used were recorded in the table below.

Titration number	1	2	3	4
Volume of $KMnO_4$ (mL)	22.03	20.25	21.97	21.99

a. Write a balanced half-equation, including states, for the conversion of MnO_4^- ions, in an acidic solution, to Mn^{2+} ions.

Sol. Either of:

MnO4

-(aq) + 8H+(aq) + $5e^-$ → Mn^{2+}(aq) + $4H_2O$(l)

MnO_4^- (aq) + $8H_3O$ +(aq) + $5e^-$ → Mn^{2+}(aq) + $12H_2O$(l).

b. Calculate the average volume, in mL, of the concordant liters of the potassium permanganate solution.

Sol.

(22.03 + 21.97 + 21.99)/3 = 22.00 mL

A number of students who identified the three concordant liters did not access the mark because they truncated the average (21.997) to 21.99. A significant proportion of students simply averaged all four liters, not recognising that 20.25 was not concordant with the other three liters.

c. Use your **Sol.** to **part b.** to calculate the amount, in mol, of MnO^{4-} (aq) ions used in this titration.

Sol. n(MnO^{4-}) = 0.0400 x 22.00x10^{-3}

= 8.80x10^{-4}* (mol) or 0.000880

Consequential marks were applied throughout this equation. The mark for this equation was awarded if the **Sol.** to equation 1b. was correctly converted to the number of mol.

There was a significant number of errors associated with not converting the volume to mL, and not expressing the **Sol.** to the correct number of decimal places.

d. Calculate the amount, in mol, of Fe^{2+}(aq) ions present in the 250.0 mL volumetric flask.

Sol. n(Fe^{2+}) in 20 mL aliquot = 5 x n(MnO_{4-})

= 5 x 8.80x10^{-4} = 4.40x10^{-3} (mol)

n(Fe^{2+}) in 250 mL flask = 4.40x10^{-3} x (250/20) = 5.50x10^{-2} (mol)

The marks were awarded for accurately multiplying the **Sol.** to equation 1c. by 5 and by (250/20). Some students used their liter value rather the 20.00 mL aliquot in determining the amount present in the 250 mL volumetric flask.

e. Calculate the percentage, by mass, of iron in the 80.50 g sample of alloy.

Sol. n(Fe) in 80.50 g alloy = $5.50x10^{-2}$ (mol)

m(Fe) in 80.50 g alloy = $5.50x10^{-2}$ x 55.9 = 3.07 (g)

% Fe in alloy = (3.07/ 80.50) x 100*

= 3.82 % (3.81)

The most common error was not expressing the solution to the required 3 significant figures. Students should also be reminded to use the molar masses as supplied (as relative atomic masses) in the Data Book.

Many students who incorrectly solution equation. 1b. still obtained full consequential marks for equation s 1c., 1d. and 1e. A common final solution was 3.74 %, consistent with using all four liters in 1b.

Students should be reminded that severe rounding of data in early parts of a equation, for example, 0.0009 for 0.00088 in equation 1c., can have a significant impact on the accuracy of their final solution **.**

Students should be aware of the difference between 'truncating' and 'rounding off' an solution In equation 1a. correctly rounding off 21.997 to 4 significant figures gives the solution as 22.00, not 21.99.

Q2. A standard solution of potassium permanganate ($KMnO_4$) has a concentration of 0.0240 M. It is titrated against a solution of iron (II) sulfate ($FeSO_4$).

The equation for the reaction is

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

15.60 mL of the KMnO4 solution reacts exactly with 20.00 mL of the $FeSO_4$ solution. The concentration of the $FeSO_4$ solution, in M, is

a. 0.0187

b. 0.0307

c. 0.0936

d. 0.1540

Sol. $n(MnO^{4-})$ reacting = $n(KMnO_4) = c(KMnO_4) \times V(KMnO_4)$

$= 0.0240 \times 15.60x10^{-3} = 3.74x10^{-4}$ mmol

$n(Fe^{2+})$ reacting = 5 x $n(MnO_4^-) = 5 \times 3.74x10^{-4} = 1.87x10^{-3}$ mmol

$c(FeSO_4) = c(Fe^{2+}) = n(Fe2+)/ V(FeSO_4) = 1.87x10^{-3}/ 20.00x10^{-3}$

$= 0.0936$ M

CHAPTER NINE
GRAVIMETRIC ANALYSIS

CHAPTER NINE
GRAVIMETRIC ANALYSIS

Introduction

The term gravimetric pertains to a Weight Measurement. Gravimetric method is one in which the analysis is completed by a weighing operation. Gravimetric Analysis is a group of analytical methods in which the amount of analyte is determined by the measurement of the mass of a pure substance containing the analyte, also gravimetric Methods can also be defined as quantitative methods based on the determining the mass of a pure compound to which the analyte is chemically related.

What is the Gravimetric Analysis?

Gravimetric analysis is the quantitative determination of analyte concentration through a process of precipitation of the analyte, isolation of the precipitate, and weighing the isolated product. gravimetric analysis was using in chemical analysis of ores industrial materials, calibration of instrumentation and elemental analysis of inorganic compounds.

Types of Gravimetric Analyses:

There are two main types of gravimetric analyses:

A) Precipitation

Analyte must first be converted to a solid (precipitate) by precipitation with an appropriate reagent. The precipitates from solution is filtered, washed, purified (if necessary) and weighed. Example for Precipitation;

Calcium can be determined gravimetrically as precipitation of calcium oxalate and ignition of the calcium oxalate to calcium oxide.

$CaC_2O_4 \rightarrow CaO + CO_2 + CO$

Therefor, the precipitate obtained is weighed and the mass of calcium oxide is determined.

B) Volatilization

In this method, the analyte or its decomposition products are volatilized (dried) at a suitable temperature. The volatile product is then collected and weighed, or alternatively, the mass of the

volatilized product is determined indirectly by the loss of mass of the sample.

Example for Volatilization; The analyte or its decomposition products are volatilized at a suitable temperature. The volatile product is then collected and weighed, i.e. the mass of the product is indirectly determined from the loss in mass of the sample.

Example for volatilization:

Water can be separated from most inorganic compounds by ignition, the evolved water can then be absorbed on any one of several solid absorbents. The weight of water evolved may be calculated from the gain in weight of the absorbent. Not all insoluble precipitates are well suited for gravimetric analysis.

Criteria For a Successful Determination

For a successful determination in gravimetric analysis the following criteria should be met;

1. The desired substance must be completely precipitated. In most determination the precipitate is of such low solubility that losses from dissolution are negligible. An additional factor is the common ion effect, this further decrease the solubility of the precipitate, e.g. When Ag+ is precipitated out by addition of Cl^-:

$$Ag+ + Cl^- \rightarrow AgCl$$

The low solubility of AgCl is reduced further by the excess of Cl^- which is added force to the reaction to proceed towards right side.

2. The weighed form of the product should be a known composition.
3. The product should be pure.
4. The product should be easy in handling i.e. precipitation filtering, washing drying and weighing.

It is usually difficult to obtain a product which is pure or which is free from impurities. This could be reduced by careful precipitation and sufficient washing.

Advantages of Gravimetric Analysis

a- Accurate and precise: Gravimetric analysis is potentially more accurate and more precise than volumetric analysis.

b- Possible sources of errors can be checked: Gravimetric analysis avoids problems with temperature fluctuations, calibration errors, and other problems associated with volumetric analysis.
c- It is an ABSOLUTE method.

Disadvantages of Gravimetric Analysis

a- There are potential problems with gravimetric analysis that must be avoided to get a good result.
b- Proper lab technique is critical.
c- Careful and time consuming.
d- Scrupulously clean glassware.
e- Very accurate weighing.

Properties of Precipitate

a- The precipitate should be so insoluble that no significant loss occurs during filtration and washing.
b- Physical nature of precipitate should be such that it can be easily separated by filtration.
c- The precipitate should be stable to atmospheric conditions.
d- The precipitate must be convertible to pure compound of definite composition, either by ignition or by simple chemical operations such as evaporations.
e- Have large crystals (Easier to filter large crystals).

Process of Precipitation

Precipitation is a most important step in gravimetric analysis.it is Involves both physical and chemical process, the physical process consists of three steps;
1- Super saturation: the solution phase contains more dissolved salt than at equilibrium. The driving force will be for the system to approach equilibrium (saturation).
2- Nucleation: initial phase of precipitation. A minimum number of particle will gather together to form a nucleus of particle or precipitate (solid phase). Nucleation involves the formation of ion pairs and finally a group of ions formed. The greater rates of nucleation take place at a higher degree of super saturation.

3- Crystal growth: particle enlargement process. Nucleus will grow by deposition of particles precipitate onto the nucleus and forming a crystal of a specific geometric shape. Crystal growth involved two steps diffusion of ion to surface of nucleus and deposition on surface.

Particle Size and Filterability of Precipitates

Precipitates made up of large particles are generally desirable in gravimetric work because large particles are easy to filter and wash free of impurities. In addition, such precipitates are usually purer than are precipitates made up of fine particles. Three types of precipitates are produced Crystalline, Curdy and gelatinous etc.

Co-Precipitation

Co-precipitation is the phenomenon in which soluble compounds are removed from solution during precipitate formation.

There are four types of co-precipitation:

1) Surface adsorption,
2) mixed-crystal formation,
3) Occlusion,
4) Mechanical entrapment Surface adsorption and mixed crystal formation are equilibrium processes, whereas occlusion and mechanical entrapment arise from the kinetics of crystal growth.

Coagulation of Colloids

Coagulation can be hastened by heating, stirring, and adding an electrolyte to the medium. Colloidal suspensions are stable because all the particles present are either positively or negatively charged. This charge results from cations or anions that are bound to the surface of the particles. The process by which ions are retained on the surface of a solid is known as adsorption. We can readily demonstrate that colloidal particles are charged by observing their migration when placed in an electrical field.

Mechanism of Precipitation

Induction period. The time before nucleation occurs after the addition of the precipitating agent to the solution, May range from milliseconds to several minutes.

Nucleation

Formation of small, stable aggregates or nuclei of precipitate. Nuclei have sizes down to ~1 nm, composed of a few atoms, and there may be up to 1010 nuclei per mole of analyte. Excess ions from solution collect around the nuclei. Silver nitrate is added very slowly to an acidic solution containing chloride. Silver chloride nuclei formed with a surface layer of ions. The "charged" AgCl particles (or colloidal particles) repel each other. Nucleus of AgCl(s) colloid Primary Adsorbed Ag+ Loosely associated counter ion Illustration of an Electrical Double Layer Homogeneous solution (charges balanced).

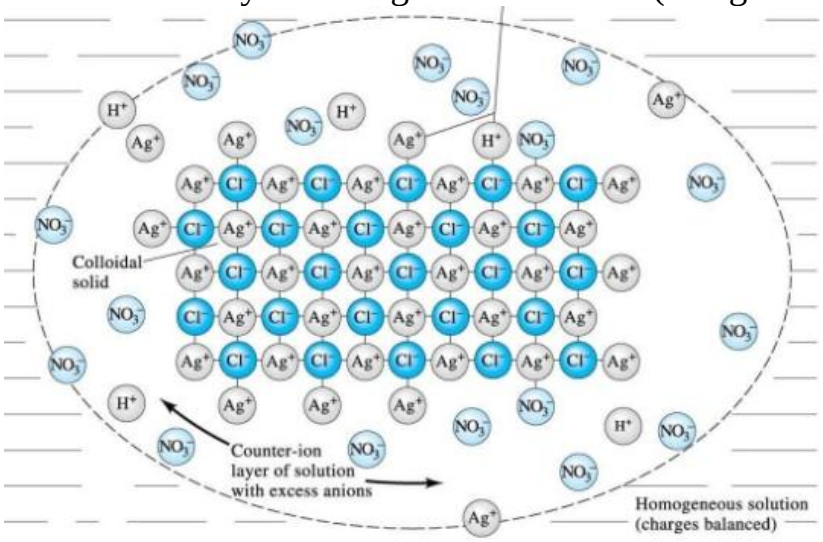


Figure 9-1 Colloidal suspensions of an electrostatic layer for AgCl-NO_3^-

In addition to the primary adsorbed silver ions, some nitrate ions forms an electrostatic layer around the nucleus. These counter ions tend to aggregate around the [AgCl:Ag]+ center because these centers have a net positive charge (excess Ag+) and additional negative charge is required to maintain electrical neutrality. Counter ions are less tightly held than the primary adsorbed ions and the counter ion layer is somewhat diffuse and contains ions other than those of the counter ions. These layers of charged ions associated with the surface of the nuclei are known as the electric double layer.

Adsorption

Adsorption is a process in which a substance (gas, liquid, or solid) condenses onto the surface of a solid. The electric double layer of a colloid consists of a layer of charge associated with the surface of the particles and a layer with a net opposite charge in the solution surrounding the particles. A colloid is a finely divided particle (typically with diameters from 10 nm to 1 μm) that forms a stable dispersion within a medium (air or liquid).

Digestion

Heating the precipitate within the mother liquor (or solution from which it precipitated) for a certain period of time to encourage densification of nuclei. During digestion, small particles dissolve and larger ones grow (Ostwald ripening). This process helps produce larger crystals that are more easily filtered from the solution.

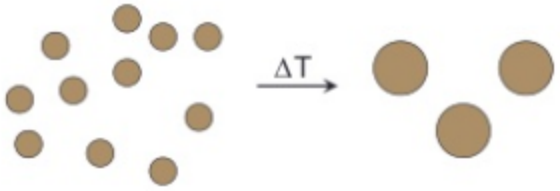


Figure 9-2 process of growth large crystals

Precipitation process (Von Weimarn eq.)

Von Weimarn showed that particle size of precipitates is inversely proportional to the relative supersaturation of the solution during precipitation.

Relative supersaturation = (Q-S)/S.

Where Q is the molar concentration of mixed reagents before any precipitation occurs (Keep it low by using dilute solutions, stirring mixture well, add reactants slowly)

S is the molar solubility of the product (precipitate) when the system has reached equilibrium. (Keep it high with high temperatures, adjusting pH).

For the best possible results, conditions need to be adjusted such that Q will be as low as possible and S will be relatively large during the precipitation process, The von Weimarn Ratio (The lower the better).

= (Q – S)/S

Measure of relative supersaturation or supersaturation ratio, if high; get excessive nucleation, lots of small crystals, large surface area. If low; get larger, fewer crystals, small surface area.

What Factors Determine Particle Size?

The particle size of solids formed by precipitation varies enormously. At one extreme are colloidal suspension, whose tiny particles are invisible to the naked eye (10^{-7} to 10^{-4} cm in diameter). Colloidal particles show no tendency to settle from solution, nor are they easily filtered. At the other extreme are particles with dimensions on the order of tenths of millimeter or greater. The temporary dispersion of such particles in the liquid phase is called a crystalline suspension. The particles of a crystalline suspension tend to settle spontaneously and are readily filtered.

The particle size of a precipitate is influenced by experimental variables as precipitate solubility, temperature, reactant concentrations, and the rate at which reactants are mixed. The particle size is related to a single property of the system called its relative super-saturation, where relative super-saturation = (Q – S)/ S. In this equation, Q is the concentration of the solute at any instant and S is its equilibrium solubility. When (Q – S)/ S is large, the precipitate tends to be colloidal. When (Q – S)/ S is small, a crystalline solid is more likely.

Steps of a gravimetric analysis:

Gravimetric analysis involved several steps which including: Preparation of the solution, Precipitation, Digestion, Filtration, Washing, Drying or ignition, Weighing and Calculations.

1. Preparation of Analyte Solution.

Gravimetric analysis usually involves precipitation of analyte from solution in two steps:

1st step- Sampling; Representative of bulk

2nd step- prepare the analyte solution (Dissolution).

May need:

a- preliminary separation to separate potential interferences before precipitating analyte.

b- Adjustment of solution condition (pH/temp/vol/conc of test substance) to maintain low solubility of precipitate & max precipitate formation. Eg. Calcium oxalate insoluble in basic medium

c- Most of the substances are readily solutes in water and can be used as such. Some required special treatment as treatment with HCl, HNO_3, Aquilegia or fusing with basic flux.

2. Precipitation process

The precipitating reagent is added at a concentration that favors the formation of a "good" precipitate. This may require low concentration, extensive heating (often described as "digestion"), or careful control of the pH. A large excess of precipitant should be avoided because this increases chances of adsorption on precipitating. Test for completeness of precipitating. No new precipitating should be formed after addition of drop of precipitating agent.

3. Digestion of the Precipitate

Let the precipitate stand in contact with mother liquor (the solution from which it was precipitated), usually at high temp. This process is called digestion, or ostwaldripening. The small particles tend to dissolve and precipitate on the surfaces of the larger crystals reduce surface contamination, reduce crystals imperfection.

4- Filtration

Sintered glass crucibles are used to filter the precipitates. The crucibles first cleaned thoroughly and then subjected to the same regimen of heating and cooling as that required for the precipitate. This process is repeated until constant mass has been achieved, that is, until consecutive weighing differs by 0.3 mg or less. The filer Media are use; Filter papers; e.g ash less filter papers – No 41 (Fast), 40 (Medium), 42(Slow).

5- Washing

Co-precipitate impurities, especially these on the substance can be removed by washing the precipitate. Wet Precipitate with mother liquid and which will also be removed by washing. Some precipitate cannot be washed with pure water, peptization occurs (reverse of

coagulation), eg: HNO_3 and NH_4NO_3 is used for washing AgCl precipitate

6- Drying or ignition

To remove solvent and wash electrolytes. a heating at 110 to 120°C for 1 to 2 hours done. it is Converts hygroscopic compound to non- hygroscopic compound. May used high temp if precipitate must be converted to a more suitable form before weighing, eg. $MgNH_4PO_4$ convert to pyrophosphate $Mg_2P_2O_7$ by heating at 900°C.

Weighing

After the precipitate is allowed to cool (preferably in a desiccator to keep it from absorbing moisture), it is weighed (in the crucible) using properly calibrated analytical balance (Good weighing technique).

Impurities in Precipitates

1- Co-precipitation.

Co-precipitaion is the precipitation of an unwanted species along with your analyte of interest which occurs to some degree in every gravimetric analysis. A major factor for precipitations of barium sulfate and those involving hydrous oxides and cannot be avoided, but can be minimized by careful precipitation and washing of the precipitate.

2- Surface adsorption: Unwanted material is adsorbed onto the surface of the precipitate. Digestion of a precipitate reduces the relative surface area and, therefore, the area available for adsorption of impurities. Washing can remove impurities bound to the surface.

3- Occlusion

Occlusion is a type of co-precipitation in which impurities are trapped within the growing crystal.

4- Post-precipitation

Sometimes a precipitate in contact with the mother liquor is contaminated by the precipitation of an impurity.

5- Inclusion

Inclusion is a type of coprecipitation in which the impurities occupy the crystal lattice sites.

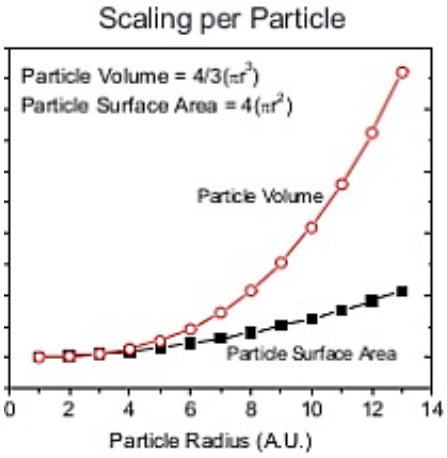


Figure 9-3 relationship between partial volume and particle surface area

6- Peptidization

A procedure where the precipitate is washed and filtered, but part of the precipitate reverts to the colloidal form because supporting electrolyte is gone. Cooling the system with an ice- water bath minimizes loss of precipitate due to dissolution.

AgCl (s) → AgCl (colloid)

Increasing Purity

1- Re-precipitation

A procedure including washing away the mother liquor, redissolving the precipitate, and precipitating the product again

2- Drying the solid

Generally, the solids are dried at 120 ^{o}C, but conditions for drying can vary considerably.

3- Precipitation in the presence of electrolyte

Columbic repulsion is diminished in the presence of electrolyte because of a compression of the volume of the ionic atmosphere.

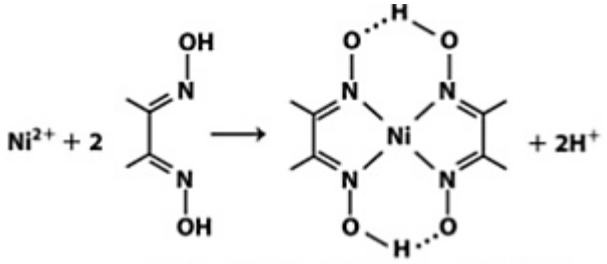
4- Digestion

Raising the temperature will increase the collision energy for colloidal particles and overcome Columbic repulsion, leading to formation of larger particles

Ex1: Ni in Steel

To measure Ni in steel, the alloy is dissolved in 12 M HCl and neutralized in the presence of citrate ion, which maintains iron in

solution. The slightly basic solution is warmed and dimethylglyoxime (DMG) is added to precipitate the red DMG-nickel complex quantitatively. The product is filtered, washed with cold water, and dried at 110 °C.



Precipitate

Organic precipitating agents have the advantages of giving precipitates with very solubility in water and a favorable gravimetric factor. Most of them are chelating agents that forms slightly insoluble, uncharged chelates with the metal ions.

Table 9-1 methods for homogeneous generation of precipitating agent

Methods for Homogeneous Generation of Precipitating Agents

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

Gravimetric Calculations

The result of a gravimetric determination usually is reported as a percentage of analyte.

$$\%\ A = \frac{\text{Weight A}}{\text{Weight of Sample}} \times 100$$

Two values are needed: the weight of the analyte and the weight of the sample. To calculate the weight of analyte from the weight of the

precipitate a gravimetric factor (GF) is used. The GF, is the weight of analyte per unit weight of precipitate.

$$GF = \frac{a}{b} \times \frac{\text{F. wt. Analyte}}{\text{F. wt. Precipitate}}$$

a,b: mole of analyte and precipitate.

$$\%A = \frac{\text{Weight of Precipitate} \times GF}{\text{Weight of Sample}} \times 100$$

Questions and Answer

Q1. If Cl_2 in a sample was converted to chloride and precipitated as AgCl. what is the weight of Cl_2 that gives 1g of AgCl?

Sol.

F.wt Cl = 35.453, F.wt Ag = 107.868

GF = F .wt analyte (g/mol) x a (mol analyte/mol precipitate)

F. wt precipitate (g/mol) b = g analyte/ g precipitate

GF = F.wt analyte (g/mol) x a (mol analyte/mol precipitate)

F.wt precipitate (g/mol) b = g analyte/ g precipitate

g Cl_2 = g AgCl x F.wt analyte (g/mol) x a

F.wt precipitate (g/mol) b = 1 AgCl x 70.906 g/mol x 1 mol

143.321 g/mol 2 mol = 0.2474 g

Q2. Calculate the gravimetric factor for each of the following:

P $\rightarrow Ag_3PO_4$, $K_2HPO_4 \rightarrow AgPO_4$, $Bi_2S_3 \rightarrow BaSO_4$, $As_2O_3 \rightarrow Ag_3AsO_4$, $K_2O \rightarrow KB(C_6H_5)_4$

Sol.

P/Ag_3PO_4 = atwt P/ Mwt Ag_3PO_4

K_2HPO_4/Ag_3PO_4= Mwt K_2HPO_4/MwtAg_3PO_4

Bi_2 S_3/BaSO4 = MWt Bi_2S_3/3MWt $BaSO_4$

As_2O_3/ Ag_3AsO_4 = Mwt As_2O_3/2MWt Ag_3AsO_4

$K_2O/KB(C_6H_5)_4$ = Mwt K_2O/ 2MWt $KB(C_6H_5)_4$

Q3. Orthophosphate ($PO4^{3-}$) is determined by weighing as ammonium phosphomolybdate, (NH_4) $PO_4.12MoO_3$. Calculate the percent P in the sample and the percent P_2O_5 if 1.1682g precipitate were obtained from a 0.2711 g sample.

Remember: Wt of analyte = Wt of ppt × Gravimetric Factor

$$wt\ of\ P = 1.1682 \times \frac{At.wt\ P}{\text{Mwt}\ (NH_4)3PO_4.3MoO_4}$$

$$= 1.1682 \times \frac{30.97}{1876.5} = 0.0193g$$

% P = (0.0193/0.2711) x 100 = 7.11%

$$\%P_4O_4 = \frac{1.1682 \times \frac{At.wt\ P}{2\text{Mwt}\ (NH_4)3PO_4.3MoO_4}}{0.2711} \times 100$$

$$= \frac{1.1682 \times \frac{141.95}{2 \times 1876.5}}{0.2711} \times 100 = 16.30\%$$

Q4. An ore is analyzed for the manganese content by converting the manganese to Mn_3O_4 and weighing it. If a 1.52 g sample yields Mn_3O_4 weighing 0.126g, what would be the percent Mn and Mn_2O_3 in the sample?

$$\%Mn_2O_3 = \frac{0.126 \times \frac{3\ \text{Mwt}\ Mn_2O_3}{2\ \text{Mwt}\ Mn_3O_4}}{1.52} \times 100$$

$$= \frac{0.126 \times \frac{3\ (157.9)}{2\ (228.8)}}{1.52} \times 100 = 8.58\%$$

$$\%\ Mn = \frac{0.126 \times \frac{3\ \text{At.wt Mn}}{\text{Mwt}\ Mn_3O_4}}{1.52} \times 100$$

$$= \frac{0.126 \times \frac{3\ (54.94)}{228.8}}{1.52} \times 100 = 5.97\%$$

Q5. If Cl_2 in a sample is converted to chloride and precipitated as AgCl, the weight of Cl_2 that gives 1g of AgCl is? F.wt Cl = 35.453, F wt Ag = 107.868

Sol.

GF = F.wt analyte (g/mol) x a (mol analyte/mol precipitate)

f wt precipitate (g/mol) b = g analyte/ g precipitate

GF = F.wt analyte (g/mol) x a (mol analyte/mol precipitate)

F.wt precipitate (g/mol) b = g analyte/ g precipitate
g Cl_2 = g AgCl x F.wt analyte (g/mol) x a
f wt precipitate (g/mol) b = 1 AgCl x 70.906 g/mol x 1 mol • 143.321 g/mol 2 mol = 0.2474 g.

Q6. Why does the procedure call for a sample containing no more than 60 mg of Mg^{2+}?
Sol.
A 60-mg portion of Mg^{2+} generates approximately 600 mg of $MgNH_4PO_4$.$6H_2O$. This is a substantial amount of precipitate. A larger quantity of precipitate may be difficult to filter and difficult to adequately rinse free of impurities.

Q7. Why is the solution acidified with HCl before adding the precipitant?
Sol.
The HCl ensures that $MgNH_4PO_4.6H_2O$ does not immediately precipitate when adding the precipitant. Because PO_4^{3-} is a weak base, the precipitate is soluble in a strongly acidic solution. If the precipitant is added under neutral or basic conditions. the resulting precipitate consists of smaller, less pure particles. Increasing the pH by adding base allows the precipitate to form under more favorable conditions.

Q8. To determine the amount of magnetite, Fe3O4, in an impure ore, a 1.5419- g sample is dissolved in concentrated HCl, giving a mixture of Fe^{2+} and Fe^{3+}. After adding HNO_3 to oxidize Fe^{2+} to Fe^{3+} and diluting with water, Fe^{3+} is precipitated as $Fe(OH)_3$ by adding NH_3. Filtering, rinsing, and igniting the precipitate provides 0.8525 g of pure Fe_2O_3. Calculate the %w/w Fe_3O_4 in the sample.
Sol.
A conservation of mass requires that all the iron from the ore is found in the Fe_2O_3. We know there are 2 moles of Fe per mole of Fe_2O_3 (FW= 159.69 g/mol) and 3 moles of Fe per mole of Fe_3O_4 (FW= 231.54 g/mol); thus

$$0.8525\ \text{g}\ Fe_2O_3 \times \frac{2\ \text{mol Fe}}{159.69\ \text{g}\ Fe_2O_3} \times \frac{231.54\ \text{g}\ Fe_3O_4}{3\ \text{mol Fe}} = 0.82405\ \text{g}\ Fe_3O_4$$

The % w/w s Fe_3O_4 in the sample, therefore, is

$$\frac{0.82405\ \text{g}\ Fe_3O_4}{1.5419\ \text{g sample}} \times 100 = 53.44\%\ \text{w/w}\ Fe_3O_4$$

Q9. A 200.0-mL sample of water was filtered through a pre-weighed glass fiber filter. After drying to constant weight at 105 o C, the filter was found to have increased in mass by 48.2 mg. Determine the sample's total suspended solids. Solution A ppm is equivalent to a mg of analyte per liter of solution; thus, the total suspended solids for the sample is

$$\frac{48.2\ \text{mg solids}}{0.2000\ \text{L sample}} = 241\ \text{ppm solids}$$

Q10. A sample of slag from a blast furnace is analyzed for SiO_2 by decomposing a 0.5003 g sample with HCl, leaving a residue with a mass of 0.1414 g. After treating with HF and H_2SO_4, and evaporating the volatile SiF_4, a residue with a mass of 0.0183 g remains. Determine the %w/w SiO2 in the sample.

Sol.

In this procedure the difference in the residue's mass before and after volatilizing SiF4 gives the mass of SiO_2 in the sample; thus the sample contains

$$0.1414\ \text{g} - 0.0183\ \text{g} = 0.1231\ \text{g}\ SiO_2$$

and the %w/w SiO_2 is

$$\frac{0.1231\ \text{g}\ SiO_2}{0.5003\ \text{g}} \times 100 = 24.61\%\ \text{w/w}\ SiO_2$$

CHAPTER TEN
Spectrophotometry and Beer's Law

CHAPTER TEN
SPECTROPHOTOMETRY AND BEER'S LAW

Introduction

Instrumental analysis testing uses a wide variety of chemical techniques and deferent methods for analysis. This technique is using in many fields such as environment, agriculture and others. Clinical laboratory testing allows us to answer commonly asked questions such as level of cholesterol and diabetes mellitus. Some of the laboratory tests use simple techniques as spectrophotometry method. Other processes involve complex equipment and computer analysis of the data in order to perform measurements on large numbers of patient samples.

Instrumental Methods

Measurement of physical properties of analylets such as conductivity, electrode potential, **light absorption** or emission, mass-to-charge ratio, and fluorescence. began to be employed for quantitative analysis of inorganic, organic, and biochemical anaylets. Efficient chromatographic separation techniques are used for the separation of components of complex mixtures. Instrumental Methods of analysis (collective name for newer methods for separation and determination of chemical species).

Regions of electromagnetic spectrum

Distribution of the continuum of all radiant energies can be plotted either as a function of wavelength or of frequency in a chart known as the electromagnetic spectrum. It ranges from shorter wavelengths (including X-rays and gamma rays) to longer wavelengths (microwaves and radio waves). The electromagnetic waves are grouped into types that have similar wavelengths and so have similar properties. Electromagnetic waves form a continuous series in order of changing wavelength, frequency and energy. This series is called the electromagnetic spectrum. Gamma rays, X-rays, ultraviolet visible light infrared microwaves radio waves 0.01nm to 100nm

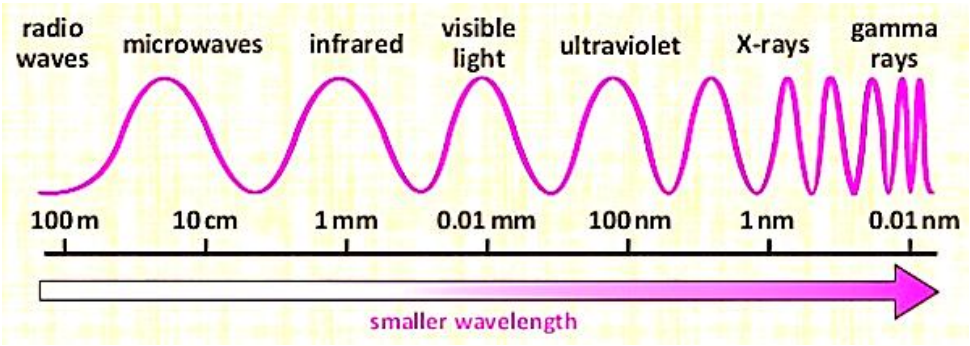


Figure 10-1 Electromagnetic spectrum

The process of separating the constituent colours in white light is known as dispersion, the light which our eyes, our sensors can detect is part of the visible spectrum. Some remote sensing instruments also detects radiations invisible to our eyes. Range of visible wavelength is from 0.4µm to 0.7µm, longest visible wavelength is red and shortest is violet.

The following figure clarify the visible region (400-800 nm) in the electromagnetic spectrum.

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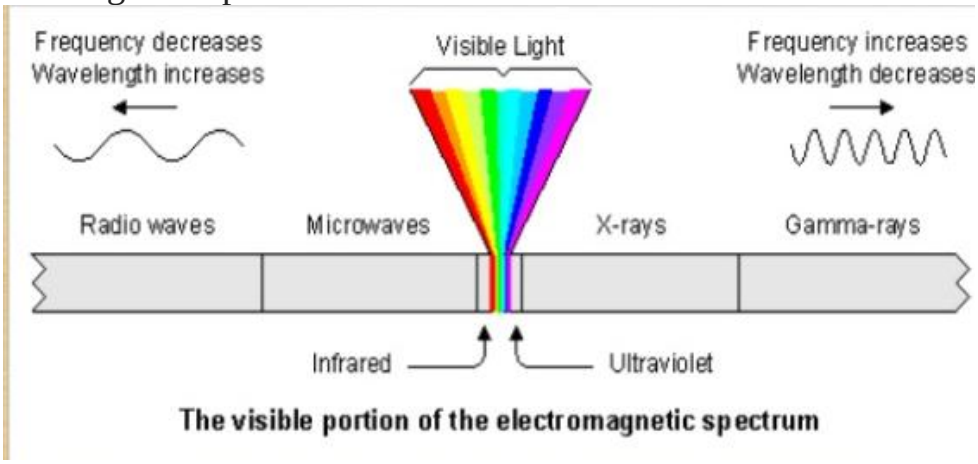


Figure 10-2 the visible portion of the electromagnetic spectrum

In general, the atoms and molecules that contain an unsaturated outer orbit covered by another electronically saturated orbit absorb the UV and visible UV rays which are falling on them, thereby quantifying and quantifying using these absorbed rays.

Quantitative Spectroscopy

Quantitative spectroscopy is one of the quickest and easiest ways to determine how many atoms or molecules are present in a sample. This is because the interaction of light with matter is a stoichiometric interaction. At any given temperature, the same number of photons will always be absorbed or emitted by the same number of atoms or molecules in a given period of time. This makes spectroscopy one of the few techniques that can provide a direct measure of the number of atoms or molecules present in a sample.

General Information

a- Matter interacts with light by absorbing and transmitting different wavelengths.
b- The specific nature of the interaction depends on a compound's molecular structure.
c- Many solutions have distinctive colours
d- Absorb/transmit different wavelengths of visible light
e- Intensity of colour is an indication of the solution's concentration
f- More concentrated = darker colour.

Spectrophotometry

A quantitative method of studying matter and studies amount of light transmitted/absorbed by matter.
Spectrophotometry quantitatively describes either the transmittance or absorbance of light by a substance.
The optimal light wavelength to use for analysis is denoted λ_{max}, and the wavelength at which maximal light absorbance occurs.

Negative Control

Other compounds in a solution (or the solvent itself) may absorb the same wavelengths as the compound being analyzed, this can complicate analysis.
Negative control = reference blank
Reference blank contains everything found in the sample solution, except the substance and being analyzed calibrates the absorbance reading to A=0.000

Q: Explain the significance of preparing a reference blank, and using it to calibrate the spectrophotometer.

Simplified shape of spectrophotometer;

The advice consists of many parts;

Light source; Tungsten Lamp, Tungsten Halogen Lamp, it is the most common light source used in spectrophotometer. This lamp consists of a tungsten filament enclosed in a glass envelope, with a wavelength range of about 330 to 900 nm, are used for the visible region.

Monochromator; Prism is type of dispersion device. Prism is used to isolate different wavelength. If a parallel beam of radiation falls on a prism, the radiation of two different wavelengths will be bent through different angles. Prism may be made of glass or quartz.

Absorption cells (Cuvettes); A cuvette is a kind of cell (usually a small square tube) sealed at one end, made of Plastic, glass or optical grade quartz and designed to hold samples for spectroscopic experiments. Cuvette should be as clear as possible, without impurities that might affect a spectroscopic reading

Photoresister tube(detector); Detectors Any photosensitive device can be used as a detector of radiant energy. The photocell and phototube are the simplest photodetectors, producing current proportional to the intensity of the light striking Them. The figure below declares that;

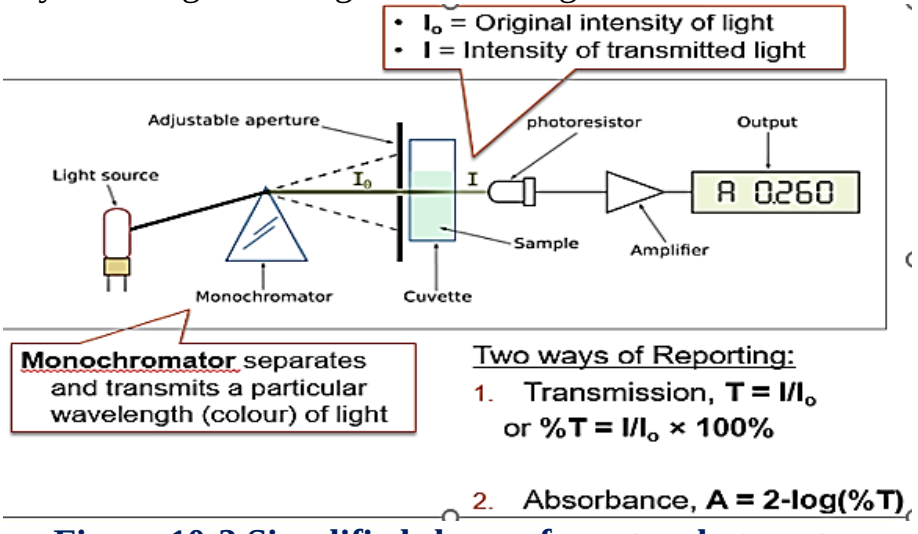


Figure 10-3 Simplified shape of spectrophotometer

Choosing a Wavelength.

use wavelength at which most light is absorbed (λ_{max}). Both organic and inorganic materials have a specific absorption in the regions of the chromogenic spectrum, and the highest wavelength, which represents the highest absorption of the material at this wavelength λ_{max} , can be chosen as in the following figure; .

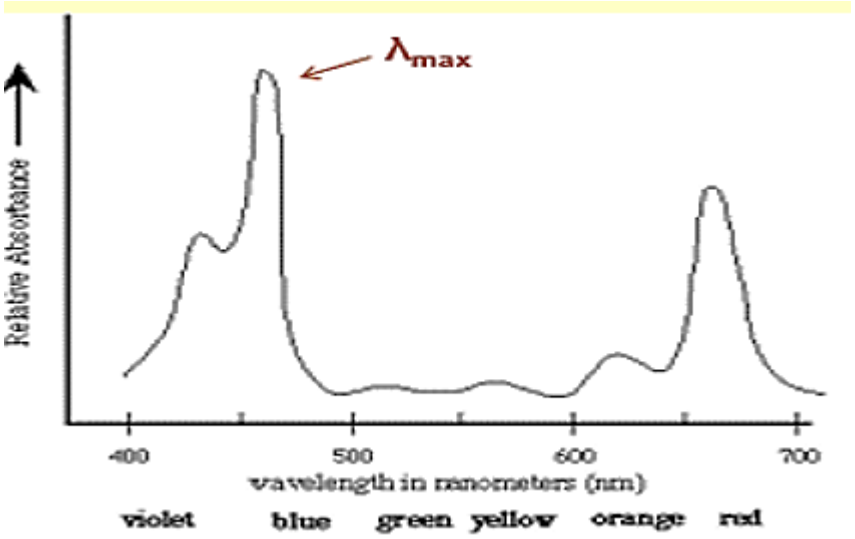


Figure 10-4 choosing λ_{max}

q1) what is the (max) for this compound? An: 450 nm

q2) what color light would you use to analyze compound? An: violet-blue

q3) what color dose this solution appear observe ? An: greenish-yellow(these colors are tranmited right through)

Lambert's Law

If material bodies are exposed to radiation, part of the incident radiation is absorbed, a part is scattered and a part is transmitted. As a result of absorption the intensity of light passing through material bodies, i.e. the intensity of transmitted light, decreases. The fraction of incident light absorbed depends on the thickness of the absorbing medium. Lambert derived a quantitative relationship between the decrease in intensity of a monochromatic light due to the passage

through a homogeneous medium of thickness dx and the intensity of light I. This law is known as Lamberts law, and may be stated as The decrease in intensity of light with thickness of the absorbing medium at any point is directly proportional to the intensity of light. Monochromatic light x, Incident beam Intensity I_o, Absorbing solution concentration c, Emergent beam Intensity I. as show in figure below;

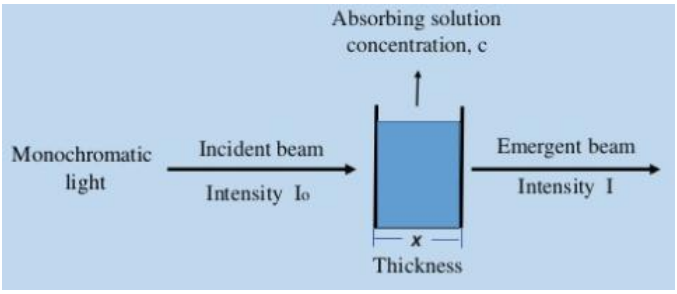


Figure 10-5 Lamberts law

Beer's Law

There are at least five conditions that must be met in order for implement Bear's law:

1. The absorbent materials in the solution must be separated.
2. The absorption medium should be uniformly distributed across the total volume and the radiation should not be scattered. Falling radiation must consist of parallel rays, each of which travels the same distance in the absorbent medium.
3. The incident light must be monochromatic, or at least have a narrower width than the absorbent medium.
4. The falling of optical flow should not affect the atoms or molecules; it should only be the excitation of the studied particles. To set the calibration curve, fix the λmax when measuring the absorbance of different concentrations of the matters.

5- Beer's Law is used for dilute solutions.

Describe the relationship between the absorbance of solution and its concentration

- Beer's Law states that a substance's absorbance value is directly proportional to its concentration.

if absorbance can be measured, it can be used to determine the concentration of an unknown solution.

A= ε LC

A= Measured absorbance, ε = molar absorptivity constant.

ε= Proportionality constant known as the molar absorptivity with units of ($M^{-1}cm^{-1}$). (depends on combination of solute/ solvent/ λ)

L= length of bath traveled by light (, is usually expressed in cm (as this is the most convenient, given the scale of the instrument)

C- Concentration of the absorbing species, mol/L

Q: can you deduce the units of the molar absorptivity constant, ε? Absorption is a unitless quantity

there is a direct relationship between absorbance and concentration.

empirical evidence: prepare solutions of known concentration and analyze them at λmax: plot of absorbance vs. concentration is linear as in figure below;

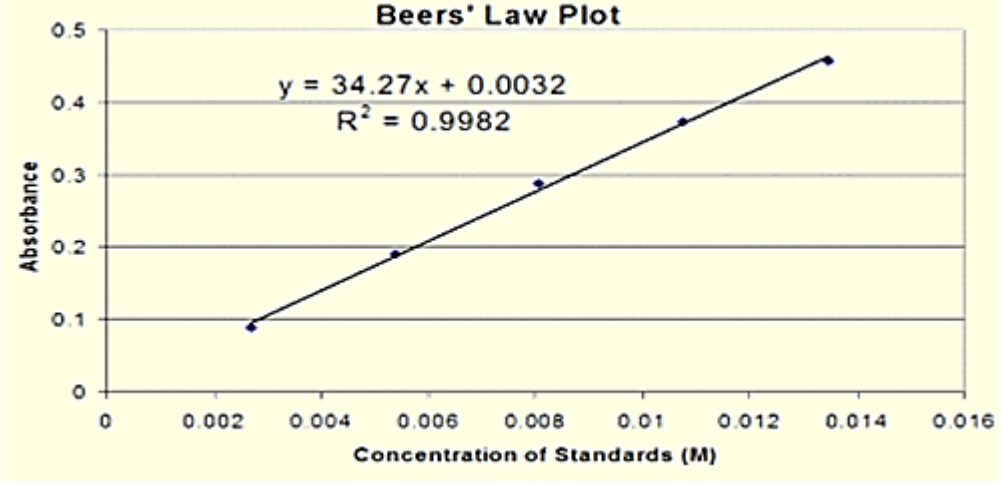


Figure 10- 6 Beer's Law using equation of line

Since A is a linear function of C,

Equation of line **A= mx+ b, A= ε LC**

Slop of best-fit line=ε L (**look to chapter thirteen**).

Using Spectrophotometry and Beer's Law to find concentration of an unknown

familiarize yourself with the three methods by which Beer's Law can be used to determine the concentration of an unknown solution.

Method 1; graphing;

Part A; prepare of standard plot

1- prepare a plot A vs. C for standard solution

2- determine of equation of line.

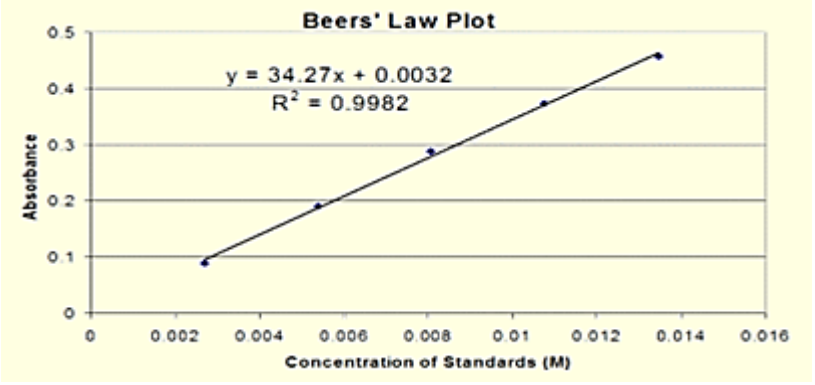
Part B; ID that unknown concentration.

3- measure absorbance of unknown solution.

4- use measurement and equation to solve for concentration unknown.

Example 1:

Use the plot to determine the concentration of a solution that has an absorbance of A = 0.25.



Recall, Y= A and X= C

Sol.

Equation of fit-best line= y= 34.27x + 0.0032

Substitute y= 0.25 and solve x

X= 0.0072m/l = c

Method 2: Proportionality

Beer's law tells us that absorption is proportional to concentration, therefore…

A1/A2 = C1/C2

Example 2:

Calculate the concentration of a solution $CoCl_2$ that has an absorbance value of 0.400 at λmax, if a 5.00×10^{-3} mol/L solution of $CoCl_2$ has an absorption of 0.175 under the same conditions.

Sol.:
A1/A2= C1/C2
Subsisted:
C2= 0.0114mol/L

Method 3: Just use the Beer's Law equation
seems simple, but ε is usually not readily available

Example 3: The molar absorptivity of ethanal in hexane at its λ_{max} is 15 $L*cm^{-1}*mol^{-1}$. Calculate the concentration of ethanal in a solution that has an absorbance of 0.652 with a path length of 1.2 cm.

Sol.: $A = \varepsilon L c$
Subsisted = 0.036 mol/L

Deviation from Bear's Law

Reasons for deviating from Bear's law:

1. The interaction or effect of solute molecules with each other, forming polymers, meaning that the greater the concentration, the greater the number of polymers, and thus the absorbance decreases, ie, a negative deviation from the Bear law.
2. It deflects when the particles are ionized by the solute.
3. The solute molecules interact with the solvent molecules such as:

$Cr_2O_7^{-2} + H_2O \leftrightarrow 2CrO_4^{-2} + 2H^+$

Yellow solvent solute (orange)

4. One of the causes of the deviation is the use of a non-monochromatic ray or spectrum, i.e. that contains linear impurities, in this case a curve occurs to the bottom (negative deviation). And the reason for this deviation is that the exit opening of the spectrum is relatively large and the smaller the exit hole the outside spectrum is Purer monochromatic more.

Limitation of Beer-Lamber's law:

1- The electromagnetic radiation should be monochromatic.
2- The light beam should not be scattered.
3- The solution should be diluted.

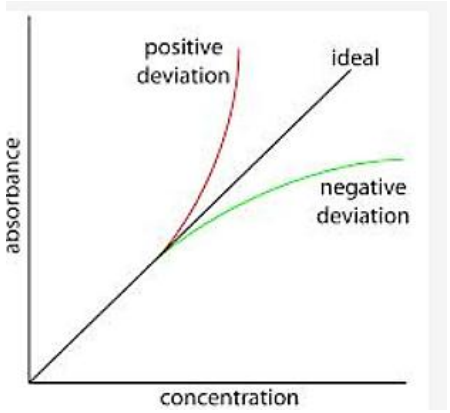


Figure 10-7 the deviation of Bear's law

Questions and Answer

Q1. An aqueous solution of copper sulfate is a clear blue colour. The concentration of this solution is to be measured using UV-visible spectroscopy. An aqueous copper sulfate solution will

a. absorbs mainly red light and therefore allow red light to pass through the solution.

b. absorbs mainly red light and therefore allow blue light to pass through the solution.

c. absorbs mainly blue light and therefore allow red light to pass through the solution.

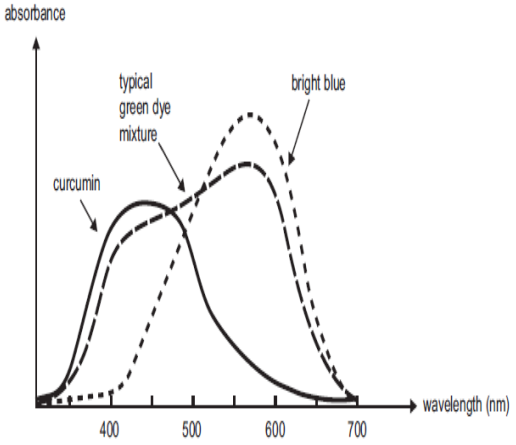
d. absorbs mainly blue light and therefore allow blue light to pass through the solution.

Q2. A green dye used to colour tinned peas is made by mixing the yellow chemical, curcumin, with another colouring agent called bright blue. The individual spectra of curcumin, bright blue and a typical green dye are represented below.

UV-visible spectroscopy is used to analyte the curcumin content of tinned peas.

a. Circle the wavelength below which would be best used for absorbance measurements to determine the curcumin content of the peas.

400 nm 450 nm 500 nm 550 nm 600 nm 650 nm



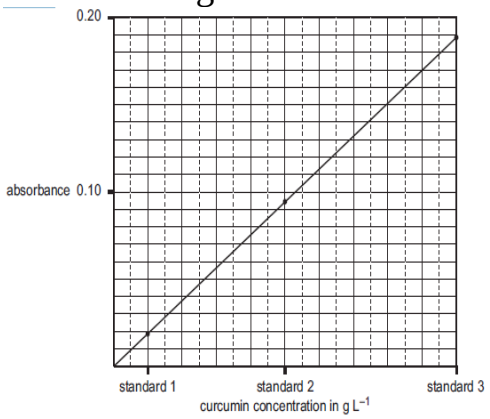
Sol. 400 nm

b. In one analysis, a stock solution of curcumin was prepared by dissolving 0.100 g of curcumin ($C_21H_{20}O_6$; molar mass = 368.0 g mol.1) in 250.0 mL of water.

The stock solution was then diluted to make the following three standard solutions.

standard solution	curcumin concentration in g L^{-1}
standard 1	1.00×10^{-3}
standard 2	5.00×10^{-3}
standard 3	1.00×10^{-2}

The absorbance of the standard solutions at the chosen wavelength were measured and the following calibration line was obtained.



i. Calculate the concentration of curcumin in the stock solution in mol L.1.

Sol.

$$n(\text{curcumin) in stock solution} = \frac{0.100}{368}$$
$$= 2.72 \times 10^{-4} \text{ mol } *$$
$$c(\text{curcumin) in stock solution} = \frac{2.72 \times 10^{-4}}{250.0 \times 10^{-3}}$$
$$= 1.09 \times 10^{-3} \text{ mol L}^{-1} *$$

Alternatively:

$$m(\text{curcumin) in 1 L} = 0.400 \text{ g } *$$
$$n(\text{curcumin) in 1 L} = \frac{0.400}{368}$$
$$= 1.09 \times 10^{-3} \text{ mol } *$$
$$c(\text{curcumin}) = 1.09 \times 10^{-3} \text{ mol L}^{-1}$$

ii. What volume of water must be added to 10.0 mL of the stock solution to make standard 3?

Sol.

$$m(\text{curcumin) in standard 3} = m(\text{curcumin) in 10 mL stock solution}$$
$$= \left(\frac{0.400}{1000}\right) \times 10 \text{ or } \left(\frac{0.100}{250}\right) \times 10$$
$$= 4.00 \times 10^{-3} \text{ g}$$

$$c(\text{curcumin) in standard 3} = 1.00 \times 10^{-2} \text{ g L}^{-1}$$
$$V(\text{stock solution}) = \frac{m(\text{curcumin})}{c(\text{curcumin})}$$
$$= \frac{4.00 \times 10^{-3} \text{ g}}{1.00 \times 10^{-2} \text{ g L}^{-1}}$$
$$= 0.400 \text{ L}$$
$$= 400 \text{ mL } *$$
$$V(\text{water}) = 400 - 10$$
$$= 390 \text{ mL } *$$

iii. The curcumin in a 9.780 g sample of peas was extracted into solution. The solution was Þ ltered and made up to 100 mL in a volumetric ß ask. The absorbance of the solution at the wavelength used in the above calibration was found to be 0.170.

Calculate the curcumin content of the peas in milligram per gram of peas.

Sol. From the graph, an absorbance of 0.170 corresponds to c(curcumin) = 9.00×10^{-3} g L^{-1}

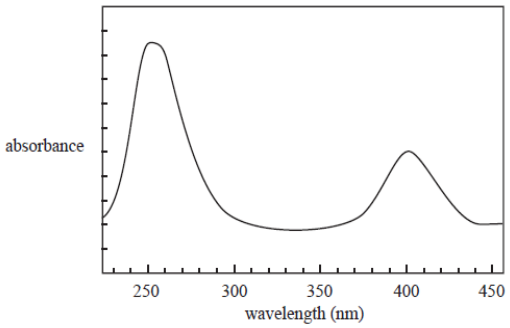
Since the curcumin from the peas was extracted into 100 mL of solution,

$$m(\text{curcumin}) \text{ in peas sample} = 0.100 \text{ L} * \times 9.00 \times 10^{-3} \text{ g L}^{-1}$$
$$= 9.00 \times 10^{-4} \text{ g}$$
$$= (0.900 \text{ mg})$$

$$\text{curcumin content} = \frac{m(\text{curcumin}) \text{ in mg}}{m(\text{peas}) \text{ in g}}$$

$$= \frac{0.900}{9.780}$$
$$= 0.0920 * \text{ mg/g}$$

Q3. The UV-visible spectrum of a solution of a certain compound is shown above. Consider the following statements about this compound and its UV-visible spectrum.



I) The amount of light absorbed by a solution of this compound depends on its concentration.

II) The amount of light absorbed by a solution of this compound depends on the wavelength of light used.

III) The spectrum is a result of electrons falling back from higher to lower electronic energy levels.

IV The concentration of a solution of this compound can only be determined by UV-visible spectroscopy at 250 nm.

Which of the above statements are true?

a. I and II

b. II and III

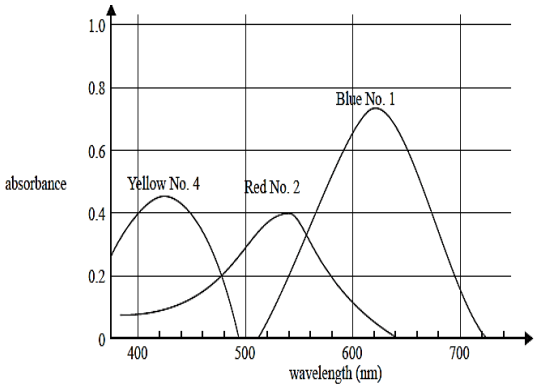
c. I, II and III

d. I, II and IV

Sol. a. Statements I and II were correct. Statement III was incorrect as energy is absorbed during the transition of electrons from lower to higher energy levels. Statement

IV was also incorrect as the spectrum shows two absorbance peaks, at wavelengths of approximately 250 nm and 400 nm. Either of those wavelengths may be used. Ideally the wavelength used should be one at which the compound absorbs strongly but other species in the solution do not.

Q4. The graph shows the absorption spectra of three food dyes: Blue No. 1, Red No. 2 and Yellow No. 4.



Which one of the following is the best wavelength to determine the concentration of Red No. 2 dye in a solution containing a mixture of all three dyes?

a. 430 nm

b. 500 nm

c. 540 nm

d. 620 nm

Sol. b. The best wavelength to use is one where Red No. 2 dye absorbs strongly but no other dye in the mixture does, i.e. 500 nm. According to the absorption spectra provided, Red No. 2 absorbs most strongly at 540 nm. However, because Blue No.1 dye also absorbs significantly at 540 nm, it is not the best wavelength to use.

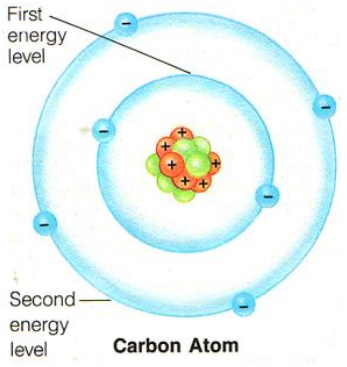
SECTION TWO
CHAPTER ELEVEN
Organic Chemistry

SECTION TWO
CHAPTER ELEVEN
ORGANIC CHEMISTRY

Introduction

Organic Chemistry is the study of the structures, properties, compositions, reactions and preparation of carbon, containing compounds, which include not only hydrocarbons but also compounds with any number of other elements.

Organic compounds are compounds composed of carbon, hydrogen, and often oxygen or nitrogen. Organic compounds are named so because they are associated with living organisms.

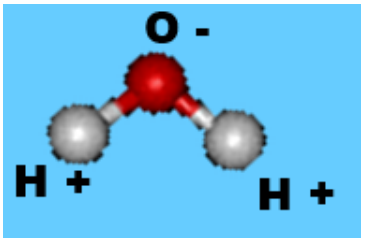


The drawing an electron dot diagram of carbon;

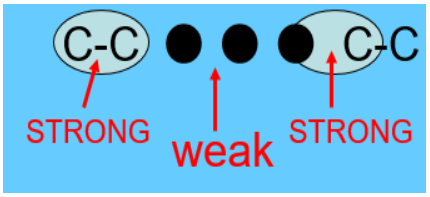
- Carbon has 6 electrons
- 2 filling in first shell
- 4 valence open for bonding
- Gives it versatility
- Typically, covalent bonds

Bonding Schemes:

Carbon is able to form 4 covalent bonds (4 valence electrons) with other carbon or other elements. Characteristics of Organic Compounds are nonpolar compounds; they do not dissolve in polar solvents like water.



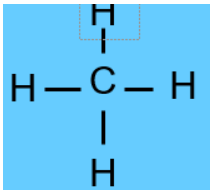
Remember the rule – "likes dissolve likes" They have low melting points due to weak intermolecular forces.



They react slower than ionic compounds – due to strong covalent bonds between atoms.

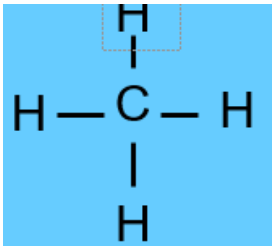
Structural Formulas

A 2D model shows' bonding patterns and shapes of molecules, Carbon is found in the center, the short line represents a pair of electrons.

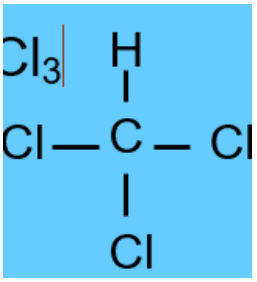


The drawing the structures for each organic:

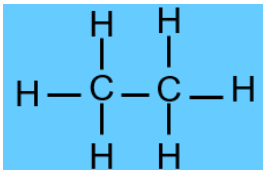
1. Methane: CH_4



2. Chloroform: $CHCl_3$



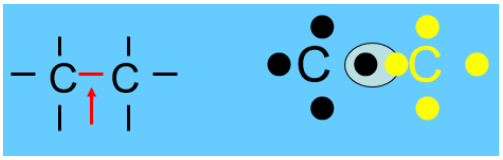
3. Ethane: C_2H_6



Notes: Carbon has 4 bonding sites

Types of Bonds

Single Bond – single covalent bond share 1 pair of electrons (2 e-).



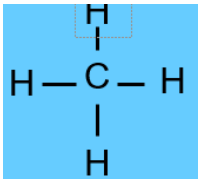
Double Bond – carbon atoms may share 2 pairs of electrons to form a double bond.

Triple Bond – carbon atoms may share 3 pairs of electrons to form a triple bond.

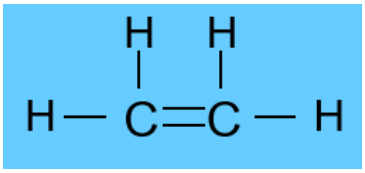
Types of Compounds:

Saturated Compound – organic compounds in which carbon atoms are bonded by single bonds.

ex. Methane: CH_4



Unsaturated Compound – compounds where carbon atoms have double or triple bonds.
ex. Ethene: C_2H_4

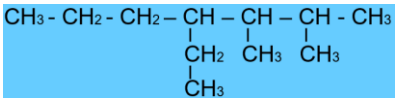


Naming Organic Compounds

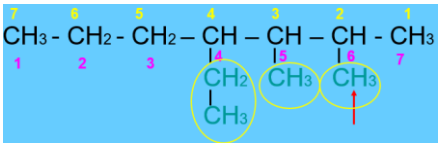
Organic compounds are named according to the IUPAC (international union of pure and applied chemistry) system of nomenclature.
Alkanes – end in… ane
Alkenes – end in... ene
Alkynes – end in… yne

IUPAC Naming Branched Hydrocarbon Chains

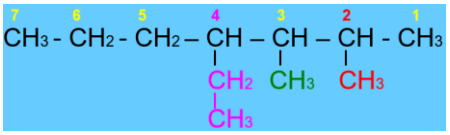
Sometimes the hydrocarbon chains are not straight and sometimes they have other elements attached to them. Here is how they are named:



Step 1: Find the longest continuous chain of carbons.
All bonds in the chain of carbons are single bonds so ending is…ane.
There are 7 continuous carbons, so the parent chain is heptane.

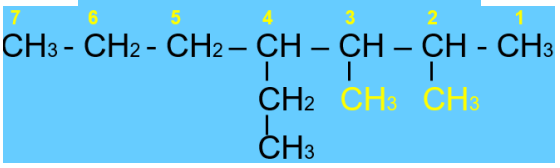


Step 2: Number the carbons in the main sequence starting with the end that will give the attached groups the smallest.
This chain is numbered from right to left because there is a substituent closest to the right.

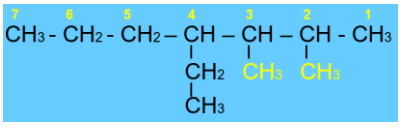


Step 3: Add numbers to the names of the groups to identify their positions on the chain. these numbers become prefixes to the parent chain. In this ex. the positions are:
methyl, 3 - methyl, 4 - ethyl-2
Step 4: Use prefixes to indicate the appearance of a group more than once in the structure.

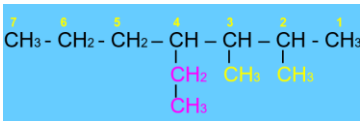
Di	=	twice
Tri	=	three times
Tetra	=	four times
Penta	=	five times



This chain has 2 methyl groups so dimethyl is used.
Step 5: List the alkyl groups in alphabetical order.
In this ex. dimethyl is listed before the ethyl.



Step 6: Use punctuation and use commas to separate numbers
-hyphens to separate numbers with words.



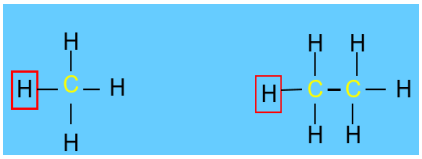
The name of this compound is 2,3-dimethyl – 4-ethyl heptane
Other Organic Compounds.

Functional Groups

A specific grouping of atoms that give characteristic properties to organic compounds.

Alkanes (C_nH_{2n+2}):

Organic compounds can be classified into groups with related structures and properties. As size of molecule increases the boiling and freezing points increase. Hydrocarbons are organic compounds that consist of only Carbon and Hydrogen atoms.

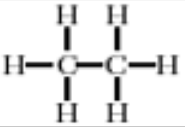


Twice as many hydrogen as Carbone +2, Alkanes = C_nH_{2n+2}.

Q) A saturated hydrocarbon contains 5 carbons, What is the formula?
$C_5H_{12}=C_5H_{2(5)+2}$

Q) A saturated hydrocarbon contains 20 carbons. What is the formula?
$C_{20}H_{2(20)+2} = C_{20}H_{42}$
Saturated = Single

Homologous Series of Hydrocarbons

Name	General Formula	Examples	
		Name	Structural Formula
alkanes	C_nH_{2n+2}	ethane	

Organic Prefixes

Prefix	Number of Carbon Atoms
meth-	1
eth-	2
prop-	3
but-	4
pent-	5
hex-	6
hept-	7
oct-	8
non-	9
dec-	10

CH_4 = methane, C_2H_6 = ethane, C_3H_8 = propane, C_4H_{10} = butane
C_5H_{12} = pentane

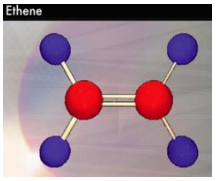
Alkanes-The smaller the compound the Lower Boiling point and Melting point is (less bonds to break) physical properties were illustrated in table below;

Table 11-1. physical properties of Alkanes

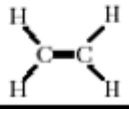
Name	BP (°C)	MP (°C)	Density
Methane	-161.7	-182.6	0.424
Ethane	- 88.6	-172.0	0.546
Propane	- 42.2	-187.1	0.582
Butane	-0.5	-135.0	0.579
Pentane	36.1	-129.7	0.626
Hexane	68.7	- 94.0	0.659
Heptane	98.4	- 90.5	0.684
Octane	125.6	- 56.8	0.703
Nonane	150.7	-53.7	0.718
Decane	174.0	-29.7	0.730

Alkenes (C_nH_{2n}):

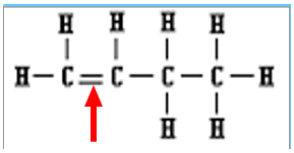
Series of unsaturated hydrocarbons having one double bond (C=C). Also called ethylene series (IUPAC) name is ethane and the general formula C_nH_{2n}.



Homologous Series of Hydrocarbons

Name	General Formula	Examples	
		Name	Structural Formula
alkenes	C_nH_{2n}	ethene	

C_2H_4 = Ethene, C_3H_6 = Propene, C_4H_8 = Buten, C_5H_{10} = Pentene
To find the number of hydrogens, double the number of carbons.
1-Butene

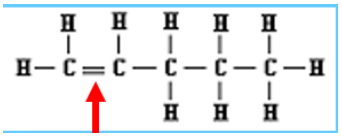


This is 1-butene, because the double bond is between the 1st and 2nd carbon from the end.

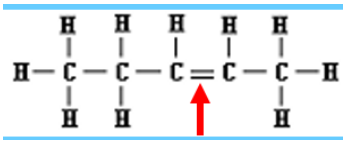
Isomers:

Molecules have the same molecular formula, but have different structural formulas.

Pentene



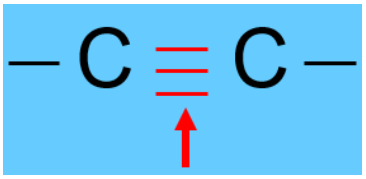
This is 1-pentene. The double bond is on the first carbon from the end.



This is not another isomer of pentene. This is also 2-pentene, just that the double bond is closer to the right end.

Alkynes (C_nH_{2n-2}):

Series of unsaturated hydrocarbons that contain 1 triple bond. Also called the acetylene series, General formula C_nH_{2n-2}



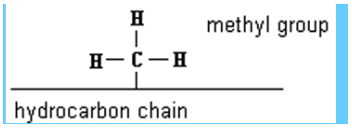
Homologous Series of Hydrocarbons

Name	General Formula	Examples	
		Name	Structural Formula
alkynes	C_nH_{2n-2}	ethyne	H—C≡C—H

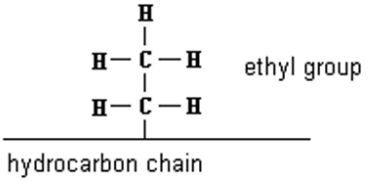
C_2H_2 = Ethyne, C_3H_4 = Propyne, C_4H_6 = Butyne, C_5H_8 = Pentyne

Alkyl Groups – have one less hydrogen than the corresponding alkane.

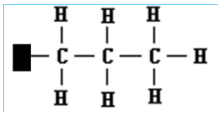
CH_3 is methyl – one less H than methane, CH_4



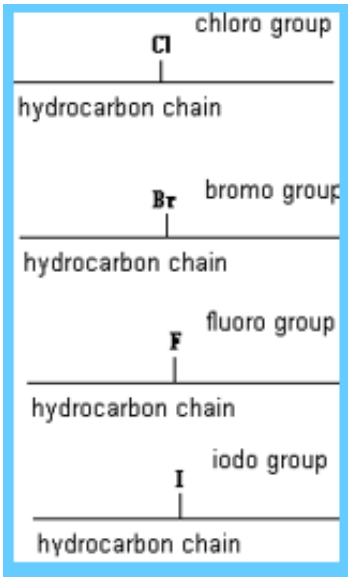
C_2H_5 is ethyl – one less H than ethane C_2H_6



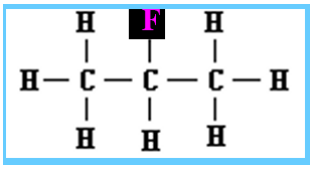
C_3H_7 is propyl – one less H than propane C_3H_8



Organohalides:



They are named by citing the location of the halogen attached to the chain
Drop the "ine" and add "o".



2- fluoropropane

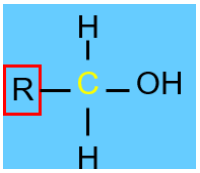
Alcohols (OH):

Are organic compounds in which one or more of the hydrogens is replaced with an – OH group. - OH group is called the hydroxyl group.

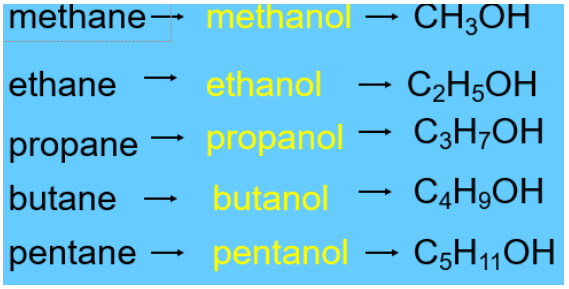
Organic Functional Groups

Class of Compound	Functional Group	General Formula	Example
alcohol	—OH	R—OH	$CH_3CH_2CH_2OH$ 1-propanol

-have one –OH group Monohydroxyl Alcohols:



IUPAC naming of alcohols
Replace the final "e" with "-ol".



Carboxylic acids (COOH):
Organic acids – have the functional group –COOH.

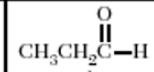
Organic Functional Groups

Class of Compound	Functional Group	General Formula	Example
organic acid	—C(=O)—OH	R—C(=O)—OH	$CH_3CH_2C(=O)—OH$ propanoic acid

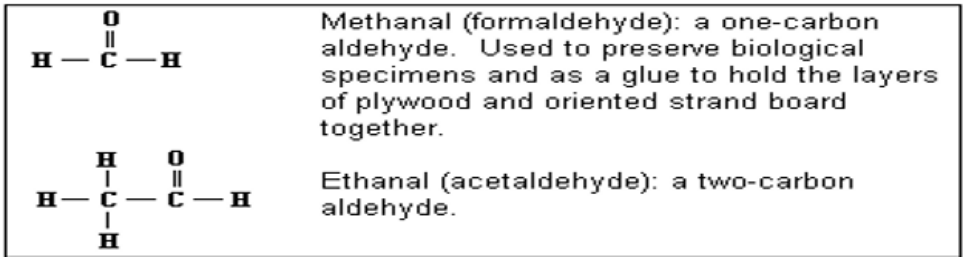
IUPAC naming of Organic Acids,Replace the final "e" with "-oic "acid. Methanoic acid - HCOOH

Aldehydes (CHO):
Aldehydes- contain the functional group –CHO.

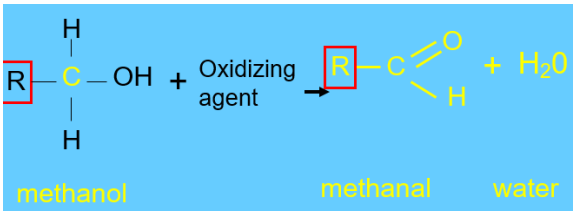
Organic Functional Groups

Class of Compound	Functional Group	General Formula	Example
aldehyde			 propanal

IUPAC naming of Aldehydes-: Replace the final "e" the the ending "al"



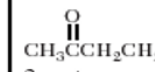
Alcohols can be oxidized to aldehydes.



Ketones:

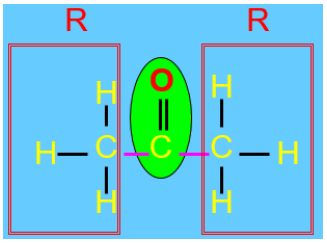
Ketones – contain the functional group R-CO-R: Replace the final "e" with "-one".

Organic Functional Groups

Class of Compound	Functional Group	General Formula	Example
ketone			 2-pentanone

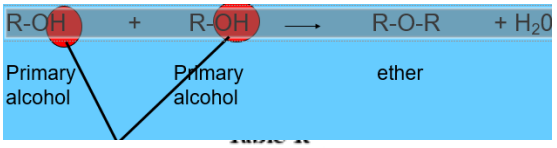
The simplest member of the ketone family is propanone.

IUPAC name is propanone but its common name is acetone, it is an important industrial solvent.



Ethers (-O-):

Ethers contain an ether group, an oxygen atom, when two primary alcohols are treated with a dehydrating agent, water is removed and the 2 alcohols are joined together by an oxygen "bridge".

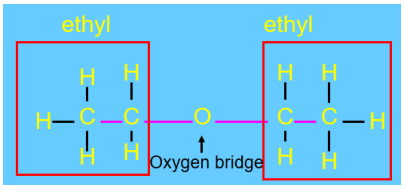


Organic Functional Groups

Class of Compound	Functional Group	General Formula	Example
ether	—O—	$R—O—R'$	$CH_3OCH_2CH_3$ methyl ethyl ether

Diethyl ether- used as a general anesthetic.

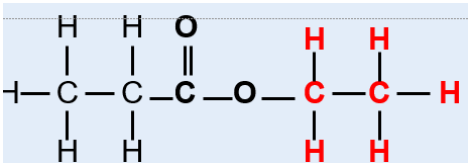
In the IUPAC name, ethers are named using general formula "alkoxyalkane".



Esters (R-CO-O-R):

Esters are organic compounds with the general formula R-CO-O-R, they are formed in a rxn between an organic acid and an alcohol. Esters have strong fragrant aromas and are what make pineapples, bananas, wintergreen and oranges so YummY ز

IUPAC naming of Esters:



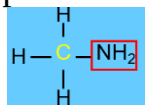
1- Look at chain after the –C-O- write its prefix
Ex. (meth,eth, etc.) and add –yl to the end of prefix
In this ex.: eth + yl = ethyl

2. Give the name of the carbon chain that includes the C=O, leave off the last letter and add –oate.
propane + oate =propanoate

Amines (-N-):

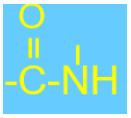
Amines contain the functional group -N-. It is a derivative of ammonia – NH_3

IUPAC naming of amines – replace the final –e with "-amine".

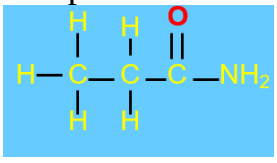


Amides:

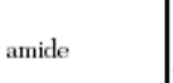
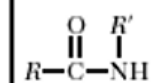
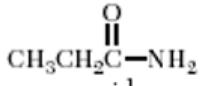
Amides are containing a carboxylic group linked to a (N), the functional group:



Found at the end of a carbon chain
IUPAC naming of amides: drop the final –e and add "amide".



Organic Functional Groups

Class of Compound	Functional Group	General Formula	Example
amide			 propanamide

Aromatic compounds

Aromatic compounds must have: -

1-High degree of unsaturation compounds.

2-Planar arrangement of P z orbitals to make high resonance

3-High degree of stability by conjugation.

4-Resistance for addition reactions.

5-Cyclic compounds

6-Obey Hückel Rule: - This is rule for aromaticity

Aromaticity Hückel Rule: - This is rule for aromaticity The number of π - electrons= 4n+2 Where n=0, 1, 2,

Benzene

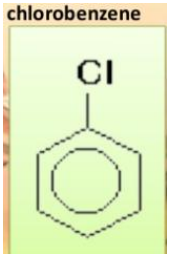
Benzene is an organic chemical compound with the molecular formula C_6H_6. The benzene molecule is composed of six carbon atoms joined in a ring with one hydrogen atom attached to each. As it contains only carbon and hydrogen atoms, benzene is classed as a hydrocarbon.

Benzene derivatives:

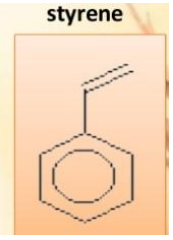
Many important chemical compounds are derived from benzene by replacing one or more of its hydrogen atoms with another chemicals groups.

a) Monosubstitution

1) Benzene as the parent name: ethylbenzene, chlorobenzene and bromobenzene



2) Common name: styrene cymene toluene



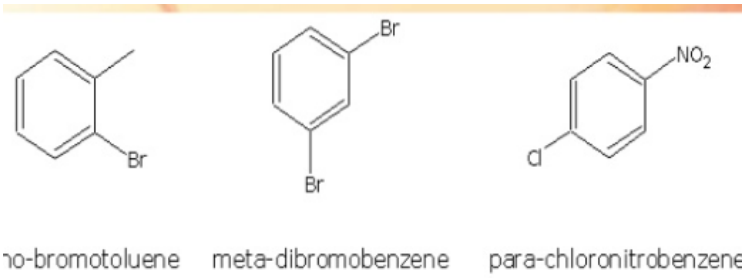
3) Alkyl substituent is larger than ring: 3-phenyldecane and 5-phenylpentanoic acid.

b) Disubstitution:

1) Ortho- disubstituted benzene has two substituents in a 1,2 positions: Principle functional group is the benzene therefore root = benzene O-dichlorobenzene. There are two chlorine substituent therefore dichloro. The substituent locants are 1 and 2 therefore ortho.

2) Meta -disubstituted benzene has two substituents in a 1,3 positions: Principle functional group is the benzene therefore root = benzene m-bromochlorobenzene. There is a chlorine substituent therefore chloro. There is a bromine substituent therefore bromo. The substituent locants are 1 and 3 therefore meta.

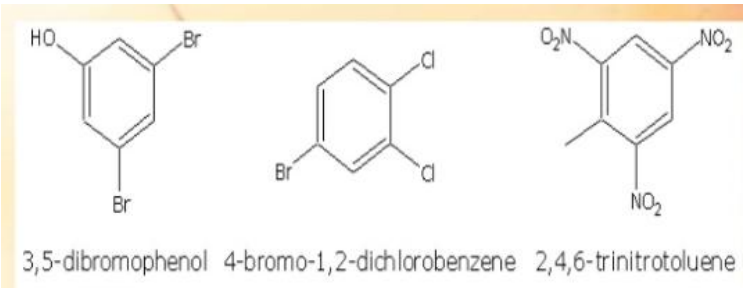
3) Para-disubstituted benzene has two substituents in a 1,4 positions.



ıo-bromotoluene meta-dibromobenzene para-chloronitrobenzene

c) Polysubstitution

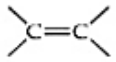
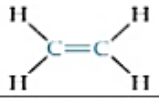
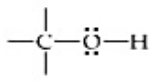
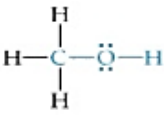
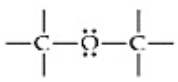
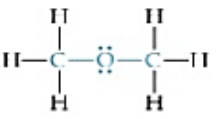
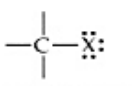
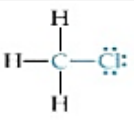
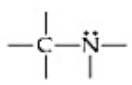
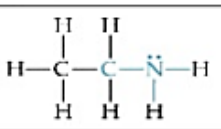
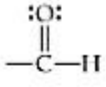
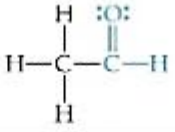
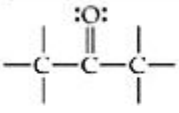
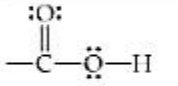
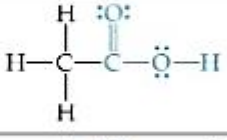
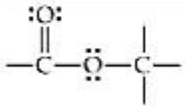
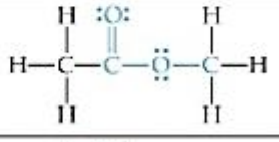
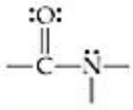
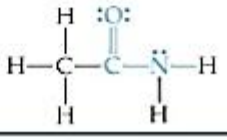
Benzene with more than 2 substituents are named by numbering the position of each substituent with lowest possible numbers: Principle functional group is the aromatic amine therefore = aniline. There is a C1 substituent therefore methyl. There is a C2 substituent therefore ethyl. Numbering from the -NH_2 (priority group at C1) gives the substituents the locants =2 and 3.



3,5-dibromophenol 4-bromo-1,2-dichlorobenzene 2,4,6-trinitrotoluene

Functional groups

Functional Groups; specific group of atoms within molecules that are responsible for the characteristic chemical reactions of those molecules and attached to the carbon backbone of organic molecules. They are determining the characteristics and chemical reactivity of molecules. The table below showing the important of function groups to indicated type of compound and its reaction.

Functional Group	Type of Compound	Suffix or Prefix	Example	Systematic Name (common name)
	Alkene	*ene*		Ethene (Ethylene)
	Alkyne	*-yne*		Ethyne (Acetylene)
	Alcohol	*-ol*		Methanol (Methyl alcohol
	Ether	*ether*		Dimethyl ether
 (X = halogen)	Haloalkane	*halo-*		Chloromethane (Methyl chloride)
	Amine	*-amine*		Ethylamine
	Aldehyde	*-al*		Ethanal (Acetaldehyde)
	Ketone	*-one*		Propanone (Acetone)
	Carboxylic acid	*-oic acid*		Ethanoic acid (Acetic acid)
	Ester	*-oate*		Methyl ethanoat (Methyl acetate
	Amide	*-amide*		Ethanamide (Acetamide)

Organic Reactions

Organic reactions are chemical reactions involving organic compounds. The basic organic chemistry reaction types are addition reactions, elimination reactions, substitution reactions, pericyclic reactions, rearrangement reactions and redox reactions.

Types of Organic Reactions

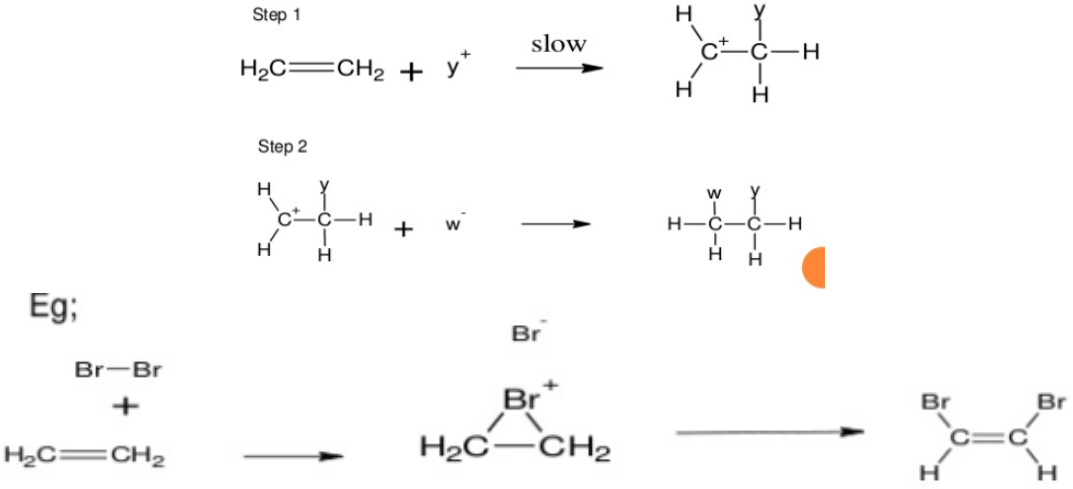
Organic reactions can be organized into several basic types. Some reactions fit into more than one category. For example, some substitution reactions follow an addition-elimination pathway. This overview isn't intended to include every single organic reaction. Rather, it is intended to cover the basic reactions.

Types of Reactions

Addition reactions. Addition reaction is defined as that reaction in which all the reagent atoms are added to the reactant and thusthe product contains all the atoms of the reactant as well as that of the reagent.

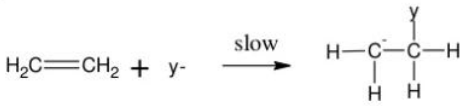
Types of addition reaction:

1- Electrophilic addition.

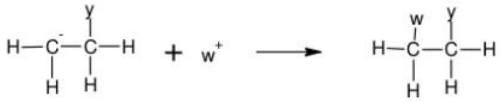


2- Nucleophilic addition

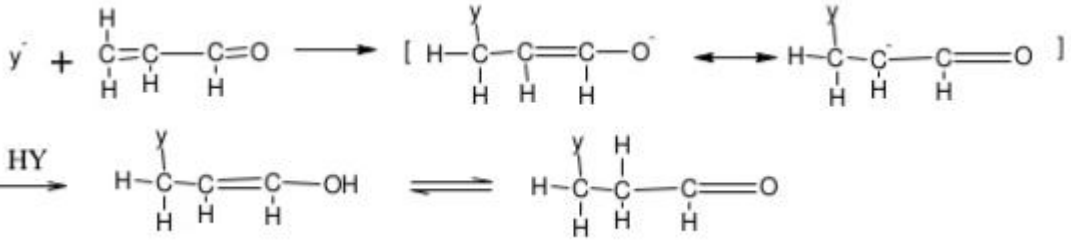
step 1



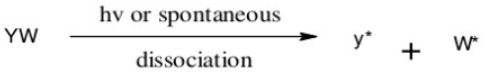
step 2



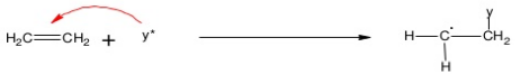
Eg.



3- Free radical addition

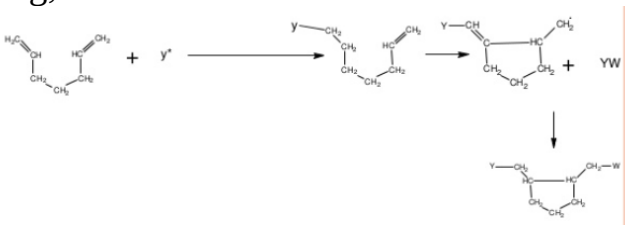


step 1



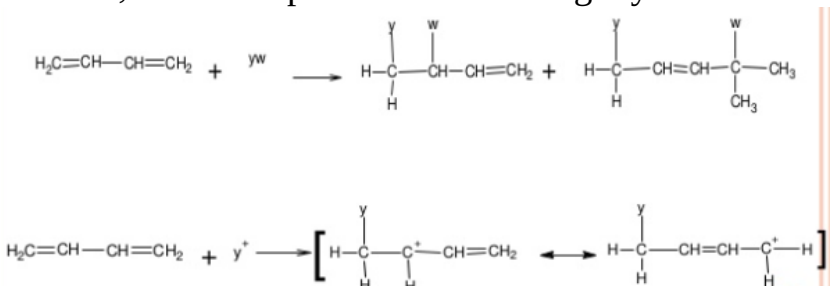
step 2

When free radicals are added to 1, 5 or 1, 6 dienes, the initially formedradical can add intramolecularly to the other bond leading to a cyclicproduct. Eg;



4- Addition to conjugated system.

Electrophillic addition on a compound with two double bonds in conjugation 1,2 addition product is often obtained, but in most cases there is also a 1,4 addition product often in larger yield.



Substitution Reactions

Definition, Reactions which involve the replacement or substitution of one or more atoms or groups of a compound by other atoms or groups are known as substitution reactions.

Classification, Based on the nature of substituents involved:

1. Free Radical Substitution,

$A{:}B + Q\cdot \longrightarrow A{:}Q + B^{\cdot}$

2. Electrophilic Substitution,

$A{:}B + Q^{-} \longrightarrow A{:}Q + B^{-}$

3. Nucleophilic Substitution,

$A{:}B + Q^{+} \longrightarrow A{:}Q + B^{+}$

Free Radical Substitution

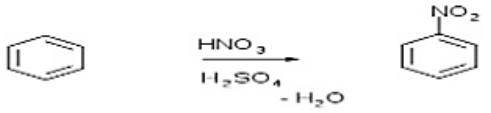
Radical substitution reactions are initiated by radicals in the gas phase or in non-polar solvents. For example, methane and chlorine react in presence of sunlight or heat to give methylchloride;

Electrophilic Substitution

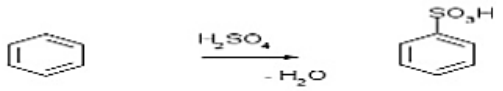
When the substitution involves attack by an electrophile, it is electrophilic substitution. This occurs in both aliphatic and aromatic compounds and hence classified as: Electrophilic Aliphatic Substitution and Electrophilic Aromatic Substitution.

Examples;

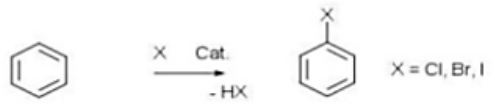
Nitration:



Sulphonation:

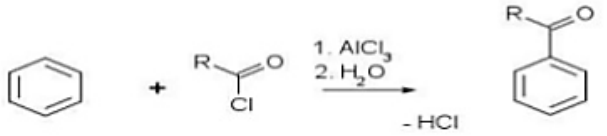


Halogenation:



Friedel-Craft's alkylation:

Friedel-Craft's acylation:



Nucleophilic Substitution

Nucleophilic substitution involves the displacement of a nucleophile by another. Nucleophilic substitution may be any one of the following:

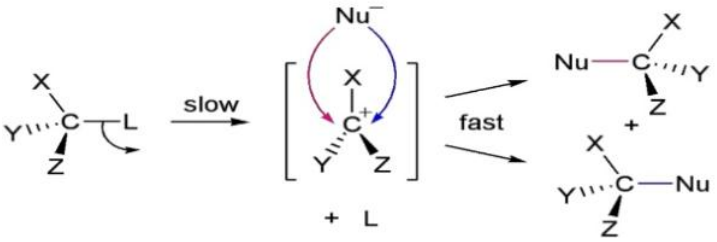
1- Nucleophilic aliphatic substitution
2- Nucleophilic aromatic substitution

Aliphatic Nucleophilic substitution

In 1935, Edward D. Hughes and Sir Christopher Ingold studied nucleophilic substitution reactions of alkyl halides and related compounds. They proposed two main mechanisms; the S_N1 reaction and the S_N2 reaction. S stands for chemical substitution, N stands for

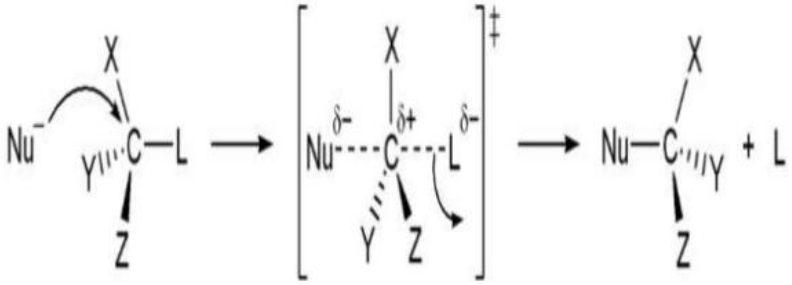
nucleophilic, and the number represents the kinetic order of the reaction.

S_N1 reaction mechanism



L= leaving group, Nu^- = attacking nucleophile

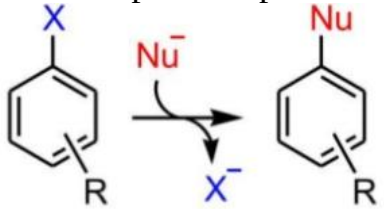
S_N2 reaction mechanism



L= leaving group, Nu^- = attacking nucleophile

Aromatic Nucleophilic substitution

A nucleophilic aromatic substitution is a substitution reaction in which the nucleophile displaces a good leaving group, on an aromatic ring.



x- halogen, Nu^- = attacking nucleophile

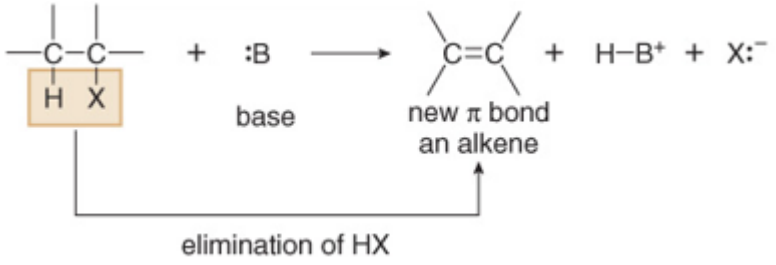
Elimination Reactions

Just as there are two mechanisms of substitution (S_N2 and S_N1), there are two mechanisms of elimination (E2 and E1).

E2 mechanism is bimolecular elimination, but E1 mechanism is unimolecular elimination. The E2 and E1 mechanisms differ in the timing of bond cleavage and bond formation, analogous to the S_N2 and

S_N1 mechanisms. E2 and SN2 reactions have some features in common, as do E1 and SN1 reactions.

general elimination reaction

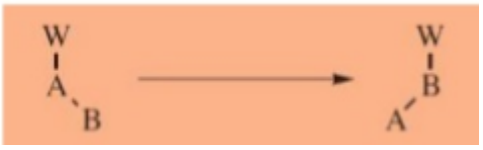


Rearrangement Reactions

In chemistry a rearrangement is a chemical reaction in which the carbon skeleton of a molecule is rearranged to give a structural isomer of the original molecule.

The rearrangement is like the substitution reaction and the addition reaction - one of the basic operations of chemical synthesis. Specific reaction types are listed under the heading of name reactions.

In a rearrangement reaction an atom or group moves from one atom to another in the same molecule i.e. connectivity of atoms changed within the molecule. Most of the migrations are from an atom to an adjacent one (called 1,2-shifts), but some are over longer distances.



The migrating group (W) may migrate with electron pair (nucleophilic rearrangement) or without electron pair (electrophilic rearrangement) or with one electron (free radical rearrangement).

These rearrangements can take place in two possible modes;

1. Intramolecular: In these migrating group do not completely detach from the migration origin and occurs within the same molecule.

W- A -B ⟶ A –B- W

2. Intermolecular: In these migrating group is detached from the migration origin. In this case, migration of a group/atom can take place to different molecule.

W- A -B + U-A- C ⟶ A- B -U + A- C- W

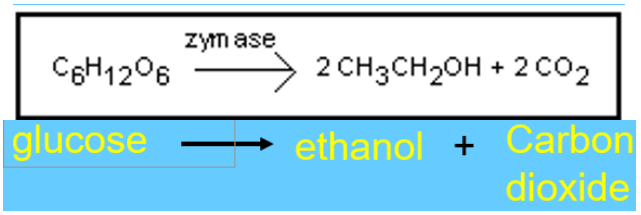
Organic Redox Reactions

Redox reactions are a vital class of chemical reactions confronted in daily processes. These reactions take place all around us. Iron corrodes, batteries produce electricity, and wood, oil and coal which are hydrocarbon fuels are scorched to produce energy. Oxidation-reduction reactions are significant for biochemical reactions and industrial procedures. The system in cells that transfers electron and the process of oxidation of glucose in the humans are common examples of redox reactions. Using redox reactions, the ores are condensed to attain metals, to manufacture electrochemical cells, to transform ammonia into nitric acid for fertilizers and also compact discs coating.

Table 11-2 illustrated types of reaction for organic compounds Fermentation

Reaction Type	Sub-type	comments
Addition reactions	Electrophilic Nucloephilic radical	halognenation, hydrohalogenation and hydration
Elimination reaction		Dehydration
Substitution reactions	nucleophilic aliphatic Substitution nucleophilic aromatic substitution nucleophilic acyl substitution electrophilic substitution electrophilic aromatic substitution radical substitution	with SN^1, SN^2 and SNi reaction mechanisms
Organic Redox reactions		redox reactions specific to organic compounds
Rearrangements reactions	1,2-rearrangements pericyclic reactions metathesis	

Ex.



Esterification:

Is the general name for a chemical reaction in which two reactants (typically an alcohol and an acid) from ester as the reaction product.

Ex.

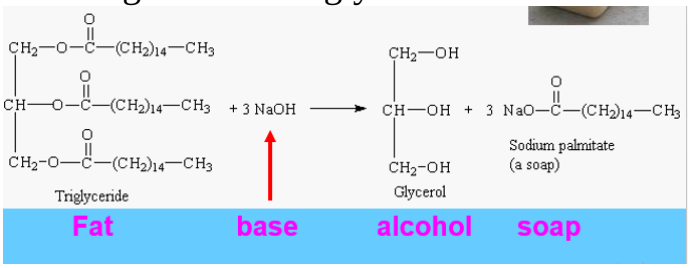
Organic Acid + Alcohol → Ester + Water

Saponification:

is a process that involves conversion of fat or oil or lipid into soap and alcohol by the action of heat in the presence of aqueous alkali.

Ex.

Fat + water = organic acid + glycerol



Polymers:

They are composed of many repeating units of monomers

Natural polymers (look in chapter twelve)

-starch – long chains of sugars

-proteins – long chains of amino acids

-cellulose – made of repeating units of sugar

Isomers

What is Isomerism?

The organic compounds having the same molecular formula but different structures are known as Isomers. This phenomenon is known as Isomerism. In other words, the organic compounds having the same molecular formula but different arrangements of carbon atoms in them, are known as Isomers. It is a phenomenon where two or more compounds have the same chemical formula but possesses different structural formulas, that is, different properties. This is mainly because of different structural or spatial arrangements. Isomers are the compounds exhibiting isomerism.

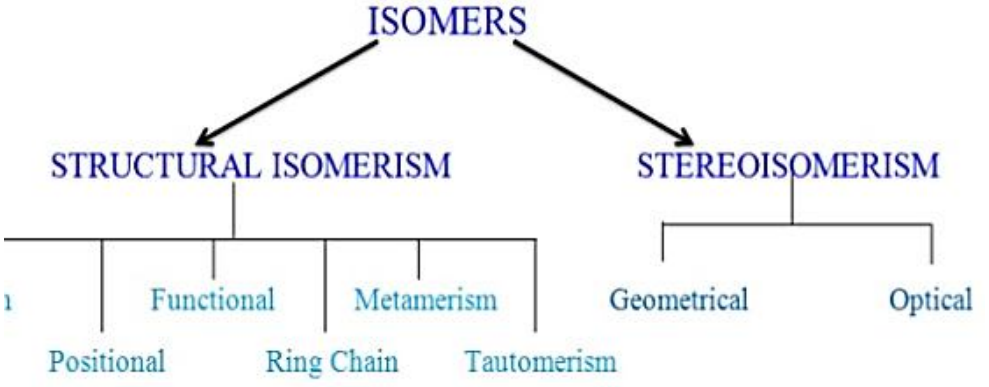
Types of Isomerism

Basically, there are two types. They are:

a- Structural Isomerism

b- Stereoisomerism

as showing in scheme bellow;



Structure isomer

Isomers are structural isomers when they have the same molecular formula but different structures, as in how they are linked to each other. Structural isomerism is further of the following types. Let's learn about these types one-by-ones.

Structure isomer classified into 6 types

1. Chain Isomerism. The same molecular formula represents two or more compounds. It differs in the nature of carbon chain (straight or

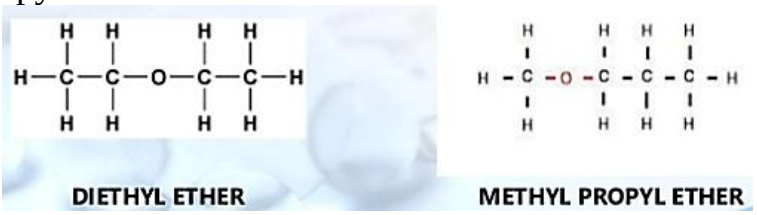
branched) Example, C_4H_{10} (Butane) has two isomers namely butane and 2- methylpropane.

2. Positional Isomerism.The same molecular formula represents two or more compounds.It differs in the position of the same functional group Example, Butene has two isomers namely But-1-ene and But-2-ene.

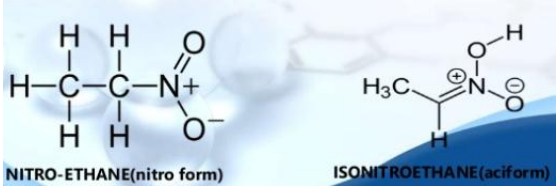
3. Functional Isomerism. The same molecular formula represents two or more compounds. It differs in the nature of the functional group. Example, $C_3H_60_2$ has two isomers namely Propanoic acid and Methyl ethanoate.

4. Ring Chain Isomerism. The same molecular formula represents two or more compounds. It differs in the mode of linkage of carbon atoms.The isomers have either open chain or closed chain. Example, Propene and cyclopropane are ring chain isomers.

5. Metamerism Isomerism. The same molecular formula represents two or more compounds.It differs in the nature of the alkyl groups attached to the same functional group.Example, Diethyl ether and Methyl propyl ether are metamerical isomers.



6. Tautomerism; The same molecular formula represents two or more compounds.It exists in dynamic equilibrium with each other. It can be present in many form such as Nitroform and Aci form, Ketoform and Enolic forms etc. Example, Nitro- ethane and Isonitroethane are Tautomerical isomers.

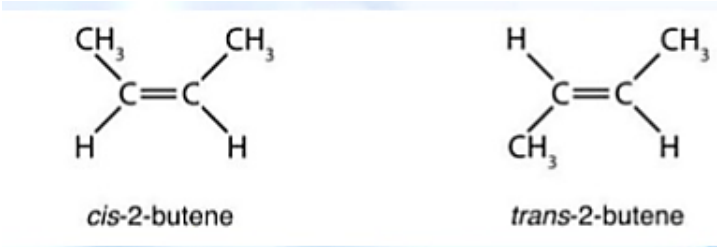


Stereo Isomerism

Stereoisomerism is a phenomenon in which compounds have the same molecular formula but differ in the relative positioning or orientation of atoms in space. Stereoisomers are the compounds exhibiting stereoisomerism. We can further classify stereoisomerism into:

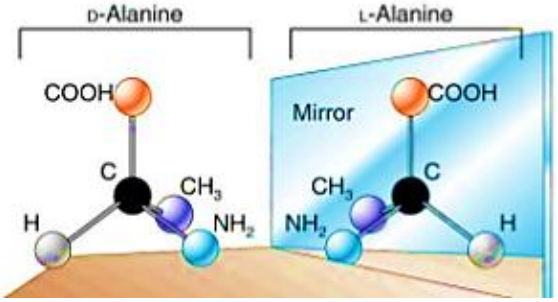
Geometric Isomerism

The same molecular formula represents two or more compounds. It differs in the spatial arrangement of atoms or groups around carbon-carbon double bond. It is of two types-If same group are on same side then, it is called ‘cis’ isomers and if it is on opposite sides, then it is called ‘trans’ isomers. Example, cis-2-butene and trans-2-butene are ‘cis’ and ‘trans’ isomers.



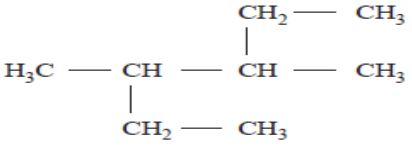
Optical Isomerism

Optical Isomers are named like this because of their effect on plane polarized light. Optical Isomers, which are non-superimposable mirror images of each other, are called Enantiomers. Example, d-Alanine and l-Alanine, lactic acid etc.



Questions and Answer

Q1. What is the correct systematic name for the following compound?



a. 2-ethyl-3-methylpentane
b. 3-methyl-4-ethylpentane
c. 3,4-dimethylhexane
d. 2,3-diethylbutane

Q2. For which one of the following molecular formulas is there only one possible structure?

a. C_2HCl_3
b. $C_2H_4Cl_2$

c. $C_2H_2Cl_2$
d. C_4H_9OH

Q3. When two mole of an organic compound is burnt in oxygen, eight mole of carbon dioxide gas is formed. In a second test, when a few drops of bromine are added to the compound and shaken, the bromine rapidly decolorizes. The formula of the compound could be:

a. C_4H_8
b. C_4H_{10}
c. C_8H_{16}
d. C_8H_{18}

Q4. How many hydrogen atoms are there in a molecule of 3-nonanol?

a. 9
b. 19
c. 20
d. 21

Sol. C: 3-nonanol → 9 C atoms with –OH on carbon number 3.
$CH_3CH_2CH_2CH_2CH_2CH_2CHOHCH_2CH_3$ → 20 H atoms

Q5. The number of structural isomers with the formula C4H9Cl is:

a. 1
b. 2
c. 3
d. 4

Sol. d. 4 structural isomers
$CH_3CH_2CH2CH2Cl$, 1-chlorobutane
$CH_3CH_2CHClCH_3$, 2-chlorobutane
$(CH_3)_2CHCH_2Cl$, 2-methyl-1-chloropropane
$(CH_3)_3CHCl$, 2-methyl-2-chloropropane

Q6. A 2L sample of a gaseous hydrocarbon is burnt in excess oxygen. The only products of the reaction are 8 L of $CO_2(g)$ and 10 L of $H_2O(g)$, all at 100ºC and 1 atm pressure. The formula of the hydrocarbon is

a. CH
b. C_2H_4
c. C_4H_{10}
d. C_8H_{10}

Sol. Since all gases are measured at the same temperature and pressure, the volumes of CxHy, CO_2 and H_2O are in the same ratio as the mole ratio.

$CxHy \rightarrow CO_2 + H_2O$

2 L 8 L 10 L

2 mol 8 mol 10 mol

1 mol 4 mol 5 mol

So 1 mol CxHy → 4 mol CO_2 (4 mol C. and 5 mol H_2O (10 mol H)

Molecular formula is C_4H_{10}

Q7. a. Give the systematic names of the following organic compounds.

i. $CH_3CHOHCH_3$

Sol. 1. 2-propanol or propan-2-ol

ii. HCOOH

Sol. 1. methanoic acid

iii. $CH_3CH_2CHClCH_3$

Sol. 1. 2-chlorobutane

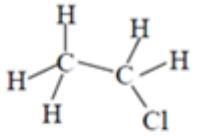
iv. $CH_3CH_2COOCH_2CH_3$

Sol. 1. ethyl propanoate

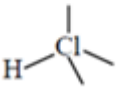
b. Complete the following chemical equation by giving relevant structural formulas in the boxes provided

$C_2H_6 + Cl_2 \rightarrow$

Sol.



or CH_3CH_2Cl;



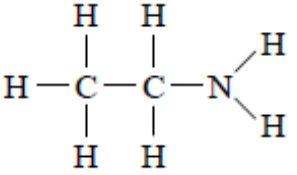
or HCl or H — Cl

Q8. The number of structural isomers that are carboxylic acids with the formula $C_4H_8O_2$ is:

a. 1

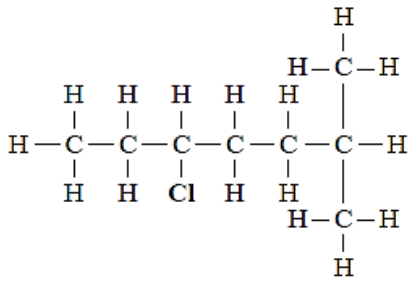
b. 2

c. 3
d. 4
Sol. b. There are two (alternative b. carboxylic acids with molecular formula $C_4H_8O_2$,
$CH_3CH_2CH_2COOH$ – butanoicacid
$(CH_3)_2CHCOOH$ – methylpropanoic acid.
Q9. Which of the following statements would apply to compounds that belong to the same homologous series?
I they have similar physical properties
II they have similar chemical properties III they contain the same functional group
IV they have the same molecular formula but different structures
a. III only
b. IV only
c. II and III only
d. I, II, III and IV
Sol. c. Since all members of an homologous series contain the same functional group (statement III) they will have similar chemical properties (statement II). However, since successive members of an homologous series differ by CH_2, they have different physical properties (e.g. boiling temperature) and different molecular formulae, therefore statements I and IV are incorrect.
Q10. a. Give a systematic name for each of the following compounds.
Sol.

i. 

Sol. Any of:
- aminoethane.
- ethylamine.
- ethanamine

ii.

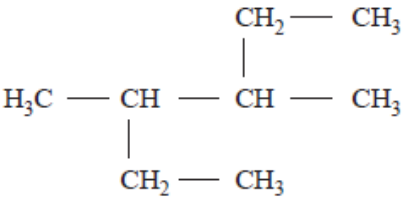


Sol. Either of:

- 5–chloro–2–methylheptane
- 3–chloro–6–methylheptane.

The ester methyl propanoate has a characteristic fruity odour and has been isolated from many fruits including pineapple. A sample of this ester is to be prepared in the laboratory.

Q11. What is the correct systematic name for the following compound?



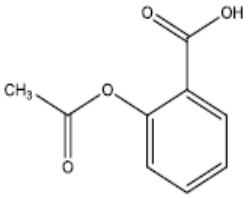
a. 2-ethyl-3-methylpentane
b. 3-methyl-4-ethylpentane
c. 3,4-dimethylhexane
d. 2, 3-diethylbutane

Q12. An organic compound reacts with both dilute hydrochloric acid and dilute sodium hydroxide solution.
The compound could be:
a. C_3H_7Cl
b. $C_3H_7NH_2$
c. C_4H_9COOH
d. H_2NCH_2COOH

Sol. d. H_2NCH_2COOH will react with both dilute HCl(aq) and dilute NaOH(aq) because the amino group,
NH_2, is basic and the carboxyl group, COOH, is acidic.

Q13. The triple bond between the carbon atoms causes acetylene, C_2H_2, to have which of the following shapes?
a. trigonal planar (pron: try-gon-al)
b. linear
c. tetrahedral
d. trigonal bipyramidal

I acid II alcohol III ester IV ether



(A) I and III (B) II and III
(C) II and IV (D) I, II, III and IV

Sol. A

Q14. Azo (pron: A-zo) Compounds characteristically are compounds containing the group:
a. C_2
b. N_2
c. O_2
d. C_{l2}

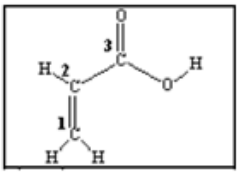
Q15. The compounds C_3H_8, CH_3CH_2OH, and CH_3OCH_3 have very similar molar masses. When they are arranged in order of increasing strength of their intermolecular forces, what is the correct order?
a. C_3H_8, CH_3OCH_3, CH_3CH_2OH
b. CH_3CH_2OH, CH_3OCH_3, $C3H8$
c. CH_3OCH_3, C_3H_8, CH_3CH_2OH
d. CH_3CH_2OH, C_3H_8, CH_3OCH_3

Q16. Which formula can be used to represent alkynes?
a. C_nH_{2n-2}
b. C_nH_{2n}
c. C_nH_{2n+2}
d. C_nH_{2n+4}

Q17. A reaction in which a carboxylic acid reacts with an alcohol to form an organic compound and water is called

a. esterification
b. hydrolysis
c. neutralization
d. saponification

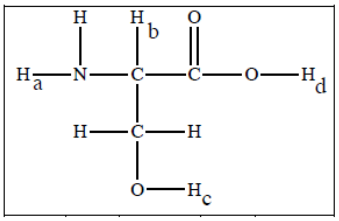
Q18. What is the hybridization of carbon atoms 1, 2 and 3 respectively in the structure?



(A) sp^3, sp, sp^2 (B) sp^2, sp, sp^2
(C) sp^3, sp^2, sp^2 (D) sp^2, sp^2, sp^2

Q19. Which term describes the formation of acetic acid from ethyl alcohol?
a. addition
b. esterification
c. neutralization
d. oxidation

Q20. Which hydrogen is the most acidic in the molecule?



a. H_a b. H_b c. H_c d. H_d

SECTION THREE
CHAPTER TWELVE
Biochemistry

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CHAPTER TWELVE
BIOCHEMISTRY

Introduction

Biochemistry is the application of chemistry to the study of biological processes at the cellular and molecular level.

It emerged as a distinct discipline around the beginning of the 20th century when scientists combined chemistry, physiology and biology to investigate the chemistry of living systems by:

A-Studying the structure and behavior of the complex molecules found in biological material.

B- The ways these molecules interact to form cells, tissues and whole organism

Principles of Biochemistry

Cells (basic structural units of living organisms) are highly organized and constant source of energy is required to maintain the ordered state.

Living processes contains thousands of chemical rxns. Precise regulation and integration of these rxns are required to maintain life.

Certain important rxns E.g. Glycolysis is found in almost all organisms.

All organisms use the same type of molecules: CHO, proteins, lipids and nucleic acids.

Instructions for growth, reproduction and developments for each organism is encoded in their DNA.

General Properties of Cells

a- Basic building blocks of life.

b- Smallest living unit of an organism.

c- Grow, reproduce, use energy, adapt, respond to their environment.

d- Many cannot be seen with the naked eye.

e- A cell may be an entire organism or it may be one of billions of cells that make up the organism.

Basis Types of Cells

Cells May be Prokaryotic or Eukaryotic

Prokaryotes include bacteria and lack a nucleus or membrane-bound structures called organelles.

Eukaryotes include most other cells & have a nucleus and membrane-bound organelles (plants, fungi, and animals)

Bio-molecules

General properties;

a- Just like cells are building blocks of tissues likewise molecules are building blocks of cells.

b- Animal and plant cells contain approximately 10, 000 kinds of molecules (bio-molecules).

c- Water constitutes 50-95% of cells content by weight. Ions like Na+, K+ and Ca+ may account for another 1%.

d- Almost all other kinds of bio-molecules are organic (C, H, N, O, P, S). Infinite variety of molecules contains C.

e- Most bio-molecules considered to be derived from hydrocarbons.

f- The chemical properties of organic bio-molecules are determined by their functional groups.

i- Most bio-molecules have more than one.

Macromolecules

Introduction

Organic Compounds; Compounds that contain CARBON are called organic.

Macromolecules are large organic molecules. Also called polymers.

They are made up of smaller "building blocks" called monomers.

These are larger organic molecules formed from many repeating units of smaller organic molecules. For further discussions we will focus on the macromolecules:

Examples:

1- Carbohydrates
2- Lipids
3- Proteins
4- Nucleic acids (DNA and RNA).

1- Carbohydrates;

Introduction

Nutrition is defined as the science of how the body utilizes food to meet requirements for development growth, repair and maintenance.

Daily Intake;

Nutrient quantity per day Energy equal 8,700 kilojoules (total). They are Distributed according to the body's need for food as follows; Protein = 50 grams, Fat = 70 grams, Carbohydrates = **310 grams**, Sugars = 90 grams, Sodium (salt) = 2.3 grams, Dietary Fibre = 30 grams and Saturated Fatty Acids = 24 grams.

Carbohydrates are defined as aldehyde or ketone derivatives of polyhydric alcohols. For example: Glycerol on oxidation is converted to D-glyceraldehyde, which is a carbohydrate derived from the trihydric alcohol (glycerol). All carbohydrates have the general formula $C_nH_{2n}O_n$ [or it can be re-written as $C_n (H_2O)_n$].

Carbohydrates are sugars and provide energy when consumed. Our bodies break down carbohydrates to extract energy. Carbon dioxide and water are released in the process.

Glucose is the primary carbohydrate our bodies use to produce energy. Carbohydrates are classified as biomolecules.

Simple carbohydrates are referred to as **simple sugars** and are often sweet to the taste. Consumption of more sugar than is needed for energy results in conversion of these sugars to fat.

Complex carbohydrates include starches and the plant and wood fibers known as **cellulose**. Carbohydrates are found on the surface of cells where they act as “road signs” allowing molecules to distinguish one cell from another.

ABO blood markers found on red blood cells are made up of carbohydrates. They allow us to distinguish our body’s blood type from a foreign blood type. Carbohydrates in our body prevent blood clots. They are also found in our genetic material.

Classes of Carbohydrates:

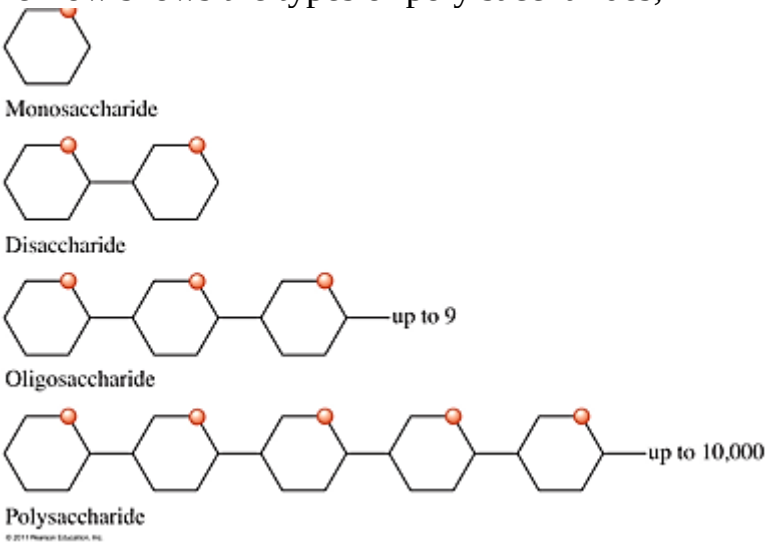
a- Monosaccharides are the simplest carbohydrates. They cannot be broken down to smaller carbohydrates.

b- Disaccharides consist of two monosaccharide units joined together; they can be split into two monosaccharides. Sucrose, table sugar, can be broken down into glucose and fructose.

c- Oligosaccharides contain anywhere from three to nine monosaccharide units. ABO blood groups are oligosaccharides.

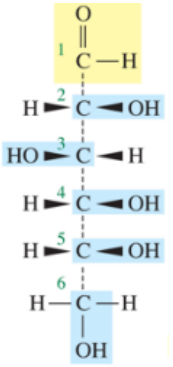
d- Polysaccharides are large molecules containing 10 or more monosaccharide units. Carbohydrate units are connected in one continuous chain or the chain can be branched.

The scheme flow shows the types of poly saccharides;



Monosaccharides contain the elements carbon, hydrogen, and oxygen, and have the general formula $C_n(H_2O)_n$, where *n* is a whole number 3 or greater. Monosaccharides contain several functional groups. They contain the hydroxyl group represented as –OH. They also contain a ***carbonyl group***, which is an oxygen double bonded to a carbon atom. The carbonyl group may be an aldehyde or a ketone.

The functional groups of glucose are shown in the figure below.

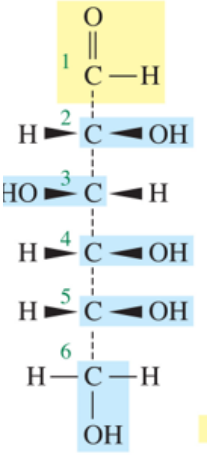


Functional Groups in Monosaccharides-Alcohols, Aldehydes, and Ketones

Alcohols

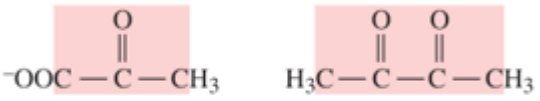
Alcohol is an organic compound containing the –OH group. Ethanol is one of the simplest alcohols and is prepared from the fermentation of simple sugars in grains and fruits. Ethanol is present in beer and liquors, and is used as an alternative fuel blend, such as gasohol and E85 (85% ethanol and 15% gasoline).

Aldehydes. Monosaccharides can contain an aldehyde group on one end of the molecule in addition to multiple hydroxyl groups**.**



Ketones

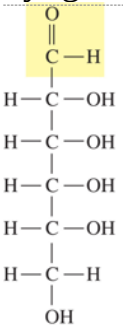
A wide variety of biologically important compounds contain a ketone group. Pyruvate is a ketone-containing compound formed during the breakdown of glucose. Butanedione, the flavor of butter, contains two ketone groups.



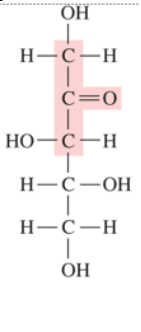
Pyruvate

Butanedione
(butter flavor)

Monosaccharides that contain an aldehyde group are referred to as an ***aldose***. Those that contain a ketone group are referred to as a ***ketose***.
Monosaccharides are classified according to the number of carbon atoms. Most common monosaccharides have three to six carbon atoms;
Triose contains three carbons.
Tetrose contains four carbons.
Pentose contains five carbons.
Hexose contains six carbons.
Carbohydrates are further classified on whether they contain an aldehyde or ketone group.
For example, glucose, the most abundant monosaccharide found is nature, contains six carbons and an aldehyde group. It is classified as an aldohexose. Fructose, known as fruit sugar, contains six carbons and a ketone group. It is classified as a ketohexose.
Aldohexose and ketopentose differ in the number of carbon atoms and in the type of carbonyl group they contain.

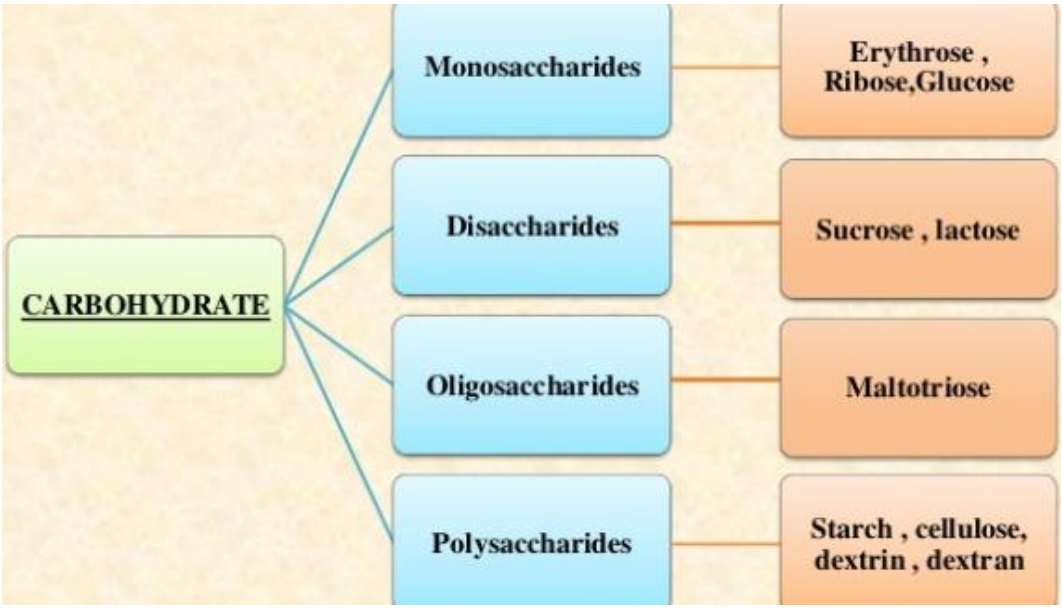


An aldohexose



A ketopentose

Classification of carbohydrate; It can be illustrated according to the following diagram;



Functions of carbohydrates;

a- These are major source of energy for living organisms.

b- Energy production from carbohydrates will be 4 k calories/g (16 k Joules/g).

c- Storage form of energy (starch and glycogen).

d- Excess carbohydrate is converted to fat.

e- Glycoproteins and glycolipids are components of cell membranes and receptors.

f- Structural basis of many organisms. For example, cellulose of plants, exoskeleton of insects etc.

i- Supplying a huge array of metabolic intermediates for biosynthetic reactions.

j- The structural elements in cell coat or connective tissues.

Digestion

a- It is Partly digested in mouth by salivary amylase.

b- In stomach there is no digestion takes place.

c- Complete digestion and absorption will be taken place at small intestine.

Biomedical Importance of Glucose;

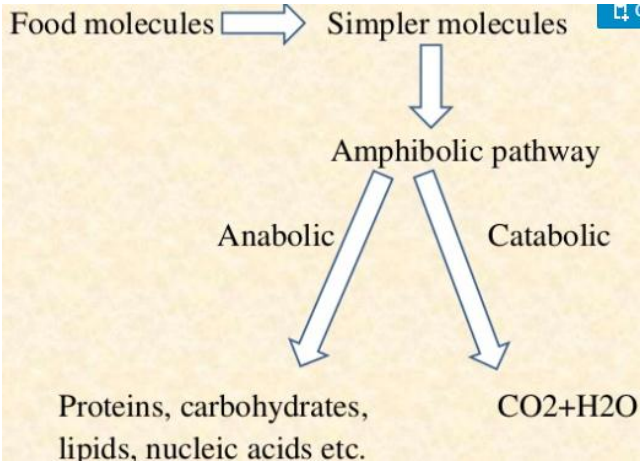
a- Glucose is a major carbohydrate.
b- It is a major fuel of tissues.
c- It is converted into other carbohydrates such as Glycogen for storage, Ribose in nucleic acids, Galactose in lactose of milk, They form glycoproteins and proteoglycans, They are present in some lipoproteins (LDL), and Present in plasma membrane.

Metabolism

Metabolism Thousands of chemical reactions are taking place inside a cell in an organized, well co-ordinated and purposeful manner; all these reactions are called as metabolism**.**

types of metabolic pathway: there are three pathways, Catabolic Pathway, Anabolic Pathway and Amphibolic Pathway**.**

stages and phases of metabolism: there are three phases, primary, secondary and tertiary**.**



Sugars

Introduction

Carbohydrates give the body energy. They are the best source of fuel for the body. Carbohydrates also help to digest protein and fat.
45-65% of our food should come from carbohydrates. If we eat more carbohydrates than are needed for energy, the extra is stored in the liver or in the tissues as fat. Simple carbohydrates are quick energy sources. They come from sugar. They do not usually supply any other

nutrients or fiber. Glucose or blood sugar is the basic source of energy for all living things. Sucrose or table sugar is made from sugar beets or sugar cane. Fructose is sugar found in fruit, honey and vegetables. Maltose is grain starch broken down into sugar. Lactose is ilk sugar.

What is sugar?

The white stuff we know as sugar is sucrose, a molecule composed of 12 atoms of carbon, 22 atoms of hydrogen, and 11 atoms of oxygen ($C_{12}H_{22}O_{11}$). Like all compounds made from these three elements, sugar is a carbohydrate. It's found naturally in most plants, but especially in sugarcane and sugar beets—hence their names.

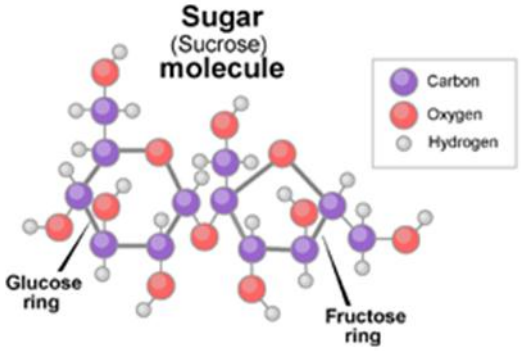


Figure 12-1 structure of sugar

Sucrose is actually two simpler sugars stuck together: fructose and glucose. In recipes, a little bit of acid (for example, some lemon juice or cream of tartar) will cause sucrose to break down into these two components.

If you look closely at dry sugar, you'll notice it comes in little cubelike shapes. These are sugar crystals, orderly arrangements of sucrose molecules.

Abstract;

a- Carbohydrates most abundant organic molecule found in nature.

b- Initially synthesized in plants from a complex series of reactions involving photosynthesis.

c- Basic unit is monosaccharides.

d- Monosaccharides can form larger molecules e.g. glycogen, plant starch or cellulose.

Functions

a- Store energy in the form of starch (photosynthesis in plants) or glycogen (in animals and humans).
b- Provide energy through metabolism pathways and cycles.
c- Supply carbon for synthesis of other compounds.
d- Form structural components in cells and tissues.
e- Intercellular communications.

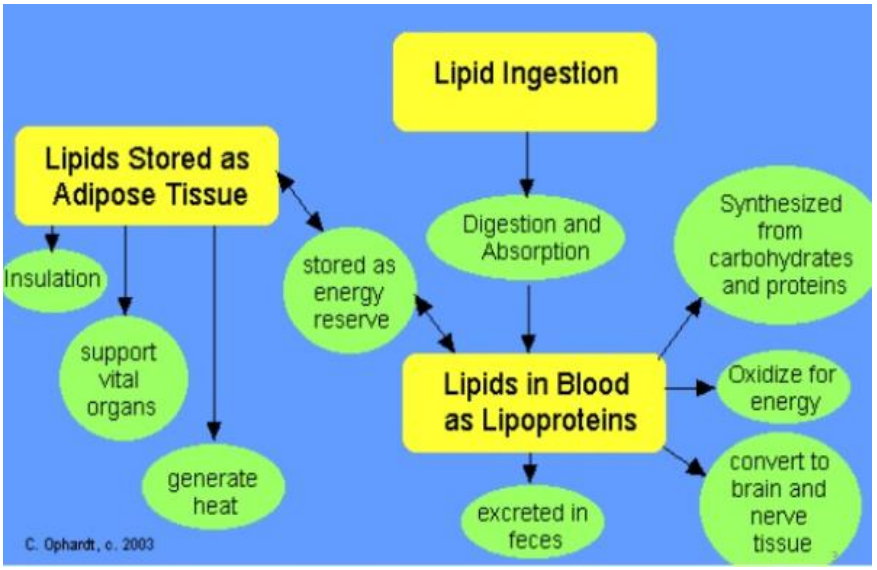
2-Lipids

These are nonpolar organic compounds. Generally, it is insoluble to water, but soluble to nonpolar solvent like; chloroform, acetone, ether and benzene. It contains a carboxyl group (-COOH).

Classification and Functions of Lipids in human

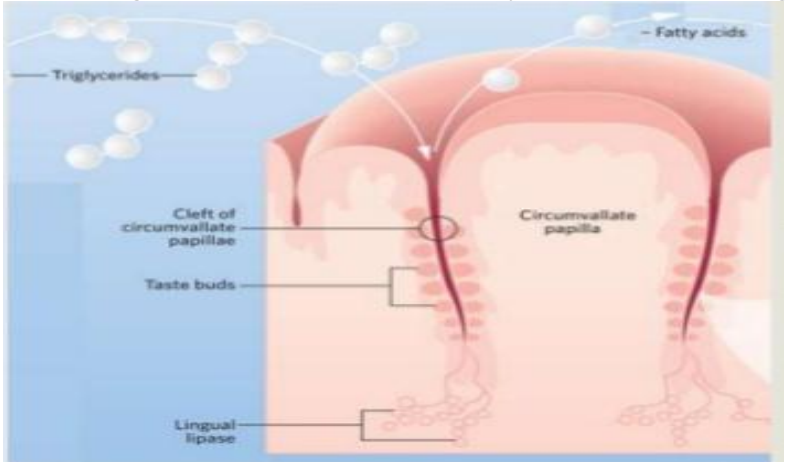
a- Triglyceride, TG （ Variable lipids ）: - As storage and transport form of metabolic fuel;
- To keep the body temperature
- Fats are solids
- Oils are liquids
b- Cholesterols - As structural components of biological membranes.
- Cholesterol serves the precursor of bile salt and steroid hormones 3.
C- Phospholipids: As constituents of cell membrane
d- Fatty Acids: Precursor for energy and other macromolecules
e- Other Lipids: Glycolipids

Lipid function and metabolism are illustrated in diagram below;



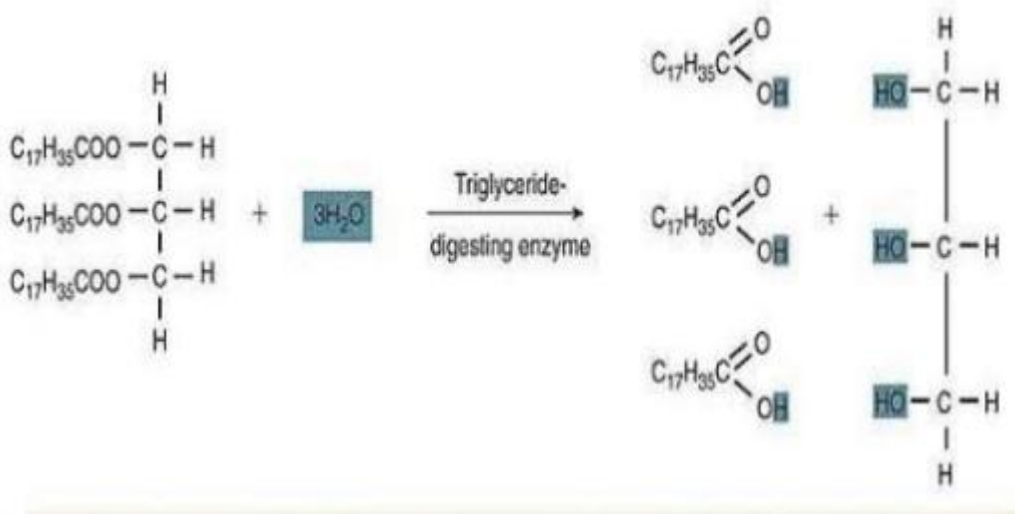
Digestion of lipids;

It is initially starts in the mouth. The dietary lipid like the triglycerides will activate the tastes buds connecting to the Von Ebner's gland will secrete the enzyme called the lingual lipase.



Triglyceride degradation

Triglycerides are degraded by lipases to form free fatty acids and glycerol.



Fat + water → fatty acids + glycerol

Fatty acids

Introduction

Lipids are organic molecules essential for life that are composed mostly of C, H, O. There are 4 types of lipids:

1- fats (triglycerides)
2- phospholipids
3- steroids
4- waxes

3 fatty acids chains linked to glycerol.it is functions are long term energy storage and insulation for animals and
can be saturated or unsaturated.

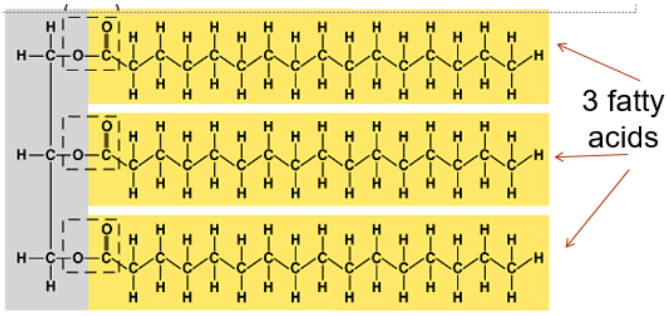


Figure 12-2 structure of fatty acids

What is fatty acid?

Fatty acids are basic building blocks of lipids(simplest lipids) & they are amphipathic. Fatty acids are naturally occurring carboxylic acids with an unbranched carbon chain and an even number of carbon atoms. *Long-chain fatty acids (12 to 26 carbon atoms) are found in meats and fish. *Medium-chain fatty acids (6 to 10 carbon atoms) are found in Coconut oil. *Short-chain fatty acids (fewer than 6 carbon atoms) occur primarily in dairy products.

Oils and fats are liquids or solids having a greasy feel. When pure, they are colorless, odorless and tasteless. • They are insoluble in water but soluble in organic solvents such as ether, chloroform, benzene and hot alcohol. • They have lower specific gravity than water and consequently will float on the surface when mixed with it.

Classification of fatty acid;

Biological Importance of Fatty Acids

Unsaturated fatty acids are found in membranes as phosphoglycerides (also known as phospholipids). Without Fatty acids the Phospholipids can't formed. So the bilayer can't be construct. Fatty acid composition results more fluids in a cell membrane but also one that is "leakier" to various ions (H+ & Na+). However, polyunsaturation of cell membranes occur in response to chronic cold temperatures. In fish increasingly cold environments lead to increasingly high cell membrane content of both monounsaturated and polyunsaturated fatty acids, to maintain greater membrane fluidity (and functionality) at the lower temperatures.

Essential fatty acids, or EFAs, are fatty acids that humans and other animals must ingest because the body requires them for good health but cannot synthesize them. Only two fatty acids are known to be essential for humans: alpha-linolenic acid (an omega-3 fatty acid) and linoleic acid (an omega-6 fatty acid). Omega 3 Fatty acid- Omega 6 Fatty acid- ϖThey act on DNA (activating or inhibiting transcription factors such as NF-κB, which is linked to pro- inflammatory cytokine production) ϖHigh intakes of omega-3 fatty acids are linked to

decreased rates of major depression. ϖWithout omega 3 and omega 6 human or animal will suffer in sick.

- Omega-3 fatty acids in algal oil, fish oil, fish and seafood have been shown to lower the risk of heart attacks.
- Omega-6 fatty acids in sunflower oil and safflower oil may also reduce the risk of cardiovascular disease.
- One gram of fat gives you nine calories of energy, which is over twice that provided by carbohydrates or protein. Fat enables your body to transport, store and absorb the fat-soluble vitamins A, D, E and K.

Cell Membranes: Require (50%) fatty acids to be "waterproof" and function properly.

• Heart: Prefers saturated long chain 16-carbon palmitic and 18-c stearic acid (over carbohydrates) for energy.
• Bones: Need fats to assimilate calcium effectively.
• Liver: They protect it from the adverse effects of alcohol and medications like acetaminophen.
• Lungs: Lung surfactant, which prevents asthma and other breathing disorders, is composed entirely of 16-c palmitic acids.
• Hormones: They function as signaling messengers for hormone production.
• Immune system: Saturated fatty acids play an important role here. They prime white blood cells to destroy invading bacteria, viruses and fungi and to fight tumors. Medium chain 12-c lauric acids and 14-c myristic acid (in butter) kill bacteria and candida in the gut.

Abstract;

1- monocarboxylic acids are containing even number C atoms.
2- Two types: saturated (C-C sb) and unsaturated (C-C db).
3- Fatty acids are components of several lipid molecules.
4- E.g. of lipids are triacylglycerol, streiods (cholestrol, sex hormones), fat soluble vitamins.

Functions

1- Storage of energy in the form of fat.
2- Membrane structures.
3- Insulation (thermal blanket).

4- Synthesis of hormones.

C- Biochemical Reactions

Metabolism: total sum of the chemical reaction happening in a living organism (highly coordinated and purposeful activity):

a- Anabolism- energy requiring biosynthetic pathways

b- Catabolism- degradation of fuel molecules and the production of energy for cellular function

c- All reactions are catalyzed by enzymes.

The primary functions of metabolism are:

a. acquisition & utilization of energy.

b. Synthesis of molecules needed for cell structure and functioning (i.e. proteins, nucleic acids, lipids, and CHO).

c. Removal of waste products.

And complex in a tiny cell:

a- The types of rxn are small

b- Mechanisms o biochemical rxns (abbreviation of reactions) are simple.

c- Reactions of central importance (for energy production and synthesis and degradation of major cell components) are relatively few in number.

Frequent reaction encountered in biochemical processes;

1. Nucleophilic Substitution;

One atom of group substituted for another.

2. Elimination Reactions;

Double bond is formed when atoms in a molecule is removed.

3. Addition Reactions:

a- Two molecules combine to form a single product.

b- A. Hydration Reactions

c- Water added to alkene > alcohol (common addition rxn)

4- Isomerization Reactions. Involve intramolecular shift of atoms or groups.

5- Oxidation-Reduction (redox) Reactions. Occur when there is a transfer of e- from a donor to an electron acceptor

6- Hydrolysis reactions. Cleavage of double bond by water.

D- Energy for Cells

a- Living cells are inherently unstable.

b- Constant flow of energy prevents them from becoming disorganized.

c- Cells obtains energy mainly by the oxidation of bio-molecules (e- transferred from 1 molecule to another and in doing so they lose energy) d- This energy captured by cells & used to maintain highly organized cellular structure and functions

E- How does complex structure of cells maintain high internal order?

1- Synthesis of bio-molecules

2- Transport Across Membranes. Cell membranes regulate the passage of ions and molecules from one compartment to another.

3- Cell Movement. Organized movement- most obvious characteristics of living cells. The intricate and coordinated activities required to sustain life require the movement of cell components.

4- Waste Removal. Animal cells convert food molecules into CO_2, H_20 and NH_3. If these not disposed properly can be toxic.

3- Proteins

Introduction

Proteins Are most abundantly distributed organic compounds. Seventy (70) kg man equal protein weight constitute 12 kg.

Skeleton and connective tissue contains half. Body protein and other half is intracellular.

Protein Turnover: The total amount of protein in the body remains constant (i.e Rate of protein synthesis is constant) Is equal to protein degradation. This process is called as protein turnover. The intake of protein is range 300 to 400 gm/day.

Proteins rich in Proline, Glutamate, Serine and threonine are rapidly degraded and short half-lives.

Structure of proteins

Proteins contain carbon, hydrogen, oxygen, nitrogen, and sometimes other atoms. They form the cellular structural elements, are biochemical catalysts, and are important regulators of gene expression.

Nitrogen is essential to the formation of twenty different amino acids, the building blocks of all body cells. Amino acids are characterized by the presence of a terminal carboxyl group and an amino group in the alpha position, and they are connected by peptide bonds.

Digestion breaks protein down to amino acids.

If amino acids are in excess of the body's biological requirements, they are metabolized to glycogen or fat and subsequently used for energy metabolism.

If amino acids are to be used for energy their carbon skeletons are converted to acetyl CoA, which enters the Krebs cycle for oxidation, producing ATP. The final products of protein catabolism include carbon dioxide, water, ATP, and urea.

Amino acids:

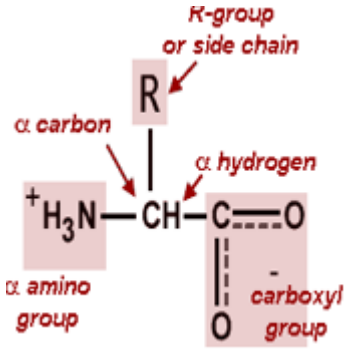
Introduction

Protein is a complex nutrient essential to many important functions in the body. Protein needs can be met by eating a variety of food sources. Protein is an energy-yielding nutrient composed of carbon, hydrogen, oxygen, and nitrogen. It is Differs from carbohydrates and fats because of the presence of nitrogen.

The body has at least 30,000 types of protein, each with a different job. The building blocks of all protein molecules are amino acids. There are 20 different amino acids that create different combinations for specific functions in the body. DNA provides the instructions for how the amino acids will be linked to form the proteins in your body.

What is the amino acid?

Amino acid, any of a group of organic molecules that consist of a basic amino group (—NH_2), an acidic carboxyl group (—COOH), and an organic R group (or side chain) that is unique to each amino acid. The term amino acid is short for α-amino [alpha-amino] carboxylic acid. Each molecule contains a central carbon (C) atom, called the α-carbon, to which both an amino and a carboxyl group are attached. The remaining two bonds of the α-carbon atom are generally satisfied by a hydrogen (H) atom and the R group. The formula of a general amino acid is:



General properties

a- Building blocks of proteins.

b- 22 commonly occurring.

c- Contains amino group and carboxyl group function groups (behavioral properties)

d- R Group (side chains) determines the chemical properties of each amino acid.

e- Also determines how the protein folds and its biological function.

f- Individual amino acids in protein connected by peptide bond.

i- Functions as transport proteins, structural proteins, enzymes, antibodies, cell receptors.

Table 12-1 Essential vs. Dispensable Amino Acids

Amino Acids	
Essential	**Non-Essential**
Histidine	Alanine
Isoleucine	Arginine
Leucine	Asparagine
Lysine	Aspartic Acid
Methionine	Glutamic Acid
Phenylalanine	Glutamine
Threonine	Glycine
Tryptophan	Proline
Valine	Serine
	Tryosine
	Tyrosine

4- Nucleic Acids

There are two kinds of nucleic acids in cells:

1) ribonucleic acids (RNA)
2) deoxyribonucleic acids (DNA)

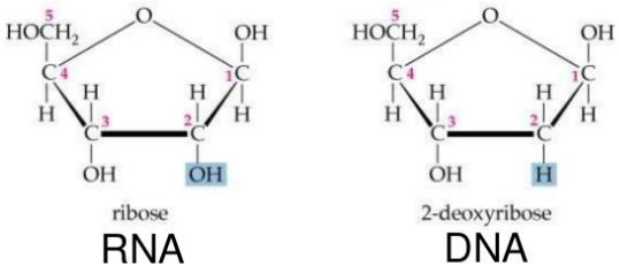
Both RNA and DNA are polymers built from monomers called nucleotides. A nucleotide is composed of a base a monosaccharide and a phosphate.

Nucleic Acids made up of nucleotides and found in all living cells except RBC. DNA is in the nucleus while the RNA is in the cytoplasm. It is function in the storage and transmission of genetic material with control and direct all protein synthesis.

each nucleotide contains:

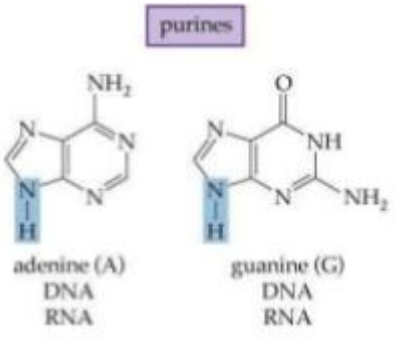
1) a sugar
2) a base
3) phosphoric acid unit

1) Ribose and Deoxyribose

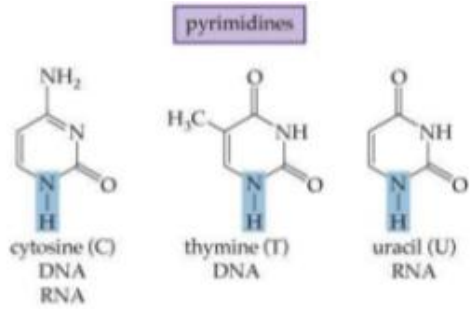


Bases in Nucleic Acids;

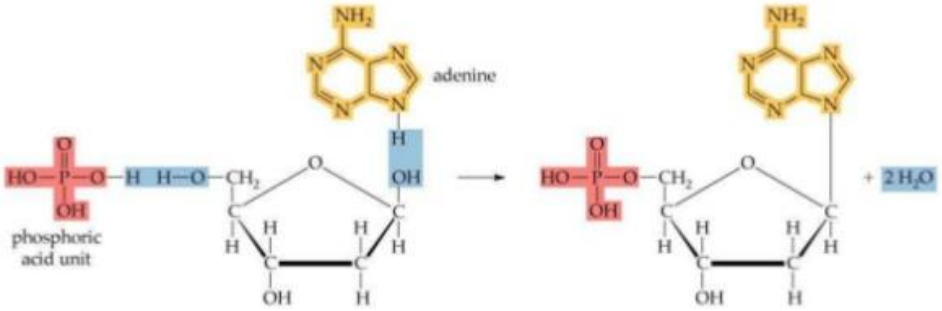
Bases for DNA: A, G, C, T



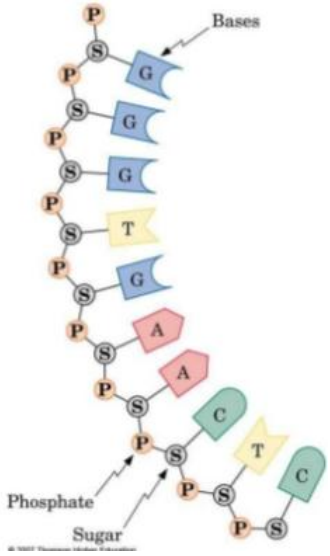
and Bases for RNA: A, G, C, U



Formation of a Nucleotide, alternating phosphate, sugar molecules form the backbone. The rxn between phosphate and sugar forms an ester bond with the elimination of water. The sugar bonds with a base, forming tertiary amine, with the elimination of water.



Structure of DNA and RNA



Water and Electrolytes

Water is balance and ImbalanceIn Human Body. Water is the chief constituent of human body. Water is the chief solvent of body. Water comprises 60-70% of total body weight. Human body cannot exist without Water.

Sources of Body Water

Exogenous Sources of Water

a- Drinking Water, Beverages -1000-1500 ml

b- Water from Cooked Foods

Water intake through mouth is highly variable 1-5 Liters this depend on:

a- Social habits.

b- Climatic condition.

Endogenous Sources of Water

a- Metabolic Water - 400 ml

b- Produced during metabolism oxidation of food substances.

Distribution of Body

Water in an adult of 70 kg body

Total Body Water 60- 70% L

Intracellular Fluid 35-65 % L

Extracellular Fluid14 35% L

Interstitial Tissue Fluid 11-25% L

Plasma /Intra Vascular Fluid 3 -8% L

Transcellular Fluid 2%

Functions of Body Water:

1- Involved in Biochemical reactions. Water act as reactant in many hydration Hydrolytic reactions of metabolic pathways.

2- Transporting media of body: Transportation of nutrients and waste metabolites through aqueous media of blood and tissue floods.

3- Regulates body temperature.

4- Water transports Hormones, Enzymes, blood platelets, and red and white blood cells.

5- Water act as a solvent for Electrolytes and Non electrolytes.

6- Water Facilitates Digestion and promoting Elimination of ingested food.
7- Water serve as a tissue Lubricant.

Body Water Input

Body can gain water by;
1- Ingestion of liquids and moist foods (2300mL/day)
2- Metabolic synthesis of water during cellular respiration (200mL /day)

Body Water Output

Body losses water through:
1- Kidneys (1500mL/day)
2- Evaporation from Skin (600mL/day)
3- Exhalation from Lungs (300mL/day)
4- Feces (100mL/day)

Body Electrolytes

What Are Electrolytes?
Substance when dissolved in solution dissociates into ions. These ions are able to carry an electrical current. An Electrolyte is a substance
Which develops an electrical charg**e** when dissolved in water.
Salts like **NaCl** and **KCl** in aqueous solutions gets dissociated to;
a- Charged Ions Na^+ and Cl^- called as Electrolytes.
b- The concentration of these Electrolytes is expressed as mEq/L.

Types of Electrolytes

a- Cation - Positively charged Electrolyte
b- anion - Negatively charged Electrolyte

Water molecules completely surround these dissociated ions. These prevent union of Cations and Anions.

Table 12-2 electrolytes in body fluid compartments

INTRACELLULAR Electrolytes	EXTRACELLULAR Electrolytes
POTASSIUM	SODIUM
MAGNESIUM	CHLORIDE
PHOSPHOROUS	BICARBONATE

Functions of Body Electrolytes

a- Electrolytes are well distributed in the body compartments.

b- Electrolytes in the medium/compartments produce osmotic pressure.

This osmotic pressure helps in maintaining water balance.

Electrolytes:

1- (Na+)- Most abundant electrolyte in the extracellular fluid (ECF). Sodium creates most of the osmotic pressure of extracellular fluid. It is essential for electrical activity of neurons and muscle cells.

2- K+- Essential for normal membrane excitability for nerve impulse

3- Cl^-- Regulates osmotic pressure and assists in regulating acid-base balance.

4- Ca^{+2}- Promotes nerve impulse and muscle contraction/relaxation.

5- Mg^{+2}- Plays role in carbohydrate and protein metabolism, storage and use of intracellular energy and neural transmission. Important in the functioning of the heart, nerves, and muscles.

Enzymes

Introduction

Enzymes are biological catalysts that speed up the rate of the biochemical reaction. Most enzymes are three dimensional globular proteins (tertiary and quaternary structure). Some special RNA

species also act as enzymes and are called Ribozymes e.g. hammerhead ribozyme. Hammerhead enzyme.

Structure of enzymes

The active site of an enzyme is the region that binds substrates co-factors and prosthetic groups and contains residue that helps to hold the substrate. Active sites generally occupy less than 5% of the total surface area of enzyme. Active site has a specific shape due to tertiary structure of protein. A change in the shape of protein affects the shape of active site and function of the enzyme.

Active site

Active site can be further divided into: Active Site Binding Site Catalytic Site It chooses the substrate It performs the catalytic and binds it to active site. action of enzyme.

Active site can be further devided in to;

It is the catalyst of biological systems. The remarkable molecular device that determine the patterns of chemical reactions. Catalytic power and specificity. Mainly proteins, but ribozyme (RNA)

the characteristics of enzymes:

1- Higher efficiency.
2- Milder conditions.
3- Greater reaction specificity.
4- Capacity for regulation.

Factors influencing enzyme activity:

There are pH, temperature, concentration of enzyme and substrate.

The figure fllowig declear the high efficiency of enzyme;

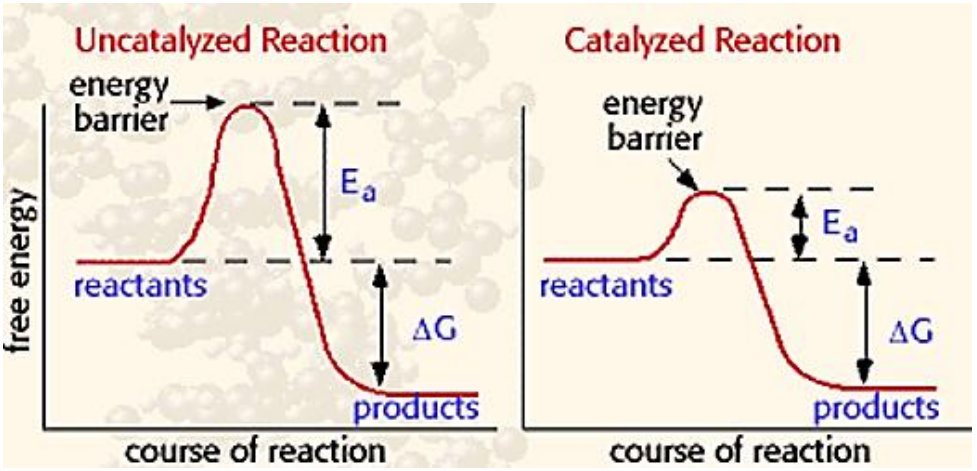


Figure 12-3 efficiency of enzyme

Table 12-3 Catalytic power and specificity

Enzyme	Nonenzymatic half-life	Uncatalyzed rate (k_{un}, s^{-1})	Catalyzed rate (k_{cat}, s^{-1})	Rate enhancement (k_{cat}/k_{un})
OMP decarboxylase	78,000,000 years	2.8×10^{-16}	39	1.4×10^{17}
Staphylococcal nuclease	130,000 years	1.7×10^{-13}	95	5.6×10^{14}
AMP nucleosidase	69,000 years	1.0×10^{-11}	60	6.0×10^{12}
Carboxypeptidase A	7.3 years	3.0×10^{-9}	578	1.9×10^{11}
Ketosteroid isomerase	7 weeks	1.7×10^{-7}	66,000	3.9×10^{11}
Triose phosphate isomerase	1.9 days	4.3×10^{-6}	4,300	1.0×10^{9}
Chorismate mutase	7.4 hours	2.6×10^{-5}	50	1.9×10^{6}

Enzymes and Cofactors

Most other enzymes are named for their substrates and for the reactions that they catalyze, with the suffix "ase" added,(ATPase).

Many enzymes require cofactors for activity. Cofactors are small molecules or metal ions.

Figure below is show relationship between cofactor and coenzyme.

Table 12-4 relationship between cofactor and coenzyme.

Cofactor	Enzyme
Coenzyme	
Thiamine pyrophosphate	Pyruvate dehydrogenase
Flavin adenine nucleotide	Monoamine oxidase
Nicotinamide adenine dinucleotide	Lactate dehydrogenase
Pyridoxal phosphate	Glycogen phosphorylase
Coenzyme A (CoA)	Acetyl CoA carboxylase
Biotin	Pyruvate carboxylase
5′-Deoxyadenosyl cobalamin	Methylmalonyl mutase
Tetrahydrofolate	Thymidylate synthase
Metal	
Zn^{2+}	Carbonic anhydrase
Zn^{2+}	Carboxypeptidase
Mg^{2+}	*Eco*RV
Mg^{2+}	Hexokinase
Ni^{2+}	Urease
Mo	Nitrate reductase
Se	Glutathione peroxidase
Mn^{2+}	Superoxide dismutase
K^{+}	Propionyl CoA carboxylase

Six major classes of enzymes are:

1- Oxidoreductases
2- Transferases
3- Hydrolases
4- Lyases
5- Isomerases
6- Ligases

Mechanism of enzyme action

The catalytic efficiency of enzymes is explained by two perspectives:

1- Thermodynamic change.

All chemical reactions have energy barriers between reactants and products. The difference in transitional state and substrate is called activational barrier.

Only a few substances cross the activation barrier and change into products. That is why rate of uncatalyzed reactions is much slow. Enzymes provide an alternate pathway for conversion of substrate into products. Enzymes accelerate reaction rates by forming

transitional state having low activational energy. Hence, the reaction rate is increased many folds in the presence of enzymes. The total energy of the system remains the same and equilibrium state is not disturbed.

2- processes at active site.

There are four processes, Covalent catalysis, Acid base catalysis, Catalysis by strain, and Catalysis by proximity

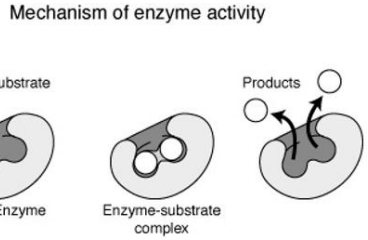
Enzyme is active in catalytic action of biochemical reaction. They act on substrate and forms a complex after interactions with the enzyme is called active center. The enzyme and substrate forms a complex at the active centre.

This binding action makes both enzyme and substrate stable. The interaction between substrate and enzyme may be either ionic bonds and hydrogen bonds or Van der Waal forces.

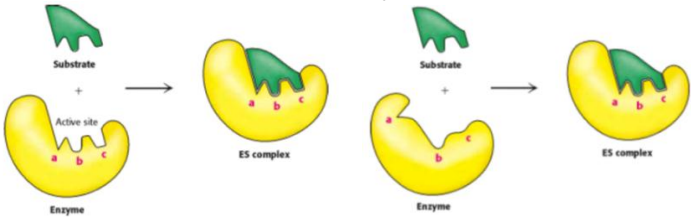
Types of Mechanisms of Enzymes:

There are two types of mechanisms involved to explain substrate-enzyme complex formation; lock and key theory (template model), and induced-fit theory.

Following figures are show in types of mechanism of enzyme.



Lock-and–Key Model



Induce-Fit Model

Questions

1- Which statement is correct about enzyme classification?

a. Enzymes are usually classified on their structures.
b. Enzymes are usually classified on their mechanism
c. Enzymes are classified into 5 classes
d. Enzymes are classified into 7 classes

2- Enzymes are sensitive to these following factors except:
a. pH value
b. Temperature
c. Concentration of enzyme and substrate
d. Light

3- The molecules which decrease the enzyme activity are called:
a. Activators
b. Initiators
c. Indicators
d. Inhibitors

4- Which statement is not the character of enzyme?
a. High efficiency
b. Mild condition
c. Specificity
d. Turnover the reaction

5- Enzymes don't change quantitatively in the biochemical reactions, but they change in structures temporarily.
a. This statement is false
b. This statement is completely true
c. This statement is only true partially

6- How do animals make light?
a. They heat themselves
b. They eat special chemicals which can give off light
c. They make light from an enzyme-catalyzed reaction
d. All are correct

7- If you are going to do an experiment, but it is very slow at room temperature. Which way can speed it up most?
a. Increase the temperature
b. Increase the external pressure
c. Add enzymes
d. Add inhibitors

8- There are __ kinds of inhibitor(s)?
a. 6
b. 5
c. 2
d. 1
9- Cofactors aren't:
a. Enzymes
b. Metal ions
c-small molecule

Hormones

Hormone, organic substance secreted by plants and animals that functions in the regulation of physiological activities and in maintaining homeostasis.

classification of hormones

The following Three categories of classification of hormones.

1. According to Chemical Nature.
2. According to Origin.
3. According to Nature of Action

1- According to Chemical Nature

a-Steroid Hormones e.g. Testosterone, Estrogen, Progesterone
b- Amine Hormones e.g. T3, T4, epinephrine, norepinephrine.
C- Peptide Hormones e.g. Oxytocin and vasopressin
d- Protein Hormones e.g. Insulin and glucagon
e- Glycoprotein Hormones e.g. LH, FSH
i- Eicosanoids Hormones e.g. Prostaglandins

Chemical Classes of Hormones

Three major classes of molecules function as hormones in vertebrates;

a- Polypeptides (proteins and peptides)
b- Amines derived from amino acids
c- Steroid hormones

Lipid-soluble hormones (steroid hormones) pass easily through cell membranes, while water-soluble hormones (polypeptides and amines) do not.

The solubility of a hormone correlates with the location of receptors inside or on the surface of target cells.

Hormones are typically grouped into three classes: steroids, amines, and peptides. Nearly all the steroid hormones are lipids synthesized from cholesterol; they are responsible for the development of many male and female sex characteristics. Amine hormones are (all) derived from the amino acid tyrosine secreted by the thyroid. Most hormones are peptides, thus each with only a short chain of amino acids; they are synthesized largely as proteins first as the following figure.

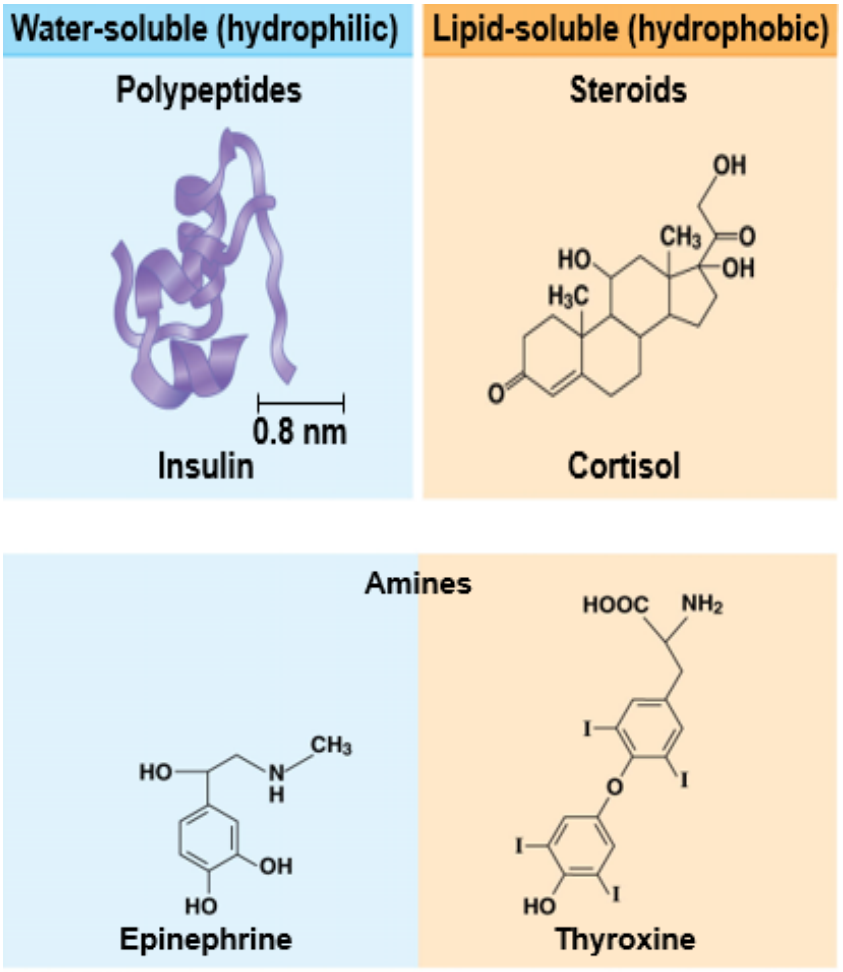


Figure 12-4 types of hormones

2- **On the Basis of Origin**

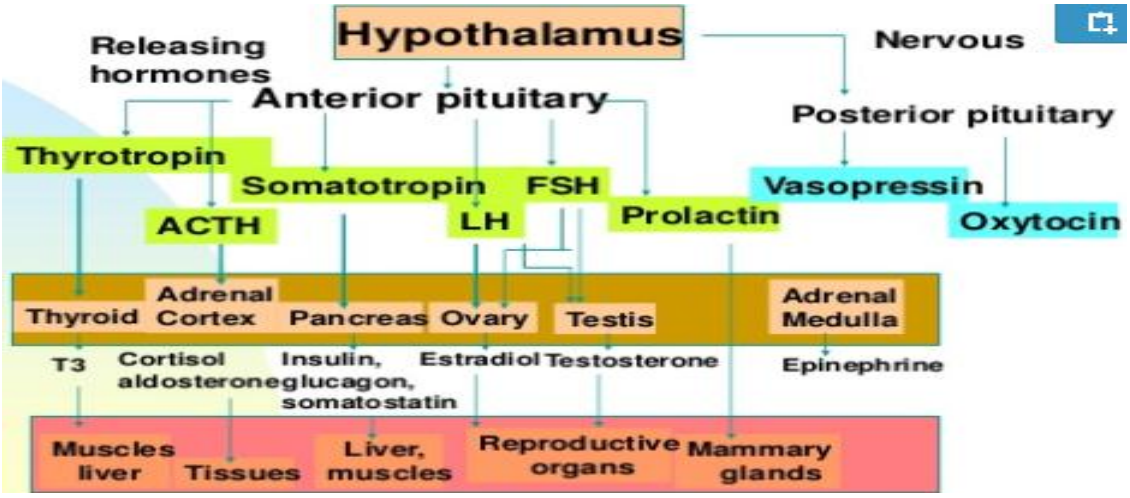
Reproductive hormones primarily derived from four major organ or system;

a- Hypothalamus

b- Anterior and posterior lobe of pituitary gland.

c- Gonads (testis and ovary including their interstitial tissues and corpus luteum).

d- Placenta and Uterus



3- **According to Nature of Action**

There are three types;

a- General Hormones: Growth hormone influence nearly all the body tissues, similar is the case with Thyroid and Insulin hormones, hence they fall in general category.

b- Specific Hormones: these hormones affect functions of specific organs, e.g. FSH and androgens.

c- Local Hormones: Prostaglandins, Acetyl choline, Histamine act locally to their site of production.

Mechanism of Action

1- The first step of a hormone's action is to bind to specific receptors at the target cell.

2- Some receptors are located on cell membrane while some are located in cytoplasm and nucleus.

3-These receptors are protein in nature and usually 2000-100,000 receptors are present on each cell.
4- Receptors are located on specific in/on target cells.

Cellular Response Pathways

Water- and lipid-soluble hormones differ in their paths through a body.
Water-soluble hormones are secreted by exocytosis, travel freely in the bloodstream, and bind to cell-surface receptors.
Lipid-soluble hormones diffuse across cell membranes, travel in the bloodstream bound to transport proteins, and diffuse through the membrane of target cells.

Pathway for Water-Soluble Hormones

Binding of a hormone to its receptor initiates a **signal transduction** pathway leading to responses in the cytoplasm, enzyme activation, or a change in gene expression.
The hormone **epinephrine** has multiple effects in mediating the body's response to short-term stress. Epinephrine binds to receptors on the plasma membrane of liver cells. This triggers the release of messenger molecules that activate enzymes and result in the release of glucose into the bloodstream. the following figure declare that.

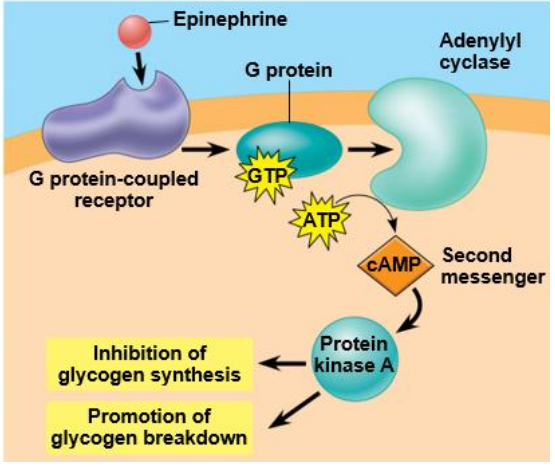


Figure 12-5 pathway of epinephrine

Pathway for Lipid-Soluble Hormones

The response to a lipid-soluble hormone is usually a change in gene expression. Steroids, thyroid hormones, and the hormonal form of vitamin D enter target cells and bind to protein receptors in the cytoplasm or nucleus. Protein-receptor complexes then act as transcription factors in the nucleus, regulating transcription of specific genes.

Multiple Effects of Hormones

The same hormone may have different effects on target cells that have;

a- Different receptors for the hormone

b- Different signal transduction pathways

UREA

Introduction

Urea is major end product of nitrogen metabolism in humans and mammals. NH3 the product of oxidative deamination reaction, is toxic even small amount and must be removed from the body. Urea cycle is the conversion reaction of NH3 to urea. This reaction occurs in the liver certain occur in cytosol and mitochondria. The urea is transported to the kidney where it is excreted.

Synthesis of urea

Urea cycle also known as kreb's hensleit urea cycle or ornithine cycle Site: Liver ′ Sub cellular organelle: two steps occur in the mitochondria, remaining in the cytoplasm. Converts NH_3 into harmless Urea. As show in figure bellow;

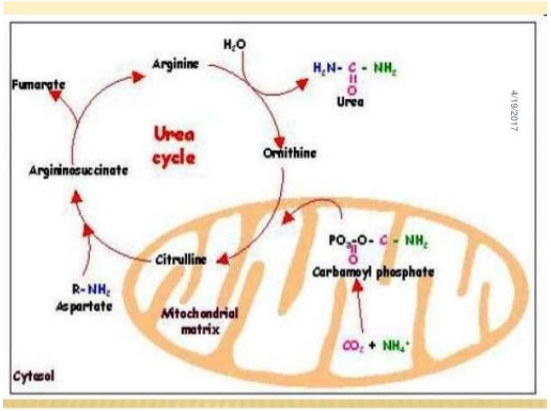
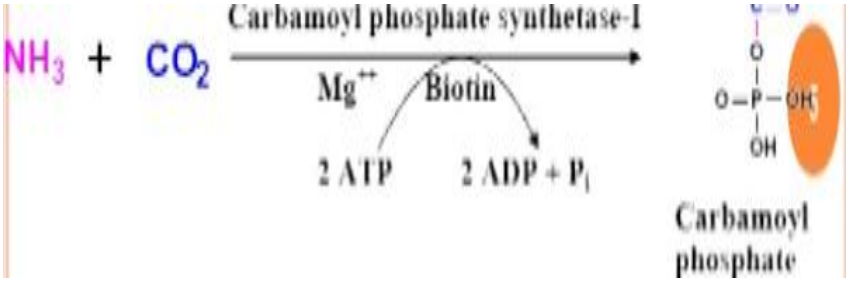


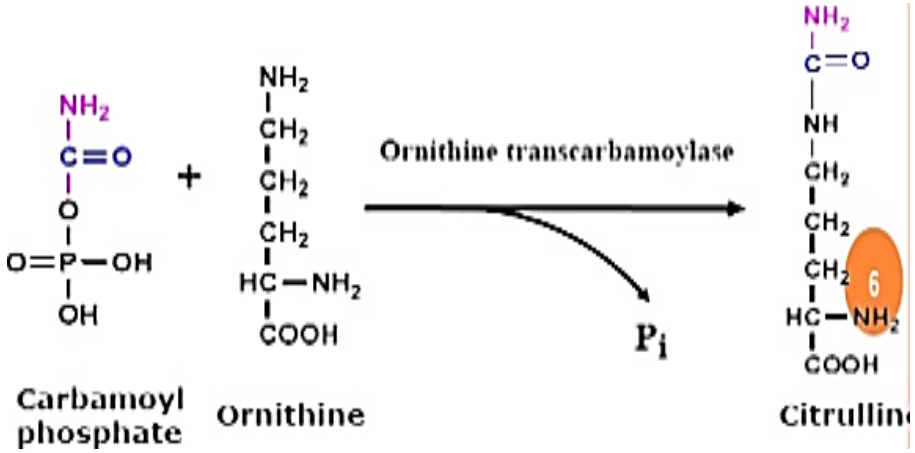
Figure 12-6 steps of Synthesis of urea

Steps in urea cycle

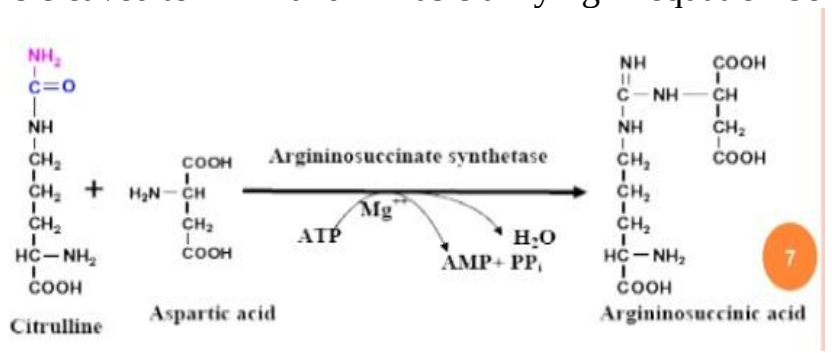
Step 1; formation of carbamoyl phosphate ′ Carbamoyl phosphate synthase one (cps I) of mitochondria catalyses the condensation of NH4 ions with CO2 to form carbamoyl phosphate. ′ This step consumes two ATP and it is irreversible. CPS I requires N-acetyl glutamate for its activity. Carbamoyl phosphate II involved in pyrimidine synthesis and it is present in cytosol. It accepts amino group from glutamine and does not require N-acetyl glutamate for its activity as show in the following equation;



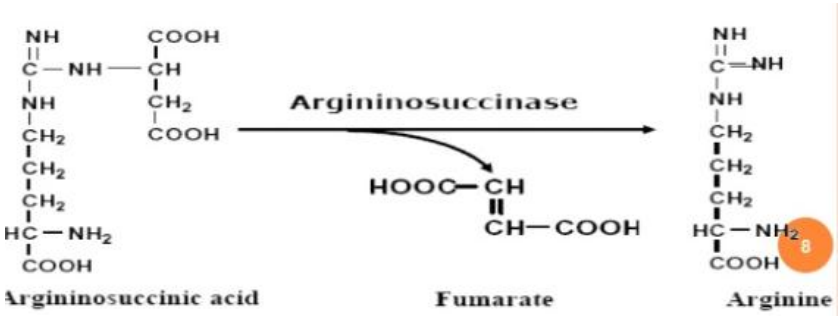
Step 2; formation of citrulline. The second reaction is also mitochondrial. Citrulline is synthesized from carbamoyl phosphate and ornithine by ornithine transcarbamoylase. Ornithine is regenerated and used in urea cycle. Citrulline is transported to cytosol by a transporter system as show in the following scheme;



Step3: formation of arginosuccinate. Citrulline condenses with aspartate to form Arginosuccinate by the enzyme Arginosuccinate synthetase. Second amino group of urea is incorporated. It requires ATP it is cleaved to AMP and PPi as clarifying in equation bellow;



Step 4; formation of arginine or cleavage of arginosuccinate. The enzyme Arginosuccinase or argininosuccinate lyase cleaves Arginosuccinate to Arginine and fumarate (and intermediate in TCA cycle) as show in the scheme following;



Step 5; formation of urea. Arginase is the 5th and final enzyme that cleaves Arginine to yield urea and ornithine. Ornithine is regenerated enters mitochondria for its reuse in the urea cycle. Ornithine and lysine compete with Arginine (competitive inhibition). Arginase is mostly found in the liver while the rest of enzymes are also present in other tissues. Arginine synthesis can occur to varying degrees in many tissues, but only liver can ultimately produce urea.

Urea cycle disorders. There are six enzyme disorders of the urea cycle, collectively known as inborn errors of urea synthesis, or urea cycle enzyme defects. Each is referred to by the initials of the missing enzyme.

Excretion of urea.

urea is filtered across the glomerulus and enters the proximal tubule. the concentration of urea in the ultra-filtrate is similar to plasma, so the amount of urea entering the proximal tubule is controlled by the GFR. In general, 30%–50% of the filtered load of urea is excreted. The urea concentration increases in the first 75% of the proximal convoluted tubule, where it reaches a value approximately 50% higher than plasma. This increase results from the removal of water, secondary to salt transport, and is maintained throughout the remainder of the proximal tubule. Urea transport across the proximal tubule is not regulated by vasopressin (also named antidiuretic hormone) but is increased with an increase in sodium transport.

Control of blood urea

Correct intake of protein If kidneys can't do their work properly, extra protein will increase the workload on kidneys. On the contrary, lack of protein may lead to malnutrition. Under this circumstance, it is necessary to restrict the amount of protein intake to 0.6-0.8g/kg every day. Supplement enough calories: This can reduce the consumption of protein in the body. Generally, it is suitable to take in 30Kca/Kg of calories every day.

Uric acid

Introduction

Uric acid is the final breakdown product of purine degradation in humans. Uric acid is synthesized from compounds containing purines, and it is a waste product derived from purines of the diet such as liver, thymus, and organ meat. Uric acid is mainly excreted in urine by glomerular filtration. A part of it is reabsorbed by the renal tubules. Serum uric acid determination is used to diagnose gout. In gout the blood levels of uric acid are increased and also abnormal deposition of uric acid crystals occur in joints, tendons bone leading to painful condition of these structures. Primary gout: is a condition in which uric acid is synthesized in excess and decreased ability of plasma to retain uric acid in solution. The cause for primary gout is unknown, but there is a metabolic disorder. Secondary gout: is accumulation of uric acid in plasma, then other tissues, due to increased purines catabolism it is not due to excessive synthesis of uric acid.

Synthesis of uric acid

The end product of purine metabolism in human is uric acid. The nucleotide monophophate (AMP, IMP and GMP) are converted to their respective nucleoside forms (adenosine, inosine and guanosine) by the action of nucleotidase. The amino group either from AMP or adenosine can be removed to produce IMP or inosine. Inosine and guanosine are converted to hypoxanthine and guanine by purine nucleoside phosphorylase. Adenosine is not degraded by this enzyme it has to be converted to inosine. Guanine undergo deamination by guanase to form xanthine. Xanthine oxidase converts hypoxanthine to xanthine and xanthine to uric acid. Xanthine oxidase liberates H2O2

which is harmful to the tissue. Catalase cleaves H2O2 to water and oxygen. Uric acid is the final product of purine metabolism.

Clinical significance of uric acid

Normal Uric acid levels are 2.4-6.0 mg/dl (female) and 3.4-7.0 mg/dl (male) Normal values will vary from laboratory to laboratory. Causes of High uric acid level Primary hyperuricemia: Increased production of uric acid from purine. When kidneys cannot get rid of the uric acid in your blood, resulting in high levels. Causes of Secondary hyperuricemia: Kidney disease and Certain cancers. Medications can cause increased levels of uric acid in the blood. certain forms of diabetes (type 2 diabetes) or acidosis can cause hyperuricemia.

Gout

Gout is due to elevated levels of uric acid in the blood This occurs due to a combination of diet and genetic factors. At high levels, uric acid crystallizes and the crystals deposit in joints, tendons and surrounding tissues resulting in an attack of gout. Gout occurs more commonly in those who eat a lot of meat, drink a lot of beer, or are overweight. follwing case of gout.

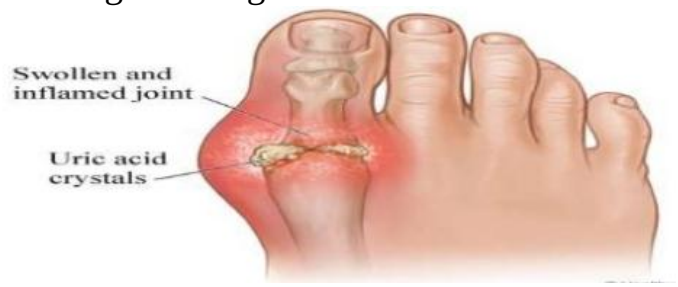


Figure 12-7 case of gout

Excretion of uric acid

It has been known for many years that the kidney plays a major role in uric acid homeostasis, as more than 70% of urate excretion is renal. Hyperuricemia in gout is most commonly the result of relative urate under excretion, as the kidney has enormous capacity for urate reabsorption.

Control of uric acid

Adjust Diet: To gain control of uric acid levels, avoid eating foods high in purine. Limit Alcohol: Because alcohol dehydrates the body, it is advisable to limit consumption, particularly when consumed with foods high in purine.

Water: Keep your body hydrated.

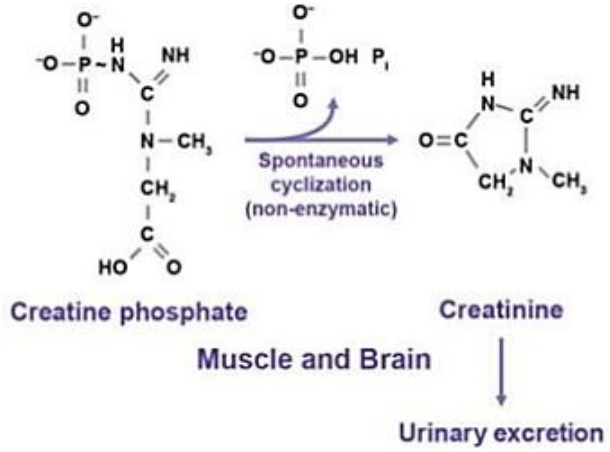
Creatinine

What's Creatine and Creatinine

Introduction

Creatinine is a chemical waste molecule that is generated from muscle metabolism. Creatinine is produced from creatine, a molecule of major importance for energy production in muscles. Creatinine is transported through the bloodstream to the kidneys. The kidneys filter out the creatinine.

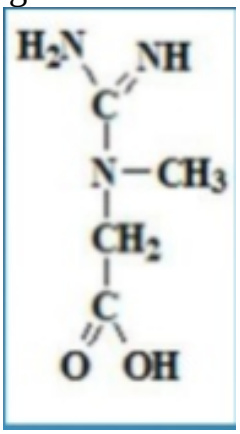
Creatine is a nitrogenous organic acid that occurs naturally in vertebrates. Its main role is to facilitate recycling of adenosine triphosphate (ATP), the energy currency of the cell, primarily in muscle and brain tissue. Creatine is not an essential nutrient as it is naturally produced in the human body from the amino acids glycine and arginine. Creatine, synthesized in the liver and kidney, is transported through the blood and taken up by tissues with high energy demands, such as the brain and skeletal muscle.as show in the following scheme;



Why is it important to check blood creatinine levels?

The kidneys maintain the blood creatinine in a normal range (male: 0.6 to 1.2 milligrams (mg) per deciliter (dL). Creatinine is a reliable indicator of kidney function. Elevated creatinine level show impaired kidney function or kidney disease.

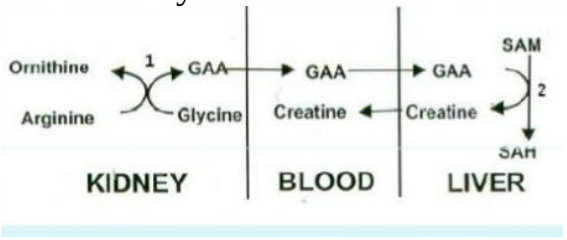
Creatine and creatinine are not the same substance. Creatine is found in the muscle. Creatinine is a break-down product (a waste product) of creatine phosphate and creatine in muscles, and is usually produced at a fairly constant rate by the body depending on muscle mass). The creatine is an amino acid that does not found in proteins. Creatine is a nitrogenous organic acid. such as in following bellow;



Three amino acids are required: Glycine Arginine Methionine (as S-adenosylmethionine). Site of biosynthesis:

Step 1: Kidneys

Step 2: Liver Creatine Biosynthesis.



Distribution of body creatine; it is from liver, transported to other tissues and 98% of creatines are present in skeletal and heart muscles. In Muscle, gets converted to the high energy source creatine phosphate (phosphocreatine).

What's the Relationship between Creatine and creatine phosphate?

Creatine and creatine phosphate exist in a reversible equilibrium in skeletal muscle. In skeletal muscle, approximately one-fourth of creatine exists as free creatine and three fourth exists as creatine phosphate.

Creatine Phosphate Is a high-energy phosphate compound and Acts as a storage form of energy in the muscle. It is Provides a small but, ready source of energy during first few minutes of intense muscular contraction. The amount of creatine phosphate in the body is proportional to the muscle mass.

Creating degradation

1. Creatine and creatine phosphate spontaneously form creatinine as an end product.
2. Creatinine is excreted in the urine.
3. Serum creatinine is a sensitive indicator of kidney disease (Kidney function test).
4. Serum creatinine increases with the impairment of kidney function Creatine Degradation.

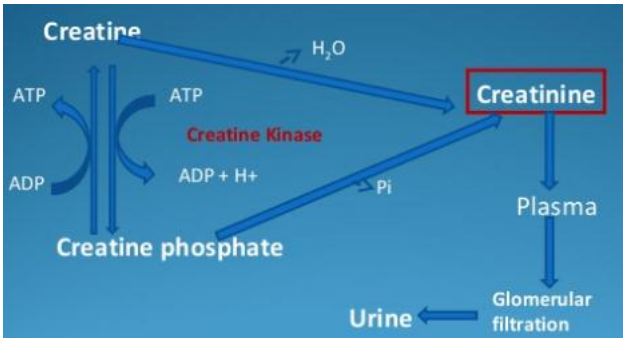


Figure 12-8 Creatine Degradation

Creatinine Excretion

The creatinine is a waste product of creatine phosphate and it will be excreted by the kidney in the urine at a rate of 1 to 2 g/day.

Serum Creatinine may be Affected Partly by;

a- The amount of muscle tissue you have. Men tend to have higher levels of blood creatinine because they have more skeletal muscle tissues than women.

B- Protein in diet. Vegetarians have been shown to have lower creatinine levels in blood.

Vitamins

Introduction

The word "vitamin" comes from the Latin word “vita”, means "life". Vitamins are organic components in food that are needed in very small amounts for growth and for maintaining good health. Everybody must eat a certain amount of vitamins to stay healthy. Vitamins are chemicals found in very small amounts in many different foods.

Characteristics

Vitamins are required in small quantities in the diet because they cannot be synthesized by the body. Water soluble vitamins cannot be stored in human tissues. Their excess is excreted with urine. ט Significant amounts of fat soluble vitamins can be stored in adipose tissue and the liver. ט Synthetic vitamins are identical to natural vitamins. Once growth and development are completed, vitamins remain essential nutrients for the healthy maintenance of the cells, tissues, and organs.

Functions

Vitamins are helpful for the health and life of the body in the following respects:

(a) They build up the resistance of the body against diseases.

(b) Prevent and cure various diseases caused by deficiency.

(c) Help the digestion and utilization of mineral salts and Carbohydrates in the body.

(d) Stimulate and give strength to digestive and nervous system.

(e) Help health protection.

(f) Help maintenance of proper health and normal growth.

Classification

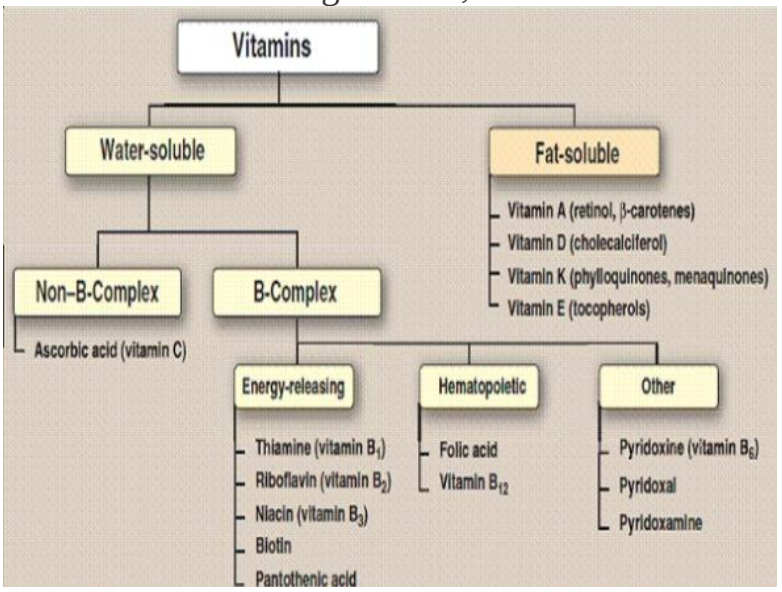
On the basis of their solubility vitamins are mainly 2 types:

Fat soluble vitamins

Vitamins that dissolve in fat. Because fat is easily stored on our body, fat-soluble vitamins can be stored within our fat. This means they can accumulate and be saved for later use. The fat-soluble vitamins are A, D, E and K.

Water soluble vitamins;

Vitamins that dissolve in water. Because our body is a watery environment, these vitamins can move through our body pretty easily, and they can also be flushed out by the kidneys. Water-soluble vitamins include the B-complex vitamins and vitamin C. There are eight B vitamins, including vitamin B1, B2, B3, B5, B6, B7, B9 and B12. As illustrated in following scheme;



Vitamin A

Vitamin A is a group of unsaturated nutritional organic compounds, that includes retinol, retinal, retinoic acid, and several provitamin A carotenoid, among which beta-carotene is the most important. Its active form is present only in Animal Tissue. daily requirement, men and women – 600 mcg and children – 600mcg.

Functions

Vitamin A plays a role in a variety of functions throughout the body, such as: ʊ Vision ʊ Gene transcription ʊ Immune function ʊ Embryonic development and reproduction ʊ Bone metabolism ʊ Hematopoiesis (the production of blood cells and platelets) ʊ Skin and cellular health ʊ Antioxidant activity

Vitamin D

Vitamin D refers to a group of fat-soluble secosteroids (a type of steroid with a "broken" ring) found in liver and fish oils, or obtained by irradiating provitamin D with ultraviolet light and are responsible for enhancing intestinal absorption of calcium, iron, magnesium, phosphate and zinc. It is also called SUNSHINE VITAMIN. it is available in 2 forms- Cholecalciferol (vitamin D3) is made from 7-dehydrocholesterol in the skin of animals and humans. Calciferol - D2 is obtained artificially by irradiation of ergo- sterol and is called ergocalciferol.

Functions of vitamin D

They are Calcium Balance, Cell Differentiation, Immunity, Blood Pressure Regulation and Development of Bones and Teeth.

Vitamin E

Vitamin E refers to a group of compounds that include both tocopherols and tocotrienols. They are naturally occuring anti-oxidant. It is also called anti-aging factor. The word tocopherol is derived from the word toco meaning child birth and pheros meaning to bear. It is yellow oily liquid freely soluble in fat solvent. Tocopherol α, β, γ, δ have been obtained from the natural sources.

Functions of vitamin E

They are Antioxidant (most powerful natural), Free radical scavenger, protects cell membranes, Protects LDL from oxidation, Protection of double bonds in polyunsaturated fatty acids, Prevention of rancidity, and Works in conjunction with selenium. Vitamin E also plays a role in neurological functions, and inhibition of platelet aggregation. Vitamin E also protects lipids and prevents the oxidation of polyunsaturated fatty acids.

Vitamin K

Vitamin K refers to a group of structurally similar, fat- soluble vitamins the human body needs for complete synthesis of certain proteins that are required for blood coagulation, and also certain proteins that the body uses to manipulate binding of calcium in bone and other tissues. ʊ Vitamin K is naturally produced by the bacteria in the intestines. ʊ It is essential for production of a type of protein called prothrombin and other factor involve in blood clotting mechanism. Hence it is known as anti – hemorrhagic vitamin. Vitamin K includes two natural vitamers: vitamin K1 (phylloquinone) and vitamin K2 (menaquinones)

Functions of vitamin K

It is essential for the hepatic synthesis of coagulation factor II, V, VII, IX, X.

it prevents hemorrhage only in cases when there is defective production of prothrombin it acts as a co- factor in oxidative phosphorylation associated with lipid. Vitamin-K is needed for carboxylation of glutamyl residue of Ca++ binding transport between the flavin coenzyme and the cytochrome system.

Vitamin b1 (thiamine)

It is also called Anti Beri-Beri factor, Anti Neuritic factor, and also Aneurin. ʊ It is colorless basic organic compound composed of a sulfated pyramiding ring. ʊ All living organisms use thiamine, but it is synthesized only in bacteria, fungi, and plants. ʊ Contains sulfur and nitrogen group ʊ Destroyed by alkaline and heat ʊ Coenzyme: Thiamin pyrophosphate (TPP).

Functions of thiamine

Vitamin B1, is very essential for converting carbohydrate into energy. The most important use of thiamine is in the treatment of beriberi, a condition caused by a deficiency of thiamine in the diet. Symptoms include swelling, tingling or burning sensation in the hands and feet, confusion, difficulty breathing. Vitamin B1, helps in maintaining the healthy nervous system. Vitamin B1, is necessary for healthy mucous membranes. It helps in the digestion of food. It

provides strength to muscles. It is very useful for the proper functioning of heart.

Vitamin c (ascorbic acid)

- It is also called ascorbic acid and antibiotic vitamin.
- It is the most active reducing agent.
- It is powerful antioxidant.
- Synthesized by most animals (not by human).

Functions of vitamin C

They are Synthesis of collagen, Maintenance, necessary for maintenance of bones and proper functioning of the adrenal and thyroid gland, and Antioxidant. It stimulates immune function, combats bacterial infection, reduces effects of allergy-producing substances and protects vitamins, A, E and some B complex vitamins from oxidation.

Questions and Answers

Q1. Stearic acid, $CH_3(CH_2)_{16}COOH$, is a common saturated fatty acid.

a. What is meant by the term 'saturated'?

Sol. No C to C double bonds.

b. Stearic acid can be used as a source of energy. Write a chemical equation for the complete reaction between oxygen and stearic acid.

Sol. $CH_3(CH_2)_{16}COOH + 26O_2 \rightarrow 18CO_2 + 18H2O$; correct reagents and products, correct stoichiometry

c. The fats and oils in food are usually made up of a complex mixture of saturated and unsaturated fatty acids. During processing, additives are often added to prevent spoiling.

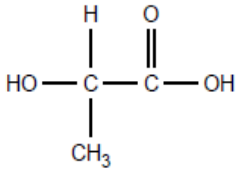
i. What class of food additive is used specifically to prevent oils becoming rancid?

Sol. Antioxidants

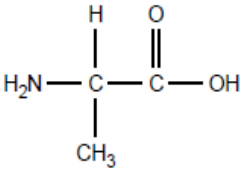
ii. How does the additive prevent oils becoming rancid?

Sol. Reacting preferentially with O_2

Q2. Lactic acid and alanine are both important chemicals in living systems. Their structures are



lactic acid



alanine

a. Give the name of the functional group common to both compounds.

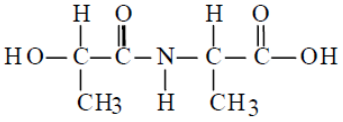
Sol. Carboxy (no other choice acceptable)

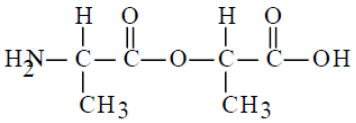
b. Why is alanine classified as an amino acid but lactic acid is not?

Sol. Lactic acid has no amino group (must mention lactic acid**.**

c. In the below, draw structures of two different possible organic molecules formed by a condensation reaction between lactic acid and alanine.

Sol.





d. For **one** of the structures given in part **c.**,

i. circle the **new** functional group formed.

Sol. Circle either -CONH-OR-COO-

ii. name the functional group that you have circled.

Sol. Peptide OR ester

Q3. What is the most abundant element in the human body, weight?

Sol. oxygen

Q4. Most enzymes are a type of

a. carbohydrate

b. lipid

c. nucleic acid

d. protein

Q5. In addition to carbon, hydrogen and oxygen, which element is found in all amino acids?

a. chlorine
b. nitrogen
c. phosphorus
d. sulfur

Q6. Which of the following statements is true about a peptide bond (RCONHR')?
a. It is non-planar.
b. It is capable of forming a hydrogen bond.
c. The cis configuration is favoured over the trans configuration
d. Single bond rotation is permitted between nitrogen and the carbonyl group.
Feedback:

Statement **b.** is correct. The NH of the amide can act as a hydrogen bond donor and the carbonyl group can act as a hydrogen bond acceptor. Statements **a.**, **c.** and **d.** are false. The peptide bond has double bond character due to the interaction of the nitrogen lone pair with the carbonyl group. This prevents bond rotation and makes the bond planar. The trans isomer is favoured over the cis isomer.

Q7. Identify which of the following terms refers to the arrangement of different protein subunits in a multiprotein complex.

a. primary structure
b. secondary structure
c. tertiary structure
d. quaternary structure
Feedback: Primary, secondary and tertiary structure refers to the different structural levels of a single protein. Quaternary structure refers to the overall structure of a multiprotein complex.

Q8. Identify which of the following terms refers to the order in which amino acids are linked together in a protein.

a. primary structure
b. secondary structure

c. tertiary structure
d. quaternary structure
Feedback: Primary structure refers to the order of the amino acids in a protein. Secondary structure indicates regions of ordered structure, and tertiary structure is the overall structure of the protein. Quaternary structure refers to the structure of a multi-protein complex.

Q9. Identify which of the following terms refers to the overall three dimensional shape of a protein.
a. primary structure
b. secondary structure
c. tertiary structure
d. quaternary structure

Feedback: Primary structure refers to the order of the amino acids in a protein. Secondary structure indicates regions of ordered structure, and tertiary structure is the overall structure of the protein. Quaternary structure refers to the structure of a multi-protein complex.

Q10. Identify which of the following terms refers to 'regions of ordered structure within a protein'.
a. primary structure
b. secondary structure
c. tertiary structure
d. quaternary structure

Feedback: Primary structure refers to the order of the amino acids in a protein. Secondary structure indicates regions of ordered structure, and tertiary structure is the overall structure of the protein. Quaternary structure refers to the structure of a multi-protein complex.

Q11. Which of the following statements is incorrect regarding transport proteins?

a. They are present in cell membranes.
b. They serve to carry polar molecules across the hydrophobic cell membrane.
c. They are required to transport amino acids across cell membranes.
d. They are required to transport hydrophobic steroids across cell membranes.
Feedback: Steroids are hydrophobic molecules which can pass through the cell membrane without the need for a transport protein.

Q12. All of the individual □-amino acids that make up human proteins
a. have an $–NH_2$ and a $–CO_2H$ group attached to the same carbon atom.
b. can be made naturally in the human body.
c. contain the peptide group.
d. have an $–NH_2$ and an –OH group attached to the same carbon atom.
Q13. The amino acid, alanine, dissolves in water.
In an aqueous solution with a pH = 7, alanine is acting as:
a. an acid only.
b. a base only.
c. neither an acid nor a base.
d. both an acid and a base.

Q14. Which of the following statements is false with respect to an enzyme's ability to catalyse a reaction?
a. An enzyme provides a reaction surface and a suitable environment for the reaction to take place.
b. An enzyme binds reactants such that they are positioned correctly and can attain their transition-state configurations.
c. An enzyme allows the reaction to go through a less stable transition state than would normally be the case.
d. An enzyme can weaken bonds in reactants through the binding process.

Q15. Which of the following statements is not true regarding the active site of an enzyme?

a. An active site is normally a hollow or cleft on the surface of an enzyme.
b. An active site is normally hydrophilic in nature.
c. Substrates fit into active sites and bind to functional groups within the active site.
d. An active site contains amino acids which are important to the binding process and the catalytic mechanism.

Q16. Which of the following statements is incorrect with respect to an enzyme's ability to catalyse a reaction?

a. An enzyme provides a reaction surface and a hydrophilic environment for the reaction to take place.
b. An enzyme binds reactants such that they are positioned correctly and can attain their transition-state configurations.
c. An enzyme allows the reaction to go through a more stable transition state than would normally be the case.
d. An enzyme can weaken bonds in reactants through the binding process

Q17. Some enzymes require the presence of a non-protein substance if they are to catalyse a reaction. Which of the following terms is the best general term for such a substance?
a. prosthetic group
b. cofactor
c. co-enzyme
d. modulator

Q18. What term is used for a non-protein organic molecule that is required by some enzymes in order to catalyse a reaction on a substrate?
a. prosthetic group
b. cofactor

c. co-enzyme
d. modulator

Q19. Sucrose, ordinary table sugar, may be classified as a:
a. Monosaccharide
b. Disaccharide
c. Polysaccharide
d. Oligosaccharide

SECTION FOUR
Chapter Thirteen
Good Laboratory Practice

SECTION FOUR
CHAPTER THIRTEEN
Good Laboratory Practice:
Quality assurance of standard operating procedure
"Every day we do something new"- The quality

Introduction

We described in chapters 2-9 the volumetric analysis and gravimetric analysis while in chapter 10 we discussed application of spectrophotometric method as instrumental analysis to unknown sample determination. In all these methods, we did not review how to validate the results using analytical statistics to show the quality of the results. To confirm appropriate measurements, we will have stablished methods which are used to give accurate result. But, the results will depend on the customer's satisfaction. Here especially if the measurements are for the purpose of organizing or forensic analysis, which enables defense in court. The result, the concepts of good laboratory practice, validation of method, and quality assurance for testing laboratories have involved as that report analyzed results correct and documented limit.

Good Laboratory Practice

History

GLP is a formal regulation that was created by the FDA (United States food and drug administration) in 1978. Although GLP originated in the United States, it had a worldwide impact. Non-US companies that wanted to do business with the United States or register their pharmacies in the United States had to comply with the United States GLP regulations. They eventually started making GLP regulations in their home countries. In 1981 an organization named OECD (organization for economic co-operation and development) produced GLP principles that are international standard.

What Is Good Laboratory Practice?

GLP is an FDA regulation. Definition GLP embodies a set of principles that provides a framework within which laboratory studies are planned performed, monitored, reported and archived. GLP is sometimes confused with the standards of laboratory safety like wearing safety goggles. The GLP ensure correct result is reported.

All references of GLP contain two elements: standard operating procedure (SOP) and quality assurance unit (QAU). Standard operating procedure provide detail description of activities performed by the laboratory. Example are custody chain, sample handling preparation, the analytical method, instruments, maintenance, archiving (record keeping), and so on. Detailing sample analysis procedures are provided for laboratory analysts or technicians to follow. The quality assurance unit is generally independent from laboratory and answer to manager of the organization with which the laboratory affiliated.

Quality Assurance

Quality Assurance an overall management plans to guarantee the integrity of data (The "system").

The test facility should have a documented QA program. It should be carried out by an individual designated by and directly responsible to management and who are familiar with the test procedures. This individual should not be involved in the conduct of the study being assured. Responsibilities of Quality Assurance Program, They should- maintain copies of all approved study plan and SOPs in use in the test facility and have access to an up-to-date copy of the master schedule. Verify the study plan and the verification should be documented. Conduct inspections to determine if all studies are conducted in accordance with the principles of GLP. Inspections should also determine the study plans and SOPs have been made available to study personnel and are being followed.

Inspections are 3 types are study based, facility based and process based. Final reports are inspected to confirm that the methods, procedures and observation are accurately and completely described

and that are reported results accurately reflect the raw data of the studies. Promptly report any inspection results in writing to management and to the study director and to the principal investigator and the respective management, when applicable. Prepare and sign a statement, to be included with the final report, which specifies types of inspections, their dates, including the phase(s) of the study inspected and the dates inspection results were reported to management and the study director and principal investigator(s), if applicable. This statement would also serve to confirm that the final report reflects the raw data.

ISO-QA

All those planned and systematic actions necessary to provide adequate confidence that a product, process or service will satisfy given quality requirements ISO 2001, 3September 29, 2015.

A quality management system

A quality management system (QMS) is a formalized system that documents processes, procedures, and responsibilities for achieving quality policies and objectives. A QMS helps to coordinate and direct an organization's activities to meet customer and regulatory requirements and improve its effectiveness and efficiency on a continuous basis.

Figure 13-1 documents of quality management system

Purpose of QMS

Quality management systems serve many purposes, including: Improving processes, Facilitating and identifying training opportunities, engaging staff, and Setting organization-wide direction.

Standard Operating Procedures (SOP)

Written procedures for a laboratories program;

They define how to carry out protocol-specified activities. Most often written in a chronological listing of action steps. They are written to explain how the procedures are supposed to work.

Purpose: to ensure reproducible and correct performance of laboratory tests. Reduce inter-operator and inter-run variation. It is made specific for each laboratory.

Controlled document: need a regulated system for, Preparation, Approval, Distribution, Revision and Training. The laboratory should have SOP for every method.

Process documents: Show how everything fits together, Flow of work, across procedures and across time. Each process has SOP. The flowing figure shows the all processing in GLP with SOP for each process.

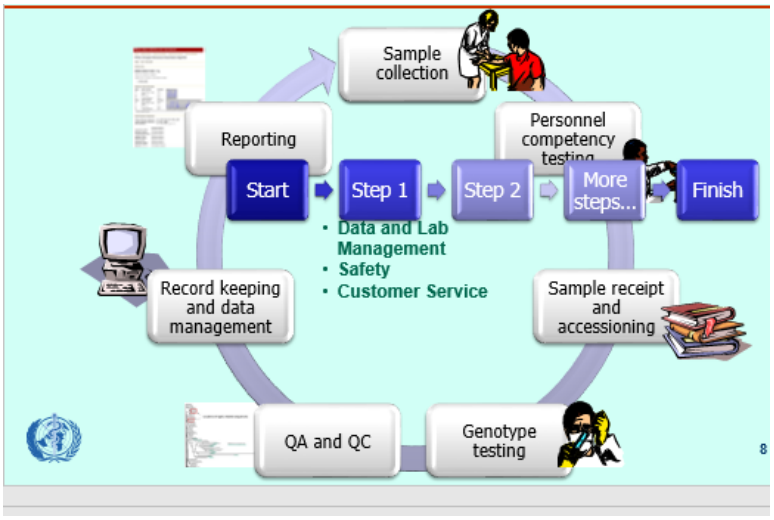


Figure 13- 2 all processing in GLP

SOPs contains:

1- Routine inspection, cleaning, maintenance, testing and calibration.
2-Actions to be taken in response to equipment failure.
3- Analytical methods
4- Definition of raw data
5- Keeping records, reporting, storage, mixing, and retrieval of data.

Who needs SOP

1- Everyone who work in lab(research).

2- Ensure compliance with GLP principles.

3- Systems with procedures that assure the quality of every aspect of the study should be implemented.

Procedure Manuals;

Procedure manuals should be organized in a way that can be easily followed by laboratory personnel and should contain the following elements:

a- Table of contents

b- Process descriptions (optional)

c- Procedures

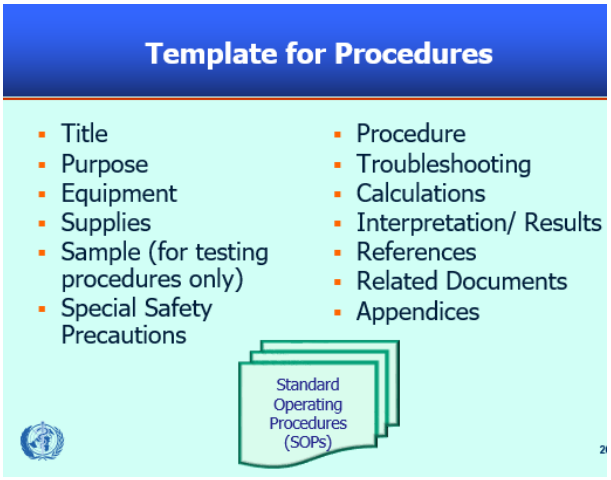


Figure 13-3 template for procedure

Associated Forms master file;

Document Identification (example)

Name of lab or institution (e.g. ABC)

Numbers for type of procedure

- 100 = General Laboratory
- 200 = Molecular

Document type and procedure number

F = Form

P = Procedure

G = Guidance or Job Aid Documents

T = Table (process)

ABC – 100 – P08

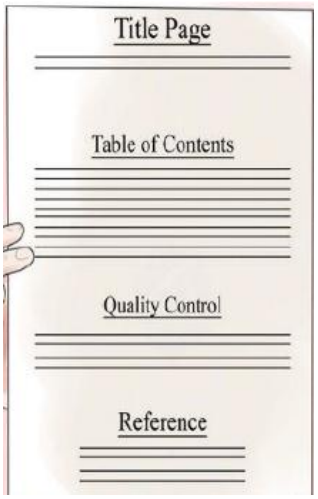
C = Flowchart (process)
Revision number
Review and Approval of New Documents;
1- Lab supervisor(s) reviews document
2- Lab Director approves all new procedures and any major modifications.
3- The Quality Assurance Manager maintains review and approval documentation in the master file hard copy binder.
Archiving, Storage, and Retention of Documents

Master file:

It is Stored by the Quality Assurance Manager, including;
1-Electronic version; it contains
a- Current version
b- All previous versions, clearly identified
c- Retired in bold on the upper right hand corner of the header
d- Watermarked diagonally across the page in order
2- Hard copy
a- Stored by the Quality Assurance Manager
b- In Master File Hard Copy Binder

Typical Structure for SOPs

1- Technical SOP
it is containing:
a- Title Page
b- Table of Contents
c- Procedures
d- Quality Control and Quality Assurance
e- Reference Section
2- Administrative SOP
it is containing the same element of Technical SOP.



Quality control in Analytical Chemistry

Quality;

In manufacturing, a measure of excellence or a state of being free from defects, deficiencies and significant variations. It is brought about by strict and consistent commitment to certain standards that achieve uniformity of a product in order to satisfy specific customer or user requirements.

Standard defines quality as "the totality of features and characteristics of a product or service that bears its ability to satisfy stated or implied needs." If an automobile company finds a defect in one of their cars and makes a product recall, customer reliability and therefore production will decrease because trust will be lost in the car's quality.

Quality control (QC)

is an essential operation of industry such as the pharmaceutical industry? Drugs must be marketed as safe and therapeutically active formulations whose performance is consistent and predictable. New and better medicinal agents are being produced at an accelerated rate. At the same time more exacting and sophisticated analytical methods are being developed for their evaluation.

Quality control means checking and directing the degree or grade of excellence of processes and products. A series of analytical

measurements used to assess the quality of the analytical data (The "tools")

ISO-Quality

The totality of features and characteristics of a product, process or service that bear on its ability to satisfy stated or implied needs.

Analytical validation;

It is referring to the evaluation and proving that an analytical method serves the intended purpose. Analytical validation ensures that the selected analytical method will give reproducible and reliable results adequate for Intended Purpose.

Considerations Prior to Method Validation

Suitability of Instrument: Status of Qualification and Calibration.

Suitability of Materials: Status of Reference Standards and Reagents.

Suitability of Analyst: Status of Training and Qualification Records.

Suitability of Documentation: Written analytical procedure and proper approved protocol with pre-established acceptance criteria.

Analyte; an analysis provides chemical or physical information about a sample. The component of interest in the sample is called the analyte, and the remainder of the sample is the matrix. In an analysis we determine the identity, concentration, or properties of an analyte. To make this determination we measure one or more of the analyte's chemical or physical properties.

True Value; The known, accepted value of a quantifiable property

Measured Value; The result of an individual's measurement of a quantifiable property.

Types of errors

The difference between the observed or calculated value and true value is known as error:

Gross errors: These errors are due to the gross blunder on the part of the experimenters or observers. These errors are caused by mistake in using instruments, recording data and calculating measurement results.

Systematic errors: These are inherent errors of apparatus or method. These errors always give a constant deviation. On the basis of the sources of errors, systematic errors may be divided into following

sub-categories: Constructional error, Determination errors, Instrument errors, and Environment errors.

Random error: After corrections have been applied for all the parameters whose influences are known, there is left a residue of deviation. These are random error and their magnitudes are not constant. The below figure show the deferent between them;

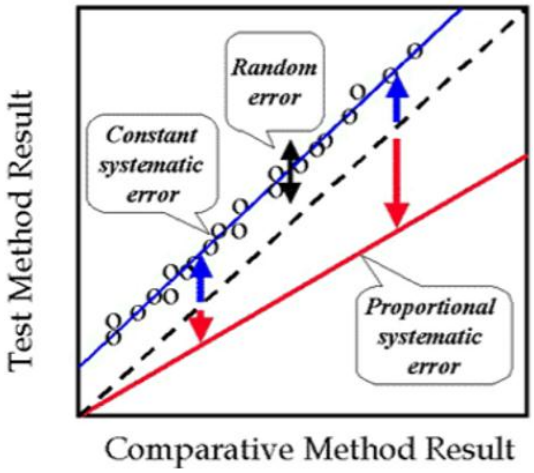


Figure 13-4 comparative method results

Experiments For Estimating Analytical Errors

There are specific experiments for estimating different types of analytical errors, as shown in the table. The first column lists the type of error. The second column is labeled "preliminary" because these experiments are generally easier to perform and take less time and effort than the "final" experiments. The final experiments are more demanding and should be performed after preliminary results have shown that everything was okay so far. However, a poor showing on a preliminary experiment can be grounds for stopping the study and rejecting a method because a specific error condition has been identified.

Table 13-1 types of error

Type of Analytic Error	Evaluation Experiment	
	Preliminary	Final
Random Error	Replication Within run	Replication Between runs
Constant Error	Interference	Comparison of Methods
Proportional Error	Recovery	

Accuracy

The agreement between the test results obtained by the proposed method and the true value. It expresses the correctness of the method. It is expressed as percentage by the assay of known amount of substance. Accuracy also evaluated by recovery studies, in which known amount of drug is added to previously analyzed pharmaceutical preparation of the drug and tested for the recovery of the added drug.

Should be established across specified range of analytical procedure.

Should be assessed using a minimum of 3 concentration levels, each in triplicate (total of 9 determinations). Should be reported as: Percent recovery of known amount added or the difference between the mean assay result and the accepted value Accuracy

The absolute error is a measure of the accuracy of the measurement, it is then calculated as, Absolute error = Mean error (True value – Measured value) / True value x 100;

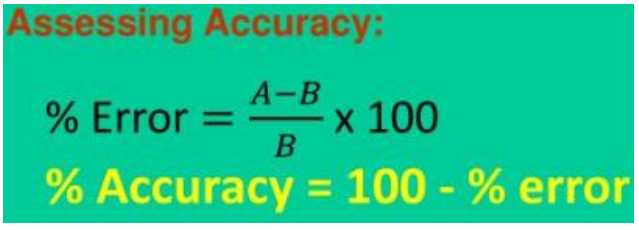
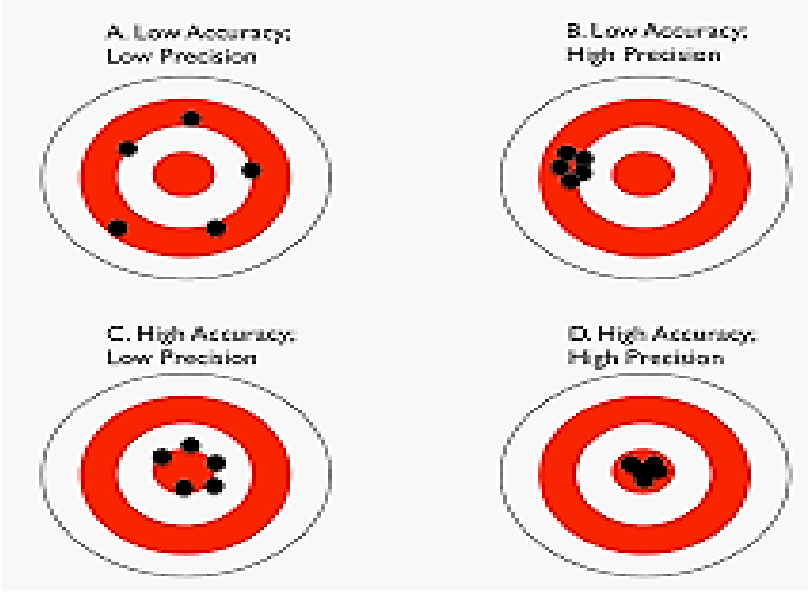


Table 13-2 calculate of recovery

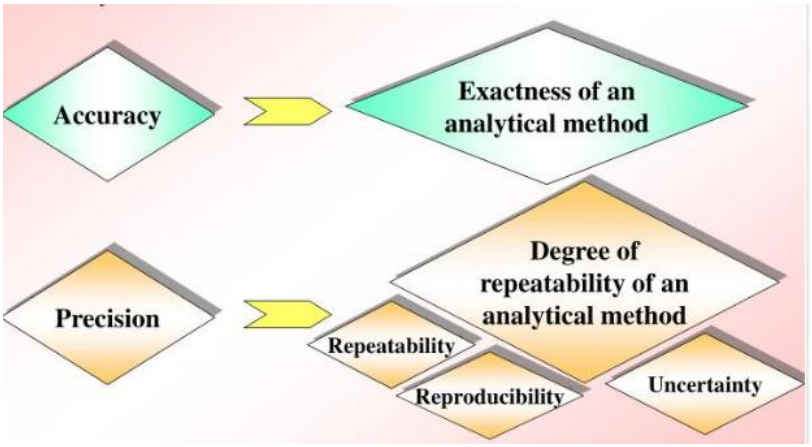
Amount Added (mg)	Amount Found (mg)	Percent Recovery
0.0	0.0	---
50.2	50.4	100.5
79.6	80.1	100.6
99.9	100.7	100.8
120.2	119.8	99.7
150.4	149.7	99.5

Precision refers to the agreement among the individual test results when a method is applied repeatedly to the same sample. It is a measure of degree of repeatability or reproducibility of a method.

The precision of an analytical procedure is usually expressed as relative standard deviation (RSD), which is calculated as, RSD = S. D. / Mean x 100. The Fugger 13-4 (a and b) below show the deferent between accuracy and precision;



(a)



(b)

Figure 13-4 (a and b) different between accuracy and precession

Specificity of a method refers to the ability of the method to measure accurately and specifically the substance of interest in the sample as impurities, degradation products. For this the test results of analysis of samples containing other ingredients is compared with the samples without containing ingredients.

Linearity

The linearity of an analytical method is ability to obtain test results which are directly proportional to the concentration of analyte in the sample.

Linearity Should Be Evaluated:

1- By Visual Inspection of plot of signals vs. analyte concentration.

2-By Appropriate statistical methods;

Linear Regression ($y = mx + b$), where, single of tool(y), concentration of variance(x), intercept (b), and slope (m)

3-Acceptance criteria: Linear regression $r^2 > 0.95$

Rang; the range of an analytical method is the interval between the upper and lower concentration of analyte in the sample.

Example;

Beer's law response – concentration curve should be linear at least 5-6 points in the range.

Plot of absorbance vs. concentration is linear as in figure below;

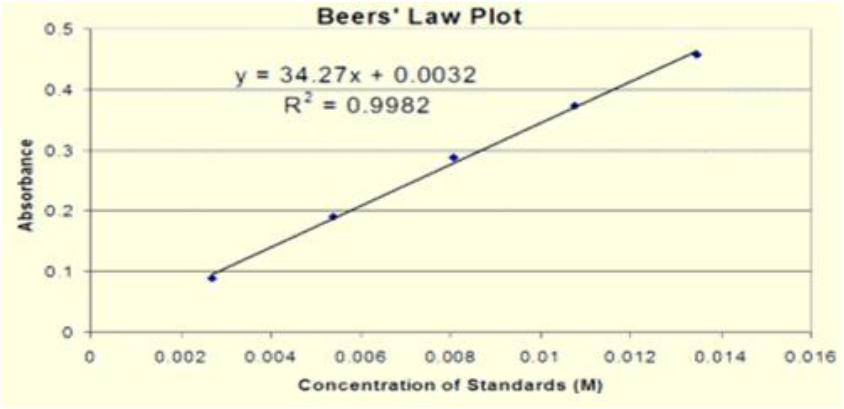


Figure 13- 5 Beer's Law using equation of line

Limit of Detection (LOD); the detection limit of an individual analytical procedure is the lowest amount of analyte in a sample which can be detected but not necessarily quantitated.

Limit of quantitation Limit (LOQ); The quantitation limit of an individual analytical procedure is the lowest amount of analyte in a sample which can be quantitatively determined with suitable precision and accuracy

Table 13-3 different between LOD and LOQ

LOD Vs LOQ

LOD	LOQ
Lowest amount of analyte in a sample that can be detected but not necessarily quantitated.	Lowest amount of analyte in a sample that can be quantified with suitable accuracy and precision.
Estimated by Signal to Noise Ratio of 3:1.	Estimated by Signal to Noise Ratio of 10:1.

LOD and LOQ Estimated by Based in Visual Evaluations: Used for non-instrumental methods;

Based on Signal-to Noise-Ratio; 3:1 for Detection Limit, 10:1 for Quantitation Limit.

Based on Standard Deviation of the Response and the Slope

$$DL = \frac{3.3s}{S} \qquad QL = \frac{10s}{S}$$

Where, S = slope of calibration curve and s = standard deviation of blank readings or standard deviation of regression line.

Robustness; Robustness is the measure of the capacity of the analytical method to remain unaffected by small but deliberate variations in procedure

Ruggedness; Degree of reproducibility of test results obtained by analysing the same sample under variety of normal test conditions is known as ruggedness.

Repeatability; Repeatability expresses the precision under the same operating conditions over a short interval of time.

Sensitivity; Sensitivity refers to the smallest quantity that can be accurately measured. It also indicates the capacity of the method to measure small variations in concentration. In the case of UV and Visible spectrophotometric methods, an estimate known as Sandell's Sensitivity' is used to evaluate the sensitivity of the method.

Laboratory Accreditation

Laboratory accreditation**,** a process or procedure by which an authoritative body gives formal recognition that a body or a person is competent to carry out specific tasks. (ISO/IEC guide 2).

eg. ISO 9000, ISO 15189; 2012, ISO 17043; 2010.

The accreditation process makes take the form quantities audit of the laboratory operations, to magnitude the policy of good laboratory followed, that is suitable documentation and record keeping, validation of method, proficiency testing and others. Finally, the laboratory undergoes the agency assessment by an accreditation body that is certified to perform laboratory accreditation.

Requirements for accreditation

The important stage is Create Quality Manual which is contains:

1- Appoint a Quality Manager.
2-Establish the Quality Management system which is contain quality, Plan, organize, staff, lead and control.
3- Appoint a technical manager.
4- Process breakdown quality identification(QI).
5- Monitor quality indicators and undertake appropriate CA/PA.
6- Documentations.
7- Technical Manager: Usually a senior technical person.
Technical workload management and work distribution among existi ng staff.
It measures how well an organization meets the needs and requiremen ts of users and the quality of all operational processes.
Appoint a person to ensure the log is maintained and updated regularl y. Formal certification of quality by an independent authorized body.

Types of Testes

1- Proficiency testing, (PT)
Unknown samples are sent for testing in a group of external laboratories and the laboratory results are compared with the relevant laboratory. PT is important because it is a tool the laboratory can use to verify the accuracy and reliability of its testing.
Data Analysis Evaluating results;
a- Quantitative evaluating; it contains, Mean ± Standard Deviation (s), Evaluating Accuracy and Precision - Evaluating Trends (graph/ diagram).
b- Qualitative evaluating; it is containing Intended response and majority of results
The mean $\overline{X}_i$, is the numerical average obtained by dividing the sum of the individual measurements by the number of measurements.

$$\overline{X} = \frac{\sum_{i=1}^{n} X_i}{n}$$

The absolute standard deviation, s, describes the spread of individual measurements about the mean;

$$s = \sqrt{\frac{\sum_{i=1}^{n}(X_i - \overline{X})^2}{n-1}}$$

Relative Standard Deviation:

$$S_r = \frac{S}{\overline{X}} \text{ X 100\%}$$

Total Test Rating is a score between 0 and 3 based on the lab's Z score for a particular test as follows:

$$z = \frac{\overline{X}_i - \dot{X}}{s}$$

Where $\overline{X}_i$ is the mean of i replicate measurement by the laboratory, $\dot{X}$ is accepted concentration, and s is the standard deviation of the accepted concentration.

Rating/Category Classification Recommendation:

Z < 1 = good Investigation not required

Z > 1 but < 2 = satisfactory Investigation not required

Z > 2 but < 3 = questionable Investigation recommended

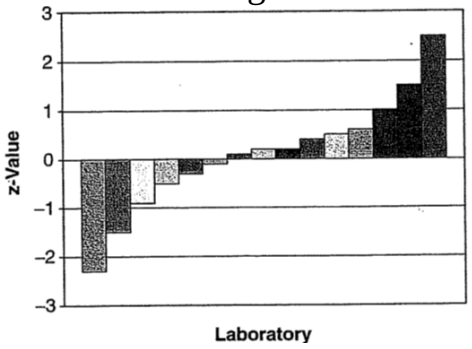


Figure 13-7 the z-distribution of the competency tests with a series of laboratories**.**

Elements of Proficiency Testing:

a- The use of internal quality control.

b- The use of validated analytical methods.

c- The use of certified reference material.

d- Participation in proficiency testing shames.

e- Accreditation to an appropriate quality standard.

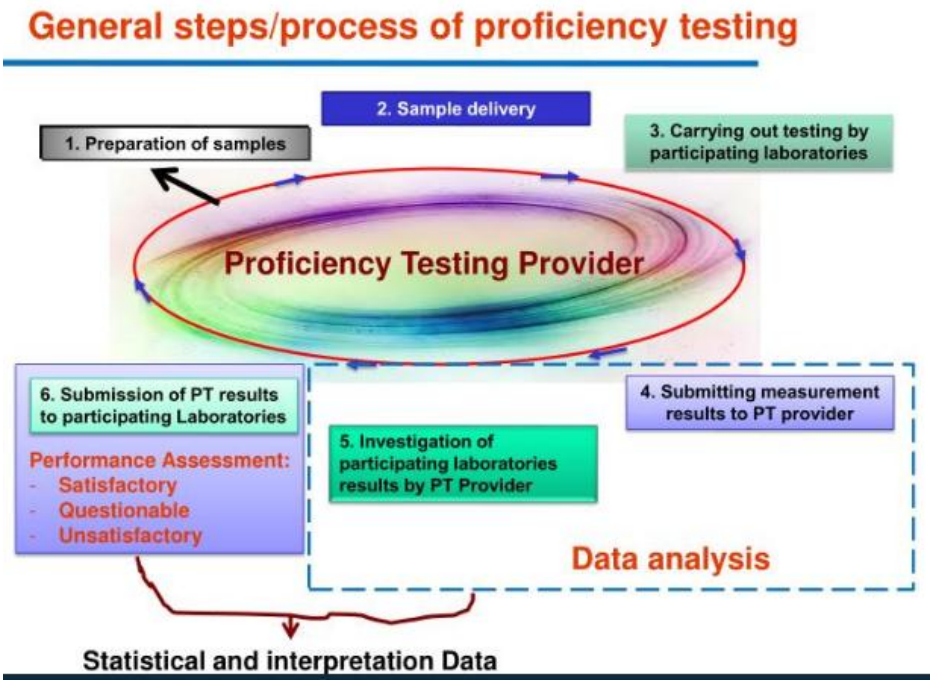


Figure 13-5 general steps of processing for proficiency test

2- (Rechecking or retesting, (RCT)

Recheck the samples analyzed by reference laboratories and compare them with the results of the internal laboratories

3- On-site evaluation

This evaluation is usually done when it is difficult to perform a traditional proficiency test or to use a re-examination method.

Audit; The following outline should be used to ensure that all applicable portions of a study are reviewed for GLP Standards compliance. Below is a simple periodic report in GLP.

Header		
phase audited	QA Comments	Responses/Corrective action planned
	Signature Date	Signature Date

Figure 13-6 a simple periodic report in GLP.

Some officinal organizations

1- International organizations for standard (ISO)
2- International conference on harmonization(ICH)
3- United states food and drug administration (FDA).
4- organization for economic co-operation and development (OECD)

Questions and Answers

Q1. A student determined the density of a solid to be 2.90, 2.91 and 2.93 g/cm^{-3}. If the actual density of this solid is 2.70 g/cm^{-3}, how should the student's results be described؟

a. high accuracy and high precision
b. low accuracy and high precision
c. high accuracy and low precision
d. low accuracy and low precision

Q2. which of the following is NOT a laboratory safety rule?

a. You should never mix acids with bases
b. You should tie back your long hair
c. You should never add water to acid
d. All of the above are valid safety rules

Q3. Accuracy is defined as:

a. A measure of how often an experimental value can be repeated.
b. The closeness of a measured value to the real value.
c. The number of significant figures used in a measurement.

d. None of these

Questions

1- what is good laboratory practice?
2- what are important element of good laboratory practice?
3- what are SOP?
4- what are the characteristics of quality assurance unit?
5- what are the aspects of validation process?
6- comparative of procedure and method.
7-declare relationship between SOP and QAU.
8- what the elements of writing GLP?
9- Where to use z score?
10- what are deferments between accuracy and precession?
11- what are deferments between quality assurance and quality control.
12- what is the accreditation of laboratory?
13- What are the safety procedures in the laboratory?
14- Why does the laboratory care more about technical methods?
15- Why does the GLP only care about SOPs?

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APPENDIX

Useful Constants

ABBREVIATIONS AND SYMBOLS					
amount of substance	*n*	equilibrium constant	*K*	milli- prefix	m
ampere	A	Faraday constant	*F*	molal	*m*
atmosphere	atm	formula molar mass	*M*	molar	M
atomic mass unit	u	free energy	*G*	mole	mol
atomic molar mass	*A*	frequency	ν	Planck's constant	*h*
Avogadro constant	N_A	gas constant	*R*	pressure	*P*
Celsius temperature	°C	gram	g	rate constant	*k*
centi- prefix	c	hour	h	second	s
coulomb	C	joule	J	speed of light	*c*
electromotive force	*E*	kelvin	K	temperature, K	*T*
energy of activation	E_a	kilo- prefix	k	time	*t*
enthalpy	*H*	liter	L	volt	V
entropy	*S*	measure of pressure	mmHg	volume	*V*

PERIODIC TABLE OF THE ELEMENTS

1 H 1.008																	2 He 4.003
3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.61	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (98)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
55 Cs 132.9	56 Ba 137.3	57 La 138.9	72 Hf 178.5	73 Ta 181.0	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra 226.0	89 Ac 227.0	104 Rf (261)	105 Db (262)	106 Sg (263)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 (269)	111 (272)	112 (277)		114 (289)				

58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (145)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np 237.0	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (260)

Nuclear Symbols

Name	Symbol
Alpha particle	α or $^{4}_{2}He$
Beta particle	β or $^{0}_{-1}e$
Gamma ray	γ
Neutron	$^{1}_{0}n$

T = temperature
P = pressure
V = volume
S = entropy
H = enthalpy
G = free energy
R = molar gas constant
n = number of moles

M = molar
m = molal
L, mL = liter(s), milliliter(s)
g = gram(s)
nm = nanometer(s)
atm = atmosphere(s)
J, kJ = joule(s), kilojoule(s)
V = volt(s)
mol = mole(s)

Common Polyatomic Ions

Ion	Ionic Formula
Ammonium	NH_4^+
Carbonate	CO_3^{2-}
Hydroxide	OH^-
Nitrate	NO_3^-
Phosphate	PO_4^{3-}
Sulfate	SO_4^{2-}

Combined Gas Law: $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$

Ideal Gas Law: $PV = nRT$

Dilution Formula: $M_1V_1 = M_2V_2$

Molar Volume of Ideal Gas at STP: 22.4 L/mol

Ideal Gas Constant: $R = 0.0821\ L \cdot atm/mol \cdot K = 8.31\ L \cdot kPa/mol \cdot K$

STP: 1 atm (101.3 kPa), 273 K (0°C)

Absolute Temperature Conversion: $K = °C + 273$

Definition of pH: $pH = -\log[H_3O^+] = -\log[H^+]$

Avogadro's Number: 6.02×10^{23} particles/mol

Analytical Signals

Molecules	Chemical reactions	
Atoms		
Ions (solvatized)	Electrochemical processes	
Electrons		
Electron beams	Particle–matter interactions	(a) Inelastic interactions (energy transfer with sample species): *SPECTROSCOPY* (b) Elastic interactions (energy transfer): *DIFFRACTION, MICROSCOPY*
Ion beams		
Electromagnetic radiation	Radiation–matter interactions	
Heat	Thermal interactions	
Directed movement energy	Interaction between phases (partition, adsorption)	

Symbols for Common Physical and Chemical Quantities

A	absorbance, area	*S/N*	signal to noise
a	absorptivity, amplifier gain, activity	*T*	transmittance, temperature
C	capacitance, concentration	*t*	time
D	diffusion coefficient	*V*	dc voltage
d	diameter, spacing	*V*	volume
deg	angular degree	*v*	ac voltage
E	electrical potential, energy	v	velocity
e	electron	*X*	reactance
f	frequency, activity coefficient	$\bar{x}$	mean
G	conductance, free energy	*Z*	impedance
H	magnetic field, enthalpy		
I	dc current		
i	ac current		
K	equilibrium constant		
L	inductance	ε	(epsilon) molar absorptivity
n	refractive index, number of equivalents	λ	(lambda) wavelength
		μ	(mu) mean
n	spectral order	ν	(nu) frequency
P	radiant or electrical power	ρ	(rho) density
Q	quantity of dc electricity	σ	(sigma) standard deviation, wavenumber
q	quantity of ac electricity	τ	(tau) period
R	electrical resistance, gas constant	ϕ	(phi) phase angle
s	standard deviation	ω	(omega) angular velocity

STANDARD REDUCTION POTENTIALS IN AQUEOUS SOLUTION AT 25°C

Half-reaction			$E°$(V)
$Li^+ + e^-$	→	$Li(s)$	−3.05
$Cs^+ + e^-$	→	$Cs(s)$	−2.92
$K^+ + e^-$	→	$K(s)$	−2.92
$Rb^+ + e^-$	→	$Rb(s)$	−2.92
$Ba^{2+} + 2\,e^-$	→	$Ba(s)$	−2.90
$Sr^{2+} + 2\,e^-$	→	$Sr(s)$	−2.89
$Ca^{2+} + 2\,e^-$	→	$Ca(s)$	−2.87
$Na^+ + e^-$	→	$Na(s)$	−2.71
$Mg^{2+} + 2\,e^-$	→	$Mg(s)$	−2.37
$Be^{2+} + 2\,e^-$	→	$Be(s)$	−1.70
$Al^{3+} + 3\,e^-$	→	$Al(s)$	−1.66
$Mn^{2+} + 2\,e^-$	→	$Mn(s)$	−1.18
$Zn^{2+} + 2\,e^-$	→	$Zn(s)$	−0.76
$Cr^{3+} + 3\,e^-$	→	$Cr(s)$	−0.74
$Fe^{2+} + 2\,e^-$	→	$Fe(s)$	−0.44
$Cr^{3+} + e^-$	→	Cr^{2+}	−0.41
$Cd^{2+} + 2\,e^-$	→	$Cd(s)$	−0.40
$Tl^+ + e^-$	→	$Tl(s)$	−0.34
$Co^{2+} + 2\,e^-$	→	$Co(s)$	−0.28
$Ni^{2+} + 2\,e^-$	→	$Ni(s)$	−0.25
$Sn^{2+} + 2\,e^-$	→	$Sn(s)$	−0.14
$Pb^{2+} + 2\,e^-$	→	$Pb(s)$	−0.13
$2\,H^+ + 2\,e^-$	→	$H_2(g)$	0.00
$S(s) + 2\,H^+ + 2\,e^-$	→	$H_2S(g)$	0.14
$Sn^{4+} + 2\,e^-$	→	Sn^{2+}	0.15
$Cu^{2+} + e^-$	→	Cu^+	0.15
$Cu^{2+} + 2\,e^-$	→	$Cu(s)$	0.34
$Cu^+ + e^-$	→	$Cu(s)$	0.52
$I_2(s) + 2\,e^-$	→	$2\,I^-$	0.53
$Fe^{3+} + e^-$	→	Fe^{2+}	0.77
$Hg_2^{2+} + 2\,e^-$	→	$2\,Hg(l)$	0.79
$Ag^+ + e^-$	→	$Ag(s)$	0.80
$Hg^{2+} + 2\,e^-$	→	$Hg(l)$	0.85
$2\,Hg^{2+} + 2\,e^-$	→	Hg_2^{2+}	0.92
$Br_2(l) + 2\,e^-$	→	$2\,Br^-$	1.07
$O_2(g) + 4\,H^+ + 4\,e^-$	→	$2\,H_2O(l)$	1.23
$Cl_2(g) + 2\,e^-$	→	$2\,Cl^-$	1.36
$Au^{3+} + 3\,e^-$	→	$Au(s)$	1.50
$Co^{3+} + e^-$	→	Co^{2+}	1.82
$F_2(g) + 2\,e^-$	→	$2\,F^-$	2.87

ADVANCED PLACEMENT CHEMISTRY EQUATIONS AND CONSTANTS

ATOMIC STRUCTURE

$$\Delta E = h\nu$$

$$c = \lambda\nu$$

$$\lambda = \frac{h}{mv}$$

$$p = mv$$

$$E_n = \frac{-2.178 \times 10^{-18}}{n^2} \text{ joule}$$

E = energy
ν = frequency
λ = wavelength
p = momentum
v = velocity
n = principal quantum number
m = mass

EQUILIBRIUM

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

$$K_b = \frac{[OH^-][HB^+]}{[B]}$$

$$K_w = [OH^-][H^+] = 1.0 \times 10^{-14} \text{ @ } 25^\circ C$$
$$= K_a \times K_b$$

$$pH = -\log [H^+],\ pOH = -\log [OH^-]$$

$$14 = pH + pOH$$

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

$$pOH = pK_b + \log \frac{[HB^+]}{[B]}$$

$$pK_a = -\log K_a,\ pK_b = -\log K_b$$

$$K_p = K_c(RT)^{\Delta n},$$

where Δn = moles product gas − moles reactant gas

Speed of light, $c = 3.0 \times 10^8 \text{ m s}^{-1}$

Planck's constant, $h = 6.63 \times 10^{-34} \text{ J s}$

Boltzmann's constant, $k = 1.38 \times 10^{-23} \text{ J K}^{-1}$

Avogadro's number $= 6.022 \times 10^{23}$ molecules mol^{-1}

Electron charge, $e = -1.602 \times 10^{-19}$ coulomb

1 electron volt per atom = 96.5 kJ mol^{-1}

Equilibrium Constants
K_a (weak acid)
K_b (weak base)
K_w (water)
K_p (gas pressure)
K_c (molar concentrations)

THERMOCHEMISTRY

$$\Delta S^\circ = \sum S^\circ \text{ products} - \sum S^\circ \text{ reactants}$$

$$\Delta H^\circ = \sum \Delta H_f^\circ \text{ products} - \sum \Delta H_f^\circ \text{ reactants}$$

$$\Delta G^\circ = \sum \Delta G_f^\circ \text{ products} - \sum \Delta G_f^\circ \text{ reactants}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$
$$= -RT \ln K = -2.303\, RT \log K$$
$$= -n\mathcal{F}E^\circ$$

$$\Delta G = \Delta G^\circ + RT \ln Q = \Delta G^\circ + 2.303\, RT \log Q$$

$$q = mc\Delta T$$

$$C_p = \frac{\Delta H}{\Delta T}$$

S° = standard entropy
H° = standard enthalpy
G° = standard free energy
E° = standard reduction potential
T = temperature
n = moles
m = mass
q = heat
c = specific heat capacity
C_p = molar heat capacity at constant pressure

1 faraday $\mathcal{F}$ = 96,500 coulombs

UNITS

Name	Symbol
meter	m
kilogram	kg
second	s
ampere	A
kelvin	K
mole	mol
hertz	Hz
newton	N
pascal	Pa
joule	J
watt	W
coulomb	C
volt	V
ohm	Ω
henry	H
farad	F
tesla	T
degree Celsius	°C
electron-volt	eV

Symbols for amino acids

Name	Symbol	Name	Symbol
Alanine	+ Ala (A)	Homocysteine	Hcy
Allohydroxylysine	aHyl	Homoserine	Hse
Alloisoleucine	aIle	Homoserine lactone	Hse >
Aminoacid residue	AA	Hydroxylysine	+ Hyl
2-Aminoadipic acid	Aad	Hydroxyproline	+ Hyp
3-Aminoadipic acid	βAad	Isoleucine	+ Ile (I)
2-Aminobutyric acid	Abu	Leucine	+ Leu (L)
ε-Aminohexanoic acid	εAhx	Lysine	+ Lys (K)
3-Aminopropionic acid	βAla	Methionine	+ Met (M)
Arginine	+ Arg (R)	Norleucine	Nle
Asparagine	+ Asn (N)	Norvaline	Nva
Aspartic acid	+ Asp (D)	Ornithine	+ Orn
Aspartic acid or asparagine	+ Asx (B)	Phenylalanine	+ Phe (F)
Cysteine (*cf.* half-cystine)	+ Cys (C)	Proline	+ Pro (P)
2,4-Diaminobutyric acid	A_2bu	5-Pyrrolidone-2-carboxylic acid (pyroglutamic acid; oxoproline)	< Glu
2,2-Diaminopimelic acid	A_2pm	Sarcosine	Sar
Glutamic acid	+ Glu (E)	Serine	+ Ser (S)
Glutamine	+ Gln (Q)	Threonine	+ Thr (T)
Glutamic acid or glutamine	+ Glx (Z)	Tryptophan	+ Trp (W)
Glycine	+ Gly (G)	Tyrosine	+ Tyr (Y)
Half-cystine (*cf.* cysteine)	+ Cys	Valine	+ Val (V)
Histidine	+ His (H)		

Symbols of carbohdrate

Carbohydrate	Symbol
N-Acetylneuraminic acid	AcNeu
Fructose	+ Fru
Galactose	+ Gal
Glucose	+ Glc
Mannose	+ Man
Muramic acid	Mur
Neuraminic acid	Neu
Ribose	+ Rib
Sialic acid	Sia
Derivatives of, e.g., *glucose*	
N-Acetylglucosamine	GlcNAc
Glucosamine	GlcN
2-Deoxyglucose	dGlc[a]
Gluconic acid	GlcA
Glucuronic acid	GlcUA

About the Author

Personal Information

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Academic Qualifications:

BSc-Baghdad university,1977
MSc-Basra University ,1989
PhD-Mustansiriya University 2001
Assist. Prof: 2005
Prof. 2014
Specialization: Analytical chemistry

Field of Research:

1-Environmental pollution problems in Iraq
2-Analysis of pharmaceutical derivatives.
3- Treatment of waste water using adsorption process.
4- Management system of laboratories.

Research Topics:

1-Teaching analytical chemistry for undergraduate studentes1996-until now.
2- Teaching postgraduate students, different subjects.
3-Successfully guided 11 research students for MS and Ph.D. in analytical chemistry.

Books Author:

1-Methods and modern techniques in instrumental chemical analysis, 2013 (Arabic)
2-Test and question in chemistry,2014(English)
3-contemporary trends in the quality system and accreditation of lab, 2015 (Arabic)
4- Concepts and principles for the application of quality of management systems and accreditation, 2016 (Arabic).
5- Extraction of Lead, Cadmium, Zinc and Rhenium ions by Liquid Membrane.2016(English).

The activities:

1- one patent
2-Establishing workshops for universities on the quality of laboratories

Publications:

Published more than 30 publications.

مكتب زاكي للطباعة
بغداد - باب المعظم
رقم الايداع في دار الكتب والوثائق ببغداد ١١٨٧ لسنة ٢٠٢٠