PREFACE

With its grounding in the "guiding pillars of Access, Equity, Equality, Affordability and Accountability," the New Education Policy (NEP 2020) envisions flexible curricular structures and creative combinations for studies across disciplines. Accordingly, the UGC has revised the CBCS with a new Curriculum and Credit Framework for Undergraduate Programmes (CCFUP) to further empower the flexible choice based credit system with a multidisciplinary approach and multiple/ lateral entry-exit options. It is held that this entire exercise shall leverage the potential of higher education in three-fold ways – learner's personal enlightenment; her/his constructive public engagement; productive social contribution. Cumulatively therefore, all academic endeavours taken up under the NEP 2020 framework are aimed at synergising individual attainments towards the enhancement of our national goals.

In this epochal moment of a paradigmatic transformation in the higher education scenario, the role of an Open University is crucial, not just in terms of improving the Gross Enrolment Ratio (GER) but also in upholding the qualitative parameters. It is time to acknowledge that the implementation of the National Higher Education Qualifications Framework (NHEQF) National Credit Framework (NCrF) and its syncing with the National Skills Qualification Framework (NSQF) are best optimised in the arena of Open and Distance Learning that is truly seamless in its horizons. As one of the largest Open Universities in Eastern India that has been accredited with 'A' grade by NAAC in 2021, has ranked second among Open Universities in the NIRF in 2024, and attained the much required UGC 12B status, Netaji Subhas Open University is committed to both quantity and quality in its mission to spread higher education. It was therefore imperative upon us to embrace NEP 2020, bring in dynamic revisions to our Undergraduate syllabi, and formulate these Self Learning Materials anew. Our new offering is synchronised with the CCFUP in integrating domain specific knowledge with multidisciplinary fields, honing of skills that are relevant to each domain, enhancement of abilities, and of course deep-diving into Indian Knowledge Systems.

Self Learning Materials (SLM's) are the mainstay of Student Support Services (SSS) of an Open University. It is with a futuristic thought that we now offer our learners the choice of print or e-slm's. From our mandate of offering quality higher education in the mother tongue, and from the logistic viewpoint of balancing scholastic needs, we strive to bring out learning materials in Bengali and English. All our faculty members are constantly engaged in this academic exercise that combines subject specific academic research with educational pedagogy.We are privileged in that the expertise of academics across institutions on a national level also comes together to augment our own faculty strength in developing these learning materials. We look forward to proactive feedback from all stakeholders whose participatory zeal in the teaching-learning process based on these study materials will enable us to only get better. On the whole it has been a very challenging task, and I congratulate everyone in the preparation of these SLM's.

I wish the venture all success.

Professor Indrajit Lahiri
Vice Chancellor

Netaji Subhas Open University

Four-Year Undergraduate Degree Programme
Under National Higher Education Qualifications Framework (NHEQF) & Curriculum and Credit Framework for Undergraduate Programmes

Course Type : Dicipline Specific Elective (DSE)
Course Title : Application Oriented Chemistry
Course Code : NEC-CH-01

First Print : March, 2025
Print Order :

Netaji Subhas Open University

Four-Year Undergraduate Degree Programme
Under National Higher Education Qualifications Framework (NHEQF)
& Curriculum and Credit Framework for Undergraduate Programmes

Course Type : Dicipline Specific Elective (DSE)
Course Title : Application Oriented Chemistry
Course Code : NEC-CH-01

Course Writer	**Course Editor**
Dr. Sanjay Roy(Unit: 1-7) Professor of Chemistry, NSOU	Dr. Sintu Ganai (Unit 1-7) Assistant Professor of Chemistry, NSOU
Dr. Simanta Kundu (Unit: 8-14) Assistant Professor of Chemistry, Shibpur Dinobundhoo Institution (College), Howrah	Dr. Sanjay Roy (Unit 8-14) Professor of Chemistry, NSOU

Format Editor

Dr. Puspal Mukherjee, Assistant Professor of Chemistry, NSOU

Notification

Ananya Mitra

Registrar (Additional Charge)

Netaji Subhas Open University

Four-Year Undergraduate Degree Programme
Under National Higher Education Qualifications Framework (NHEQF)
& Curriculum and Credit Framework for Undergraduate Programmes

Course Type : Dicipline Specific Elective (DSE)
Course Title : Application Oriented Chemistry
Course Code : NEC-CH-01

CONTENTS

Unit-1 ❑ Chemical Analysis : Principle and Application

Structure

1.1. Objectives

After reading this unit we will be able to

- Learn about different type of quantitative analysis techniques like acid base and redox titrations.
- Explain the principle of acid base titration and role of acid base indicators.

  Know about the principle of permanganometry and dichromatometry titrations.
- Learn about the principle of complexometric titration and the role of metal ion indicators.
- Determine the hardness of water.
- Learn about different chromatographic separation techniques.
- Explain the basic principle of solvent extraction.

1.2 Introduction

The need of the sophisticated analytical instruments and determinations using them is almosta routine process for the modern chemical laboratories. It has been a vast expanding area ofknowledge as the instrument and computer manufacturers are producing analytical machines,which are in ever-increase of power and scope. Further, all the manual techniques in the lineof the analytical studies had steadily been transferred to the instrumental techniques.Basically, chemical analysis can be divided into three broad categories as given below, whichare almost invariably applied to major areas such as Fundamental Research, ProductDevelopment, Product Quality Control, Monitoring & Control of Pollutants, Medical & Clinical Studies, etc.

Qualitative Analysis : Chemical analysis which just identifies one or more species present in a sample.

Quantitative Analysis : Chemical analysis which finds out the total amount of the particular species present in asample.

Structural Analysis : Chemical analysis which helps in finding the spatial arrangement of atoms in a molecule andthe presence or position of certain organic functional groups in a given compound.

Titration is a typical quantitative chemical analysis method used in laboratories to quantify the concentration of a particular analyte. Titration, also known as titrimetry or volumetric analysis, is a method in which the titrant is added from a burette until the reaction is complete, and an indicator is usually employed to mark the endpoint of the reaction. There are different types of titration such as acid-base, redox, precipitation, and complexometric titrations, however, in quantitative chemical analysis, redox titration and acid-base titration are most commonly used.

1.3 Principle of acid-base titration

What is acid-base titration?

An acid-base titration is a quantitative analysis method used to determine the concentration of an acid or base by precisely neutralizing acid or base with a known concentration standard solution, in presence of a pH indicator to monitor the reaction.

The concentration of a solution (molarity) of an analyte solution can be determined if the acid dissociation constant (pKa) of the acid or the base dissociation constant (pKb) of the base is known. If the solute solution has a known solution concentration, the pKa can be calculated by generating a titration curve.

Principle of acid-base titration :

Acid-base titrations depend on the neutralization between an acid and abase when mixed in solution. In addition to the sample, an appropriate pHindicator is added to the titration chamber, reflecting the pH range of theequivalence point. The acid-base indicator indicates the endpoint of the titrationby changing colour. The endpoint and the equivalence point are not exactly thesame because the equivalence point is determined by the stoichiometry of thereaction while the endpoint is just the colour change from the indicator. Thus, acareful selection of the indicator will reduce the indicator error. For example, if

the equivalence point is at a pH of 8.4, then the Phenolphthalein indicator wouldbe used instead of Alizarin Yellow because phenolphthalein would reduce theindicator error. Common indicators, their colours, and the pH range in which theychange colour are discussed later. When more precise results arerequired, or when the reagents are a weak acid and a weak base then a pH meter or aconductance meter are used.

Types of acid-base titration with their examples :

The acid-base titration is classified into four different types such as strong acid-strong base, weak acid-strong base, strong acid-weak base, and weak acid-weak base.

Strong acid-strong base:

As an experimental concern, it is one of the easiest titrations to perform among the four forms of acid-base titrations. It involves the complete dissociation of a strong acid and a strong base in water, resulting in a strong acid-strong base neutralization reaction. When the moles of acid and base are the same and the pH is 7, it reaches the equivalence point.

Weak acid-strong base :

In this type of titration, the protons are direct transfer from the weak acid to the hydroxide ion. In the reaction of a weak acid (acetic acid) with a strong base (NaOH), the acid and base react in a one-to-one ratio. At the equivalence point of a weak acid-strong base titration, the pH is larger than 7.

Strong acid-weak base :

In this type of titration, the acid and base will react to form an acidic solution. Throughout the titration, a conjugate acid is formed, which subsequently reacts with water to form hydronium ions. At the equivalence point of a strong acid-weak base titration, the pH is less than 7.

Weak acid-weak base :

Unlike strong acids and strong bases, the shape of a weak acid's or base's titration curve significantly depends on the acid's or base's identity and the associated acid ionization constant (Ka) or base ionization constant (Kb). In the titration of a weak acid or a weak base, the pH also changes much more gradually around the equivalence point, which is greater or less than 7, respectively.

Examples :

- Hydrochloric acid (HCl) and sulphuric acid (H2SO4) are two examples of strong acids.
- Acetic acid (CH3COOH) and formic acid (CH2O2) are the two examples of weak acids.
- Sodium hydroxide (NaOH) and potassium hydroxide (KOH) are two examples of strong bases.
- Ammonia and methylamine are the two examples of weak bases.

Applications of acid-base titration :

- Acid-base titrations are most commonly used to determine the unknown acid or base concentration of the analyte.
- It is used as a quantitative chemical analysis.
- It has the potential to be used in pharmaceutical applications.
- It can be used in environmental analysis.
- It is used to determine the barbiturates, aspirin, and amino acid.

Experimental procedure of acid-base titration :

Requirements: Conical flask, funnel, beaker, pipette, burette, burette stand, spatula, wash bottle, indicator, unknown solution, and standard solution.

Titration procedure :

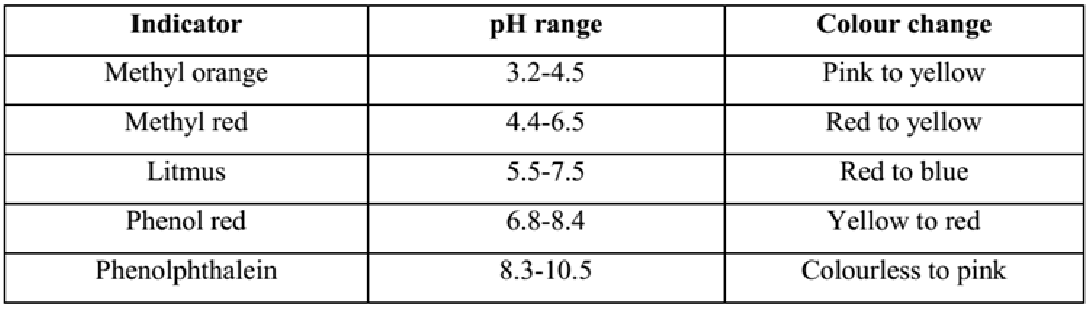
- Clean and dry all the glassware's with distilled water and rinse the burette with the standard solution.
- Fill the burette with a standardized solution, accurately measure the volume of the analyte, and add in the conical flask, also add a few drops of indicator using the pipette.
- Titrate it with the standardized solution until the indicator changes the colour. When the indicator permanently changes the colour, the endpoint reaches.

- Repeat the titration at least three more times and record the initial and final readings in the observation table and calculate the value.

Indicators used in acid-base titration :

An indicator is a substance which is used to determine the end point in a titration. Inacid base titrations, organic substances (weak acids or weak bases) are generally used asindicators. They change their colour within a certain pH range. The pH range of an indicator is the most essential property, which is reliant on the acid strength of the indicator. The pH range of an indicator is the range of pH values across which the indicator changes colour from acid to base.

It ranges from the highest pH, where only the acid form can be seen, to the lowest pH, where only the base form can be seen. Since the indicator does not change colour at certain pH levels, it is not sensitive to pH changes outside of its range.



Indicator	pH range	Colour change
Methyl orange	3.2-4.5	Pink to yellow
Methyl red	4.4-6.5	Red to yellow
Litmus	5.5-7.5	Red to blue
Phenol red	6.8-8.4	Yellow to red
Phenolphthalein	8.3-10.5	Colourless to pink

Table.1 : Colour change and the pH range of some common indicators.

Acid-base indicators are generally classified into below listed three groups.

1. The phthaleins and sulphophthaleins : example-phenolphthalein indicator

2. Azo indicators : example- methyl orange indicator

3. Triphenylmethane indicators : example- malachite green indicator

Selection of indicator in acid-base titration :

In acid-base titrations, different indicators are used. The selection of indicators depends on the type of titration and whose pH range falls within the pH change of the reaction.

- **Strong acid-strong base :** The phenolphthalein is generally preferred due to colour change seen more easily

- **Weak acid-strong base :** Phenolphthalein is more proffered for this titration because it changes sharply at the equivalence point.
- **Strong acid-weak base :** Methyl orange is more proffered for this titration because it changes sharply at the equivalence point.
- **Weak acid-weak base :** Because a vertical portion of the curve above two pH units is required, there is no indication is suitable for this titration.

1.4. Principle of oxidation-reduction titration

What is redox titration?

One of the important reactions is the oxidation-reduction reaction which occurs in volumetric titrations frequently.Oxidation means loss of electron(s) and reduction means gain of electron(s). Both the oxidation andreduction processes occur simultaneously. Titrationinvolving a complete oxidation and reductionreaction in solution is called aoxidation-reductiontitration or redox titration.

In the oxidation-reduction titration process, an oxidizing compound is titrated with the standard solution of the reducing agent, or a reducing compound is titrated with a standard solution of an oxidizing agent.It is used for the analysis of organic solutes and generally evaluating chlorination. In an oxidation-reduction (redox) titration, generally, a potentiometer or redox indicator solution is used for the determination of endpoint of the titration.

Treating an iodine solution with a reducing agent to form iodide while using a starch indicator to aid determine the endpoint of the titration is the most common example of redox titration.

What is the principle of redox titration?

The principle involved in oxidation-reduction (Redox titration) is that the oxidation process involves the loss of electrons while the reduction process involves the gain of electrons.

Oxidant + ne ? Reductant

The following are the key characteristics of redox reactions which consist of both oxidation and reduction reactions.

Oxidation reaction:

The following are examples of how a solute can be oxidation reaction:

- Oxygen atom addition
- Hydrogen atom removal
- Electron donation or loss
- An overall enhance in the substance's oxidation state

Reduction reaction :

The following are examples of how a solute can be reduction reaction:

- Hydrogen atom addition
- Oxygen atom removal
- Accepting electrons
- Reduction in the oxidation state of the analyte

Indicators used in redox titration :

Potassium permanganate, iodine, ceric ammonium sulphate, phenanthroline blue, methylene blue, ferrous ions in dichromate solution, 1, 10 phenanthroline monohydrate, 2,2'-bipyridine, 5,6-dimethyl phenanthroline, and safrannin-T. Etc. are the commonly used redox indicators. The endpoint of redox titrations can be determined in a variety of ways such as self indicators, external Indicators, redox indicators, and instrumental techniques, etc.

The redox indicators are indicators that exhibit a reversible change of colour between oxidized and reduced forms and undergo a specified colour change at a specific potential. These indicators are weak reducing or oxidizing species that have different colours in their reduced and oxidized forms. The colour changes take place within a specific redox potential transition range, which must include the redox potential at the equivalence point in the redox titration to be performed.

Types of redox titration :

There are different types of redox titration based on the titrant used, they are bromatometry, iodometry or iodimetry, permanganometry, and dichromatometry, etc., and based on the method they are classified as direct titration, and back titration.

1.4.1. Permanganometry

Potassium permanganate is a very powerful and widely used oxidising agent to oxidize manyreducing agents in different conditions to estimate the amount of reducing materials. The redoxtitration with potassium permanganate solution as an oxidant is called permanganometric titration orpermanganometry. The power of $KMnO_4$ as an oxidant depends on the pH of the medium.

(i) In acid medium it shows a very high degree of oxidizing power.

$$MnO_4^- + 8H^+ + 5e \text{ ? } Mn^{2+} + 4H_2O$$

So, the reduction potential of the MnO4-/Mn2+ system depends on H+ concentration and concentrationratio of MnO4- and Mn2+ ions in solution. At standard state the potential of the system, E = Eo = standard reduction potential = 1.51V(observed value). The equivalent weight of KMnO4 in this situation = formula weight/5 = 158.03/5 =31.606 as the number of change in oxidation number is 5.

H_2SO_4 is the most suitable acid to serve H+ in dilute solution. HCl reacts with MnO_4^- as:

$$2MnO_4\text{-} + 10Cl^- + 16H+ = 2Mn^{2+} + 5Cl_2 + 6H2O.$$

HNO_3, itself an oxidant, reacts with reducing agents used inthe permanganometry.

(ii) In neutral or faintly alkaline medium the oxidizing power of $KMnO_4$ reduces, as the standardreduction potential E_o of the reaction system is 0.59V which is lower than the above. Theequivalent weight of $KMnO_4$ is = 158.03/3 = 52.677.

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

(iii) In alkaline medium the oxidizing power is still less as is seen by the potential E_o = 0.56V of thereaction process. The equivalent weight of $KMnO_4$ in this situation is equal to its molecular weight,i.e., 158.03.

$$MnO_4^- + e = MnO4^{2-} \text{ (manganate ion)}$$

By nature $KMnO_4$ is very reactive and is not a primary standard substance due to alwayscontamination of trace MnO_2. Mn_2^+, MnO_2, light or a trace organic matter catalyses the decompositionof KMnO4 in solution:

$$4MnO_4^- + 2H2O \text{ ? } 4MnO2 + 4OH\text{-} + 3O2$$

$$2MnO_4^- + 3Mn_2^+ + 2H_2O \text{ ? } 5MnO_2 + 4H^+$$

The rate of decomposition is slow in acid medium but rapid in neutral medium. For this reason$KMnO_4$ solution cannot be stored ordinarily for a long period of time. It also reacts with the reducingmatters present in filter papers or rubber cocks etc. If required, $KMnO_4$ solution should be filteredthrough a funnel containing purified glass wool or through a sintered glass crucible. For precaution $KMnO_4$ solution is prepared by specially purified distilled water. $KMnO_4$ solution isstored in a clean glass-stoppered dark brown coloured glass bottle to avoid any decomposition by light. The solution is a secondarystandard and needs standardization each time before or after use.$KMnO_4$ solution may be standardized by titration with any one of the following primary standardsolutions: (i) oxalic acid or sodium oxalate (ii) Mohr's salt (iii) Arsenious oxide (iv) Potassiumferrocyanide.

Being a stronger oxidant it may be used to titrate many reductants having potential lower at least by0.2V with respect to MnO4-/Mn2+ system (1.51V). A few examples of such reactions are given by theequations:

$Fe^{3+} + e \; ? \; Fe^{2+}$ Eo = +0.77 V

$H_3AsO_4 + 2H^+ + 2e \; ? \; H_3AsO_3 + H_2O$ Eo = +0.56 V

$Fe(CN)_6^{3-} + e \; ? \; Fe(CN)_6^{4-}$ Eo = +0.36 V

$SO_4^{2-} + 2H^+ + 2e \; ? \; SO_3^{2-} + H_2O$ Eo = +0.17 V

$Sn^{4+} + 2e \; ? \; Sn^{2+}$ Eo = +0.15 V

$2CO_2 + 2H^+ + 2e \; ? \; H_2C_2O_4$ Eo = - 0.45 V

Due to strong charge transfer absorption, MnO_4^- itself has a very intense violet/pink colour insolution. Even the presence of one drop of $KMnO_4$ solution of strength 0.05(N) in one litre of distilledwater exhibits a distinguishable faint pink colour of the solution. As a result, permanganometry needsno redox indicator, provided the titrating medium is colourless. After the equivalence point, additionof one drop of excess $KMnO_4$ solution imparts faint pink colour of the solution indicating the endpoint of the titration. Thus, $KMnO_4$ acts as a self indicator.

1.4.2 Dichromatometry

Redox titration conducting with the use of potassium dichromate solution is called Dichromatometrictitrations or Dichromatometry. In acid medium, $K_2Cr_2O_7$ acts as a strong oxidant due to having highstandard reduction potential (Eo).

$$Cr_2O_7^{2-} + 14H^+ + 6e \; ? \; 2Cr^{3+} + 7H_2O \qquad E_o = 1.33 \text{ V}$$

Therefore, the equivalent weight is = Molecular weight/6 = 294.22/6 = 49.037

It is obtained in form of pure orange crystals, thermally stable up to its fusion point and is highlysoluble in water to form a stable orange coloured solution. Its strength remains unaltered for a longperiod of time and therefore serves as a primary standard solution.The standard reduction potential of KMnO4 in acid medium is equal to 1.51 V which is higher thanthat of $K_2Cr_2O_7$ (1.33 V) indicates that the $KMnO_4$ is stronger oxidant than $K_2Cr_2O_7$.

But the use of $K_2Cr_2O_7$ is more advantageous over $KMnO_4$ due to the following reasons:

(i) $K_2Cr_2O_7$ is obtained in a very pure state.

(ii) Aqueous solution of $KMnO_4$ is unstable towards light, heat, organic matters and also to its owncomponent Mn_2+ ion etc. to form MnO_2. Again MnO_2 also catalyzes the decomposition of $KMnO_4$. But $K_2Cr_2O_7$ solution is very stable and its strength remains unchanged for a long time.

(iii) $K_2Cr_2O_7$ solution does not react with Cl^- but $KMnO_4$ solution reacts. So Fe_2^+ or Fe_3^+ iron may beestimated by the use of $K_2Cr_2O_7$ solution directly in presence of Cl^-, but not by $KMnO_4$ solution.

Thus, a standard solution of $K_2Cr_2O_7$ is more useful and favourable oxidant than $KMnO_4$ solution.

Dichromatometric titration needs indicator to identify the equivalence point. Commonly usedindicators are (i) Diphenylamine (ii) Sodium or Barium diphenylamine sulphonate (BDS), (iii) N-phenylanthranilic acid, (iv) 5,6 dimethyl ferroin etc. Mostly used indicator is the BDS indicator whichgives a sharp colour change from colourless through green-violet to red-violet at the equivalencepoint. Diphenylamine sulphonate undergoes a reversiblechange of structure due to oxidation when higher potential avails from the titration process andtherefore, shows colour change. In estimation of Fe^{2+} by $K_2Cr_2O_7$ with the useof BDS or diphenylamine indicator, H_3PO_4 or NH_4HF_2 as complexing agent must be added prior to start of the titration to lower the reduction potential of Fe^{3+}/Fe^{2+} system so that endpoint of titration can be detected. But if N-phenylanthranilicacid or ferroin as indicator is used, there is no need of addition of H_3PO_4 or NH_4HF_2. Essentially the indicator should be oxidized as close to the equivalence point as possible, neither tooearly, nor too late. So the potential range of the indicator, for detection of equivalence point throughsudden sharp colour change, should lie within the limits of the sharp change of potentials at theequivalence point.

1.5. Principle of complexometric titration

Complexometric titration is a type of volumetric analysis in that the formation of a coloured complex is employed to determine the end-point of the titration. It is primarily used to quantify metal ions by employing complex-formation reactions.

What is a complexometric titration?

The volumetric estimation of metal ions through the formation of complex with a strong multidentatechelating ligand using suitable metal indicator is called complexometric titration or complexometry. Apolydentate ligand is able to form a very stable complex with a metal ion which is called chelate andthe ligand is called chelating ligand. So, the titration in that sense is called chelatometric titration.

For a feasible complexometric titration the following conditions should be fulfilled:

(i) The coordination number of the metal ion must be satisfied completely by the chelating ligand toform a stable water soluble complex.

(ii) The value of stability constant of the complex should be high enough.

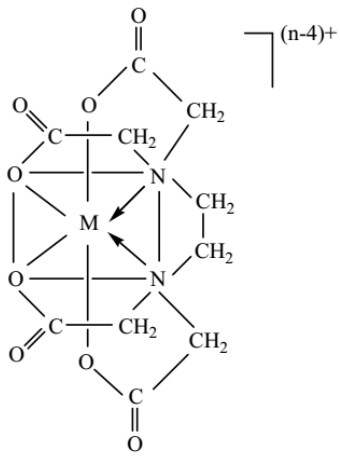
(iii) The rate of complex formation reaction should be fast.

(iv) Suitable indicator must be available to detect the sharp end point of the titration.

Ethylene diaminetetraacetic acid (EDTA) is available in form of its water soluble disodium salt,$Na_2H_2EDTA.2H_2O$ (Mol. Wt. = 372.24) which is a hexadentate chelating ligand and is able to form(1:1) stable complex with many metal ions satisfying all the above conditions. Hence, it is widelyused in complexometric titrations. It ionizes in water as H_2Y^{2-} to form (1:1) stable chelates with manymetal ions (M^{2+}) with simultaneously release of H^+ ions as:

$$Na_2H_2Y \ ? \ 2Na^+ + H_2Y^{2-}$$

$$H_2Y^{2-} + M^{n+}? \ [MY]^{(n-4)+} + 2H^+$$



$[MY]^{(n-4)+}$

Ethylene diaminetetraacetic acid (EDTA) is colourless regardless of whether it is coupled or not to a metal ion. So for detection of the endpoint of titration metal ion indicators are used. Eriochrome Black T (EBT) is the most common metal ion indicator used in the complexometric titration. When the indicator Eriochrome Black T binds with metal ions, it turns wine-red; however, when it is free from metal ions, it remains blue in colour. Addition of EBT indicator to the sample solution of metalions turns the solution colour to wine-red. Eriochrome Black T loosely binds with metal ions, whereas EDTA binds strongly with the metal ions. Therefore, when all the metal ions are bound to EDTA upon addition of EDTA during titration at the endpoint of titration, the EBT indicator in the sample solution becomes free and the solution appears blue.

Types of complexometric titration :

As a chelating titrant, the ethylene diaminetetraacetic acid (EDTA) can be used in different ways. Hence the titrations with EDTA can be performing in different types some of them are as follows.

Direct titration method :

The direct titration method is similar to the acid-base titration technique and is simple and convenient. In this method, the standard EDTA solution is gradually added using a burette to the metal ion solution until the desired endpoint is reached.

Direct titration is used to determine the copper, mercury, zinc, barium, chromium,aluminum, and lead, etc. in which the solution containing the metal ion to be measured isbuffered to the required pH and directly titrated with a standard EDTA solution.

Back titration method :

A back titration is a type of complexometric titration in which the analyte concentration is determined by reacting with a known amount of excess reagent. Metal ions that cannot be directly titrated with EDTA are determined using the back titration method.

Replacement titration method :

The replacement titration method is used when direct titration or back titration fails to produce sharp endpoints. The metal ion is determined by displacing zinc or magnesium ions from an EDTA complex with an equivalent number of metal ions, then titrating the liberated Zn or Mg ion with a standard EDTA solution.

Indirect titration method :

The indirect titration method is commonly used when normal titrations are slow, or the endpoint is difficult to determine, as well as in other applications such as weak acid-weak base reaction. Some anions (For example barium ions) precipitate when they come intocontact with metal cations, and these anions do not react with EDTA. Hence, indirect titration with EDTA can be used to determine these types of compounds.

Applications of complexometric titrations :

- The complexometric titration is used to determine the concentration of metal ions in sample solutions.
- It is used for the estimation of the amount of calcium present in food products.
- It is used to find out the total hardness of the water.
- Complexometric titration is commonly used in the pharmaceutical industries to determine the concentration metal is in a pharmaceutical dosage form (Drug).
- It is used in analytical chemistry to perform the assay.
- Complexometric titration is used in environmental analysis to determine bad metals.
- Cosmetic products are also analyzed by complexometric titration.

Which indicator is used in complexometric titration?

Complexometric indicators are water-soluble organic molecules that play an important role in the titration to indicate the endpoint. These indicators undergo a certain colour change in the presence of specific metal ions. Commonly used indicators in complexometric titration are organic dyes which are organic molecules that are soluble in water. When the endpoint is achieved, a colour change indicates that the indicator has been displaced from the metal cations in the solution.

Examples of complexometric indicators are Eriochrome Black T, calgamite, arsenazo, xylenol orange, Eriochrome red B, fast sulphon black, and calcein, etc. Eriochrome Black T, which acts as an acid/base indicator as well as a metal ion indicator, is the most often used indicator in complexometric titration.

1.6. Hardness of water

The dissolved inorganicimpurities present in water are mainly chlorides, sulphates, carbonates, andbicarbonates of sodium, potassium, calcium and magnesium. The chemical nature andphysical behaviour of the impurities present in water determine the quality of waterand also forms the basis for the procedures used in the analysis of water. Water containing carbonate, chloride and sulphate salts of heavy metals, mainly calcium andmagnesium is called hard water. When some simple soap is added to a sample of hard water, an insoluble salt is produced which decrease thecleaning efficiency of the soap.

The hardness of water due to the presence of bicarbonates of calcium and magnesiumis termed temporary hardness. Such hardness can be removed simply by boiling thewater; the soluble bicarbonates decompose on heating to give insoluble carbonates thatseparate out. On the other hand the hardness due to the presence of chlorides andsulphates of calcium and magnesium cannot be removed by boiling and is thereforecalled permanent hardness. Though calcium and magnesium present in hard waterare nutrients that are needed for good human health, hard water is not desirable for useat home or in industry.

It is not necessary to separately determine the amount of each ion contributing to the hardness of water. Instead, all ions contributing to hardness are determinedcollectively. A uniform standard has been adopted to express hardness of water. It isreported as parts per million (ppm) of CaCO3. It is equivalent to the number ofmilligrams of CaCO3 per kg of water. The hardness of water may range from zero tohundreds of ppm, depending on the source. An excellent way to determine hardness ofwater is to perform a complexometric titration using a standard solution ofethylenediaminetetraacetic acid (EDTA) solution.

The determination of the total hardness of water is based on complexometric titrationof calcium and magnesium present in it with an aqueous solution of the disodium salt of ethylenediaminetetraacetic acid at pH value of 10.EDTA is capable of forming stable 1:1 complexes with most of the metal ions. Forexample, the reaction of its disodium salt with calcium ions can be represented as :

$$Ca^{2+}(aq.) + Na_2EDTA\ (aq.)\ ?\ Ca(EDTA)\ (aq.) + 2Na^+$$

The equivalence point of a complexation titration occurs when stoichiometricallyequivalent amounts of analyte and titrant have reacted. It means that the solutionconcentrations of the metal ion and EDTA are equal. In the complexometric determination of the hardness of water we use eriochromeblack T (EBT) or solochrome black as metal ion indicator.Eriochrome black -T (EBT) forms a wine red complex with the metal ions. At the endpoint the indicator is set free and the solution becomes blue in colour, marking the endpoint.

$$\underset{\text{(Wine red)}}{M.In} \quad + \quad H_2Y^{2-} \quad ? \quad M.Y^{2-}\,(aq.) \quad + \quad \underset{\text{(Blue)}}{HIn^{2-}}$$

Here, H2Y2- represents disodium salt of EDTA and HIn2- represents eriochrome black-T in a buffer solution of pH 10.

1.7 Summary

Acid-Base Titrations

Acid-base titrations are based on the neutralization reaction between an acid and a base. These titrations help determine the concentration of an unknown acid or base using a standard solution of known concentration. Indicators such as phenolphthalein or methyl orange signal the equivalence point by changing colour. The titration curve depends on the strength of the acid and base, with strong acid-strong base titrations exhibiting a sharp pH change near the equivalence point, while weak acid-strong base or weak base-strong acid titrations show a more gradual shift.

Oxidation-Reduction Titrations

Redox titrations involve electron transfer between the analyte and titrant. They are used to determine the concentration of oxidizing or reducing agents. Two important types of redox titrations are:

Permanganometry : This method uses potassium permanganate (KMnO□) as an oxidizing agent. In acidic medium, KMnO□ is reduced to Mn^{2}□, while the analyte undergoes oxidation. The reaction is self-indicating since KMnO□ has a distinct purple colour that fades upon reduction. It is used in the determination of iron (II), oxalates, and hydrogen peroxide.

Dichromatometry : This method employs potassium dichromate (K□Cr□O□) as an oxidizing agent. In acidic medium, dichromate (Cr□O□^{2}□) is reduced to Cr^{3}□, while the analyte is oxidized. It requires an external indicator like diphenylamine or ferroin. Dichromatometry is commonly used for determining iron, organic compounds, and certain reducing agents.

Complexometric Titrations

Complexometric titrations involve the formation of a stable complex between a metal ion and a ligand, typically using ethylenediaminetetraacetic acid (EDTA). These titrations are widely used in the determination of metal ions in solution. The endpoint is detected using metal ion indicators such as Eriochrome Black T, which changes colour upon complexation. EDTA titrations are useful for determining water hardness, assessing metal content in pharmaceuticals, and analyzing industrial samples.

Hardness of Water

Water hardness is caused by dissolved calcium (Ca^2?) and magnesium (Mg^2?) ions, with contributions from iron, manganese, and other metals. It is classified into:

Temporary Hardness : Caused by bicarbonates (Ca(HCO?)?, Mg(HCO?)?), which can be removed by boiling.

Permanent Hardness : Due to sulfates and chlorides of calcium and magnesium, which cannot be removed by boiling.

Water hardness is measured using EDTA titration, where the total hardness is determined by complexing Ca^2□ and Mg^2□ with EDTA in the presence of an indicator. Hardness is expressed in parts per million (ppm) or as calcium carbonate (CaCO□) equivalents. Hard water causes scale formation in boilers and reduces the efficiency of soaps and detergents. Treatment methods include ion exchange, lime softening, and reverse osmosis.

These titration methods are essential in analytical chemistry for determining the composition of various substances in environmental, industrial, and pharmaceutical applications.

1.8 Self-assessment questions

1. Write the principle for acid base titration.
2. What are the applications of acid base titration?
3. What indicator can be used for a titration involving strong acid and strong base?
4. What is redox titration?
5. Why in permanganometry titration no indicator is added?
6. What indicator is used in dichromatometry?
7. What are temporary and permanent hardness of water?
8. What is the role of potassium permanganate in permanganometry?
9. Why is potassium dichromate used in redox titrations?
10. What is the main ligand used in complexometric titrations?
11. How can temporary hardness be removed from water?
12. How does Eriochrome Black T function in EDTA titrations?

13. What is the significance of EDTA in determining water hardness?
14. How does hard water affect industrial applications?
15. How does an indicator help in acid-base titrations?

1.9 Further Reading

A. I. Vogel, Quantitative Chemical Analysis, 1989, 5th Edition.

D. Harvey, Analytical Chemistry 2.1, 2016.

Douglas A. Skoog, Donald M. West, F. James Holler, Stanley R. Crouch, Fundamentals of Analytical Chemistry An essential textbook for understanding titration methods and analytical techniques.

Unit-2 ❑ Chromatography

Structure

2.0 Objectives

- Understand the fundamental principles of chromatographic separation
- Learn the role of mobile and stationary phases in different chromatographic techniques.
- Explain the principles of GLC
- Identify the components of a GLC system
- Discuss factors affecting separation in GLC
- Understand the basic principle of TLC and its role in analytical chemistry.
- Learn how to prepare and develop a TLC plate using different solvent systems.
- Analyze the significance of Rf values and how they are used for compound identification.
- Differentiate between GC and GLC and their respective applications.

  Understand the principles of HPLC and its advantages over conventional liquid chromatography.

- ➢ Identify the key components of an HPLC system, including the pump, injector, column, and detector.
- ➢ Explain the principle of solvent extraction based on distribution coefficient and partitioning.
- ➢ Explore applications of solvent extraction in pharmaceutical, environmental, and chemical industries.

2.1 Introduction

Chromatographic separation techniques play a crucial role in analytical chemistry, allowing for the effective separation, identification, and quantification of chemical components in complex mixtures. These techniques are based on differential interactions between the sample components and a stationary and mobile phase, leading to their separation. Various chromatographic methods, such as Gas-Liquid Chromatography (GLC), Thin-Layer Chromatography (TLC), Gas Chromatography (GC), and High-Performance Liquid Chromatography (HPLC), are widely used in research, pharmaceuticals, and industrial applications.

Additionally, solvent extraction is an essential separation technique based on the differential solubility of compounds in two immiscible solvents. It is extensively used in chemical, pharmaceutical, and environmental applications for purification and compound isolation. Understanding these principles and methods is fundamental for efficient analytical and preparative applications in various scientific fields.

2.2 Principles of chromatographic separation

Chromatography is a separation technique based on the principle where molecules in mixture applied onto the surface or into the solid, and fluid stationary phase (stable phase) is separating from each other while moving with the aid of a mobile phase. The factors effective on this separation process include molecular characteristics related to adsorption (liquid-solid), partition (liquid-solid), and affinity or differences among their molecular weights. Because of thesedifferences, some components of the mixture stay longer in the stationary phase, and they move slowly in the chromatography system, while others pass rapidly into mobile phase, and leave the system faster.

Based on this approach three components form the basis of the chromatography technique :

- **Stationary phase :** This phase is always composed of a "solid" phase or "a layer of a liquid adsorbed on the surface a solid support".

- **Mobile phase :** This phase is always composed of "liquid" or a "gaseous component."
- Separated molecules

The type of interaction between stationary phase, mobile phase, and substances contained in the mixture is the basic component effective on separation of molecules from each other. Chromatography methods based on partition are very effective on separation, and identification of small molecules as amino acids, carbohydrates, and fatty acids. However, ion-exchange chromatography is more effective in the separation of macromolecules as nucleic acids, and proteins. Paper chromatography is used in the separation of proteins, and in studies related to protein synthesis; gas-liquid chromatography is utilized in the separation of alcohol, ester, lipid, and amino groups, and observation of enzymatic interactions, while molecular-sieve chromatography is employed especially for the determination of molecular weights of proteins. Agarose-gel chromatography is used for the purification of RNA, DNA particles, and viruses.

Stationary phase in chromatography is a solid phase or a liquid phase coated on the surface of a solid phase. Mobile phase flowing over the stationary phase is a gaseous or liquid phase. If mobile phase is liquid it is termed as liquid chromatography (LC), and if it is gas then it is called gas chromatography (GC). Gas chromatography is applied for gases, and mixtures of volatile liquids, and solid material. Liquid chromatography is used especially for thermal unstable and non-volatile samples.

The purpose of applying chromatography which is used as a method of quantitative analysis apart from its separation is to achieve a satisfactory separation within a suitable timeinterval. Various chromatography methods have been developed to that end. Some of them include column chromatography, thin-layer chromatography (TLC), paper chromatography, gas chromatography, ion exchange chromatography, gel permeation chromatography, high-pressure liquid chromatography, and affinity chromatography.

2.2.1 Gas-Liquid Chromatography (GLC)

Gas-Liquid Chromatography (GLC) is a separation technique in which gas (usually inert gas, such as helium or nonreactive gas, such as nitrogen), is used as a mobile phase, and liquid as a stationary phase.Basis of this separation is difference of partition coefficient of volatilized compounds between liquid and gas phases when the desired compound is carried through the column by a carrier gas.The gaseous compounds being analyzed interact with the walls of column, which is coated with different kinds of stationary phases.This causes each compound to elute at different time (retention time), and then retention times are compared. This makes GLC analytically very useful.As compound leaves the column, they pass through a detector, which is linked to chart recorder via amplifier. Chart recorder records the peaks. Due to its high sensitivity, reproducibility, and speed of resolution, it is widely used for several qualitative and quantitative analyses.

Typical application of GLC includes testing purity of a substance; prepare new compounds from mixture (preparative chromatography), identifying and separating different components of a mixture.It is also known as Vapour-Phase Chromatography (VPC), or Gas-Liquid Partition Chromatography (GLPC).

2.2.2 Thin Layer Chromatography (TLC)

Thin-layer chromatography is a "solid-liquid adsorption" chromatography. In this method stationary phase is a solid adsorbent substance(alumina, silica gel, cellulose) coated on glass plates. In this method, the mobile phase travels upward through the stationary phase. The solvent travels up the thin plate soaked with the solvent by means of capillary action. During this procedure, it also drives the mixture previously dropped on the lower parts of the plate with a pipette upwards with different flow rates. Thus the separation of the analytes is achieved. This upward travelling rate depends on the polarity of the material, solid phase, and of the solvent.

In cases where molecules of the sample are colourless, florescence, radioactivity or a specific chemical substance can be used to produce a visible coloured reactive product so as to identify their positions on the chromatogram. Formation of a visible colour can be observed under room light or UV light. The position of each molecule in the mixture can be measured by calculating the ratio between the distances travelled by the molecule and the solvent. This measurement value is called relative mobility, and expressed with a symbol Rf(retention factor). Rf value is used for qualitative description of the molecules.

2.2.3 Gas Chromatography (GC)

In this method stationary phase is a column which is placed in the device, and contains a liquid stationary phase which is adsorbed onto the surface of an inert solid. Gas chromatography is a "gas-liquid" chromatography. Its carrier phase consists of gases as He or N_2. Mobile phase which is an inert gas is passed through a column under high pressure. The sample to be analyzed is vaporized, and enters into a gaseous mobile phase. The components contained in the sample are dispersed between mobile phase and stationary phase on the solid support. Gas chromatography is a simple, multifaceted, highly sensitive, and rapidly applied technique for the extremely excellent separation of very minute molecules. It is used in the separation of very little amounts of analytes.

2.2.4 High-Performance Liquid Chromatography (HPLC)

Using High-pressure liquid chromatography (HPLC) technique it is possible to perform structural, and functional analysis, and purification of many molecules within a short time, This technique yields perfect results in the separation, and identification of amino acids, carbohydrates, lipids, nucleic acids, proteins, steroids, and other biologically active molecules, In HPLC, mobile phase passes through columns under 10-400 atmospheric pressure, and with a high (0.1-5 cm/sec) flow rate. In this technique, use of small particles, and application of high pressure on the rate of solvent flow increases separation power, of HPLC and the analysis is completed within a short time.

Essential components of a HPLC device are solvent depot, high- pressure pump, commercially prepared column, detector, and recorder. Duration of separation is controlled with the aid of a computerized system.

2.3. Elementary idea of solvent extraction

Solvent extraction is the process in which a compound transfers from one solvent to another owing to the difference in solubility or distribution coefficient between these two immiscible (or slightly soluble) solvents. Compared with other separation methods, it gives a better separation effect than chemical precipitation, and a higher degree of selectivity and faster mass transfer than the ion exchange method. Compared with distillation, solvent extraction has advantages such as low energy consumption, large production capacity, fast action, easy continuous operation and ease of automation.

An extractant, is a substance primarily responsible for the transfer of a solute (suppose metal ion) from one phase to the other. The extractant is dissolved in a suitable diluent and together act as a solvent. The diluent is immiscible with other phase which is usually water. The extractant reacts with the solute by solvation/chelation/ion pair formation etc to extract from the aqueous phase. The distribution equilibrium between two phases is governed by Gibbs phase rule, given by

$$P+V=C+2 \qquad (1)$$

Where, P = is the number of phases, V = is the variance or degree of freedom and C = is the number of components.

In solvent extraction, we have P=2 two phases namely aqueous and organic phase, the component C=1, viz. solute, in solvent and water phase and at constant temperature and pressure P=1, thus, we therefore have

$$2+1=1+2 \text{ i.e. } P+V=C+2 \qquad (2)$$

According to Nernst distribution law,

If $[X]_1$ is concentration of solute in phase 1 and $[X]_2$ is the concentration of solute in phase 2 at equilibrium:

$$K_D = \frac{[X]_1}{[X]_2} \qquad (3)$$

Where KD is called as the partition coefficient, this partition or distribution coefficient is independent of the total solute concentration in either of the phases. In the above expression for KD, we have not considered the activity coefficient of the species in the organic as well as in the aqueous phase. We, therefore, use the term distribution ratio (D) to account for the total concentration of species in the two phases.

Distribution Ratio (D)

The distribution of a solute between two immiscible solvents in contact to each other can be described by the distribution ratio "D".

$$D = \frac{[X]_1}{[X]_2} \qquad (4)$$

Where [X] represents the stoichiometric or formal concentration of a substance X and the subscripts 1 and 2 refer to the two phases. Since in most cases, two-phase system is of analytical interest, an organic solvent and aqueous are involved, D will be understood to be;

$$D = \frac{[X]_{org}}{[X]_{aq}} \qquad (5)$$

The subscript org and aq refer to the organic and aqueous phases respectively. Distribution ratio 'D' is dimensionless quantity, separation of two solutes by solvent extraction is expressed by the term, separation factor (?), which is related to individual distribution ratios,

$$\alpha = \frac{D_A}{D_B} \qquad (6)$$

D_A and D_B are the respective distribution ratios of solute A and B.

In the simplest extraction case, the distribution ratio is constant in accordance with the classical Nernst distribution law, a solute will distribute itself between two essentially immiscible solvents so that at equilibrium, the ratio of the concentrations of the solute in the two phases at a particular temperature will be constant, provided the solute is not involved in chemical interactions in either phases. For such a solute, then $K_D=D$. Now in practical work, instead of using term K_D or D one prefers to use term percentage extraction (E).

Percent Extraction (%E)

The more commonly used term for expressing the extraction efficiency by analytical chemist is the percent extraction "E", which is related to "D" as

$$\%\text{Extraction (E)} \frac{100D}{D+V_{aq}/V_{org}} \qquad (7)$$

Where, V represent solvent volume and the other quantities remain as previously defined. The percent extraction may be seen to vary with the volume ratio of the two phases as well as with D.

2.4 Summary

Chromatographic separation techniques are essential analytical tools used to separate, identify, and quantify components in complex mixtures. These methods rely on the interaction between a mobile phase and a stationary phase, leading to differential migration of substances. Techniques such as Gas-Liquid Chromatography (GLC), Thin-Layer Chromatography (TLC), Gas Chromatography (GC), and High-Performance Liquid Chromatography (HPLC) each have unique principles and applications in fields like pharmaceuticals, forensics, and environmental analysis.

In addition to chromatography, solvent extraction is a widely used separation technique based on the selective solubility of compounds in two immiscible liquids. This method is crucial for purifying substances and is commonly applied in chemical, pharmaceutical, and industrial processes. A clear advance understanding of these techniques enhances analytical precision and efficiency in scientific research and industry applications.

2.5 Self-assessment questions

1. **What is chromatography?**

   Ans. Chromatography is a technique used to separate components of a mixture based on their interaction with a stationary phase and a mobile phase.

2. **What are the main types of chromatography?**

   Ans. The main types include liquid chromatography, gas chromatography, thin-layer chromatography, and paper chromatography.

3. **What factors influence chromatographic separation?**

   Ans. actors include the nature of the stationary phase, mobile phase composition, temperature, and flow rate.

4. **What is retention time in chromatography?**

   Ans. Retention time is the time taken for a component to travel from the injection point to the detector.

5. **What is the role of the stationary phase in chromatography?**

   Ans. The stationary phase selectively interacts with analytes, affecting their movement and separation.

6. **What is Gas-Liquid Chromatography (GLC)?**

   Ans. GLC is a type of gas chromatography where the stationary phase is a liquid-coated solid support.

7. **What is the role of the carrier gas in GLC?**

   Ans. The carrier gas (e.g., helium, nitrogen) transports the sample through the column.

8. **Which detectors are commonly used in GLC?**

   Ans. Common detectors include the Flame Ionization Detector (FID) and the Thermal Conductivity Detector (TCD).

9. **What types of compounds are analyzed using GLC?**

   Ans. GLC is used for volatile and thermally stable compounds.

10. **How does temperature affect separation in GLC?**

    Ans. Higher temperatures reduce retention time but may decrease resolution, while lower temperatures improve separation but increase analysis time.

11. **What is the principle of Thin-Layer Chromatography (TLC)?**

    Ans. TLC separates compounds based on their differential adsorption on a stationary phase coated on a glass, plastic, or metal plate.

12. **What is the stationary phase in TLC?**

    Ans. Common stationary phases include silica gel and alumina.

13. **How is the Rf value calculated in TLC?**

    Ans. Rf = (Distance traveled by the compound) / (Distance traveled by the solvent front).

14. **What are the applications of TLC?**

    Ans. LC is used for drug testing, food analysis, and purity checks.

15. **Why is a UV lamp used in TLC?**

    Ans. V light helps visualize colorless compounds that fluoresce under ultraviolet radiation.

16 How does Gas Chromatography (GC) differ from GLC?

Ans. GC generally refers to all gas-based chromatographic methods, whereas GLC specifically uses a liquid stationary phase.

17 What is the main advantage of GC over other chromatographic methods?

Ans. GC provides high-resolution separation and rapid analysis of volatile compounds.

18. **What types of samples are suitable for GC analysis?**

    Ans. GC is best for gases and volatile liquids.

19. **What is the main advantage of HPLC?**

    Ans. HPLC allows high-resolution separation of non-volatile and thermally unstable compounds with high accuracy.

20. **What type of detectors are used in HPLC?**

    Ans. Common detectors include UV-Vis, fluorescence, and refractive index detectors.

2.6 References for further reading

A. I. Vogel, Quantitative Chemical Analysis, 1989, 5th Edition.

D. Harvey, Analytical Chemistry 2.1, 2016.

Unit-3 ❑ Polymer Chemistry

Structure

3.1 Objectives

After going through this unit, we will be able to know about

- natural and synthetic polymers
- homo polymers and copolymers and their structures
- thermoplastic and thermosetting polymer and their uses

- addition and condensation polymers
- synthesis of different polymers and their uses

3.2 Introduction

A polymer (Greek poly means many and meros means parts) is defined as a large molecule of high molecular weight formed by the combination of a number of one or more types of molecules of low molecular weight. Polymers are also known as macromolecules. A monomer is a smaller molecule that can use as repeating units to form a larger polymer chain. The process by which monomers combine to form a polymer is known as polymerisation. The extent to which the number of monomer units combines to form a polymer is known as degree of polymerisation and it is represented by the ratio of the average molecular weight of polymer to molecular weight of the monomer.

3.3 Classification of polymers

Polymers are classified in a number of ways depending upon their source, structure, physical properties and synthesis.

3.3.1 On the basis of source

a) Natural Polymer: this polymer is obtained from raw materials that are found in nature. Examples : Proteins, DNA, RNA, cellulose, starch, rubber etc.

Uses: Natural polymers have been widely used in a variety of biomedical applications such as pharmaceuticals, tissue regeneration scaffolds, drug delivery agents, and imaging agents.

b) Synthetic Polymer : These polymers are made in the industry from chemical substances. Examples: Polyethylene, Nylons, Polyesters, Teflon etc.

Uses : The Polyethylene polymer is used in plastic bags and film wraps. Polyvinyl Chloride (PVC) is used in siding, pipes, flooring purposes. Polystyrene polymer is used in cabinets and in packaging.

c) Semi-synthetic polymer : These type of polymers are derived from naturally occurring polymers by means of chemical modifications. Generallythese are prepared from both petroleum and natural products. Examples: Vulcanized rubber, Cellulose diacetate, Gun Cotton etc.

Uses : S emi-synthetic polymers are frequently used for the development of drug delivery systems.

3.3.2 On the basis of Structure

The structure of a polymer depends upon

i) The composition of basis polymer unit

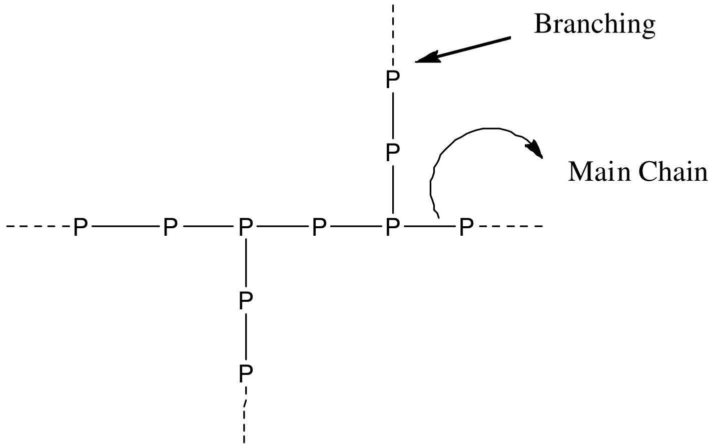
ii) The arrangement of the polymer chains.

i) Based on the composition :

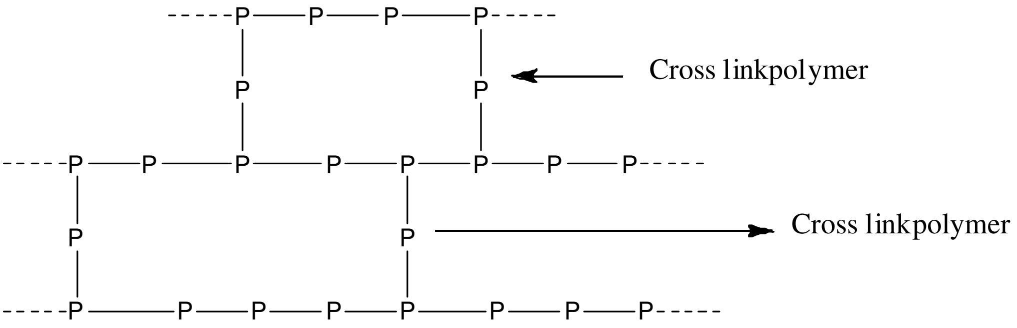
a) Homopolymers : Polymers formed from bonding of identical monomers are called homopolymers. Example : Polyethylene is a homopolymer because it is synthesized by the polymerisation of a single monomer namely ethylene.

-----P——P——P——P——P-----

Linear homopolymer



Branched Chain homopolymer



Crossedlinked homopolymer

b) Copolymer : Polymers formed from two or more different monomers are called copolymers. Examples : Synthetic rubber Buna-S (1,3-Butadiene and Styrene polymer). Again the copolymers may be linear (regular or random), branched chain and block types. In a copolymer molecule if the monomer units occur in an irregular fashion in the chain, they are called random copolymer. Sometimes, in linear copolymer molecules the similar monomeric units may occur in relatively long sequences forming block copolymers.

-----P_1——P_2——P_1——P_2——P_1-----

Linear copolymers (regular)

-----P_1——P_2——P_2——P_1——P_1——P_1——P_2——P_1-----

Linear copolymers (random)

-----P_1——P_1——P_1——P_1——P_1——P_1——P_1——P_2——P_2——P_2——P_2——P_1——P_1-----

Block Copolymers (P_1 block and P_2 block)

ii) The arrangement of the polymer chains :

a) Linear polymer : In these polymers, monomer units are held together in a long chain without any lateral linkage or branching. Examples : Polyvinyl chloride (PVC).

b) Cross-linked Polymers : In these polymers, different linear chains of monomer units are cross linked with each other through covalent bonds. Examples : Bakelite, Melamine etc.

c) Branched Polymers : These polymer contains linear chains having some branches. Examples : Low density polymer.

3.3.3 On the basis of physical properties

a) Crystalline Polymers : In crystalline polymers, there is a regular linear arrangement of polymer chain. The crystalline polymers being hard can be drawn into fibers.

b) Amorphous Polymers : In amorphous polymers, there is an irregular arrangement of polymer chain. These polymers may exhibit elasticity and such polymers are known as elastomers. Examples : Rubber etc. The amorphous solids, which do not exhibit elasticity are termed as plastics.

Depending upon the structure of the polymer and its behaviour at different temperatures, the polymers may be classified as :

i) **Thermoplastics :** These polymers soften on heating and can be moulded into different shapes. They become hard on cooling and regain their physical properties. The process of heating and cooling can be repeated a number of times without causing any change in their physical properties. Examples : Nylon, Polyethylene, PVC etc.

ii) **Thermosetting :** These polymers can be moulded into different shapes by heating and they become hard when heated. The heat treatment is given only during the preparation of various articles from these polymers. Once solidified and set, they cannot be softened or remoulded on heating. Examples : Bakelite and Melamine etc.

3.3.4 On the basis of Synthesis

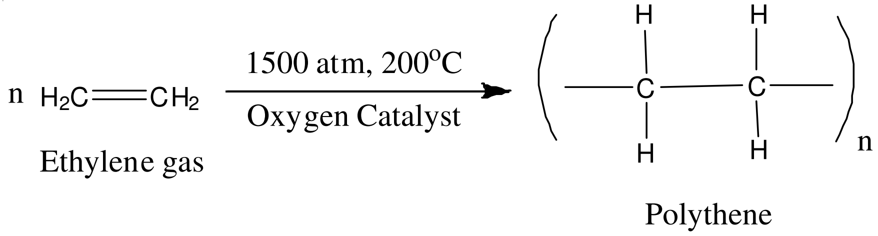
a) Addition polymerisation : Addition polymerization is when the monomer molecules bond to each other without the loss of any other atoms.These polymerisation occurs in monomer units having double or triple bonds. The monomer units are generally joined through head-tail arrangement. Examples : Polyethylene, PVC, polystyrene, polyethylene, polyacrylates, etc.

b) Condensation Polymers : Condensation polymers are any kind of polymers formed through a condensation reaction-where molecules join together and losing small molecules as by-products such as water or methanol. Examples: Nylon-6,6, Bakelite, Polyesters, polyurethanes etc.

3.4 Polythene

3.4.1 Process

In the original process ethylene was subjected to high pressure (1000-1500 atm) and 200°C in presence of trace amount of oxygen (0.01%) as catalyst. Ethylene polymerises to form low density polythene which is obtained as waxy solid. High density polythene can be prepared at low pressure (6-10 atm) by using Ziegler -Natta catalyst consisting of aluminium triethyl with TiCl4 in paraffin as diluent. The polymerisation reaction takes place at 70°C and at 7 atm pressure in a reactor. Then elimination of catalyst and solvent flakes or powered polythene.



$$n\ H_2C{=}CH_2 \xrightarrow[\text{Oxygen Catalyst}]{1500\ \text{atm},\ 200^{o}C} \left(-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}- \right)_n$$

Polythene (PE) is the simplest of all the commercial polymers and yet it is the most popular plastic in the world. High-density polyethylene (HDPE) is a thermoplastic polymer produced from the monomer ethylene. Low-density polyethylene (LDPE) is a thermoplastic made from the monomer ethylene. It was the first grade of polyethylene, produced by Chemical Industries using a high pressure process via free radical polymerization.

3.4.2 Properties

1. It is a rigid and waxy material
2. It has chemical resistance to strong acids, alkalis and salts at room temperature.
3. High density polythene (HDPE) possesses greater chemical resistance and higher softening points (125-135°C) in comparison to low density polythene (LDPE) having lower softening points (115-120°C).
4. It is a good insulator of electricity
5. High pressure polyethylene (low density) possesses branched chains in its structure and so it is flexible and tough. Low pressure polythene (high density) possesses linear polymer chains having greater strength but of low impact strength and is relatively brittle.

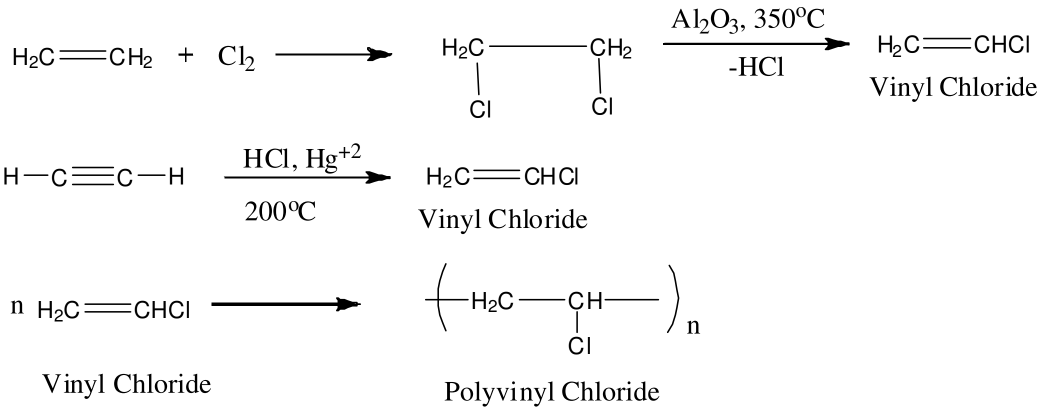
3.4.3 Uses

Polyethylene is widely used for making sheets, bags, bottles, food wrappers, caps, tubes, toys, domestic appliances, electrical insulator, coating of electric wires and cables.

3.5. Polyvinyl Chloride (PVC)

3.5.1. Process

Polyvinyl chloride is prepared by heating 50°C water emulsion of vinyl chloride in an autoclave under pressure for 72 hrs in presence of benzyl peroxide to give a linear chain polymer. A small amount of emulsifier is added for the stability of the polymer particles formed. Solid polymers may be obtained by the coagulation of vinyl latex with acid.



$$H_2C{=}CH_2 + Cl_2 \longrightarrow H_2C(Cl)-CH_2(Cl) \xrightarrow[-HCl]{Al_2O_3,\ 350^\circ C} H_2C{=}CHCl$$

$$H-C\equiv C-H \xrightarrow[200^\circ C]{HCl,\ Hg^{+2}} H_2C{=}CHCl$$

$$n\ H_2C{=}CHCl \longrightarrow \left(-H_2C-\underset{Cl}{\underset{|}{CH}}-\right)_n$$

3.5.2 Properties

1. PVC is a colourless, non-inflammable material and resistance to water and chemicals.
2. It is hard but brittle material.
3. The softening point of PVC is 148oC.
4. It does not possess any odour and also nontoxic.
5. It is a linear polymer and thermoplastic in nature.

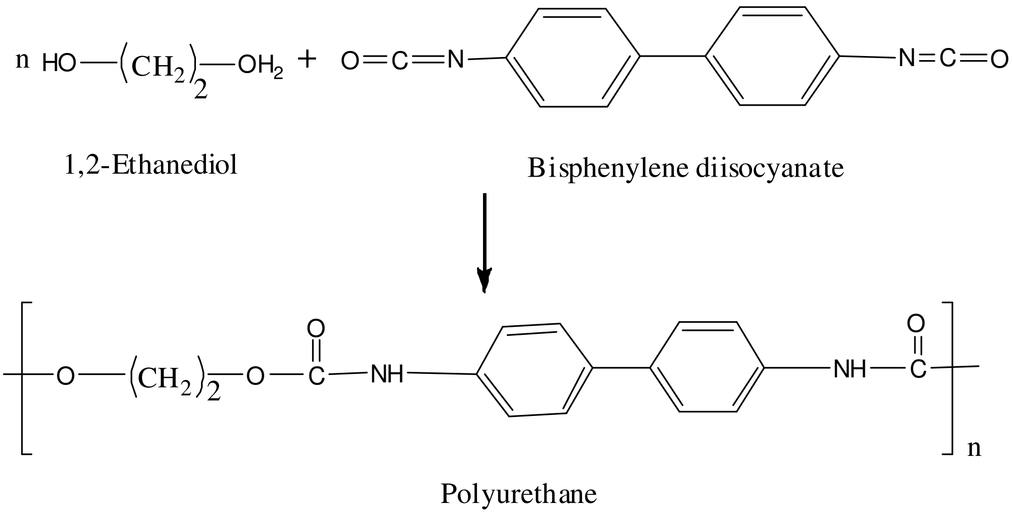
3.5.3 Uses

1. In unplasticized condition it is used as tank linings, refrigerator components, helmets, outer cover of equipments and household appliance, motor cycle, car body components, tubes and trays etc.
2. In plasticized condition the PVC becomes soft and is used in the preparation of flexible materials like electric cable cover, rain coat, sheets of different thickness, table cloth, containers, conveyor belt and foam for heat insulation etc.

3.6. Polyurethane

3.6.1 Process

Polyurathanes are prepared by the reaction between dihydric alcohol and di-isocyanate. The reaction between ethylene glycol and bisphenylene diisocyanate, a polyurethane is obtained having melting point 390oC. The melting point of the polymer varies with changing the size of the aromatic group.



3.6.2 Properties

1. It is performed very well when it is used in high fatigue applications. Flexural properties can be isolated allowing for good elongation and recovery properties.
2. It is stable in water, oil and grease. This compounds will last many years in subsea applications.

3.6.3 Uses

1. Polyurethanes are used as coating, films, foam, cushion, adhesives and elastomers.
2. Polyurethane fibres are used for foundation garments and swim-suits.
3. It is used as an artificial leather substituted.
4. It is also used to produce gaskets and seals and electric fibres.

3.7 Summary

In this unit we have discussed about the definition and different classifications of polymerslike linear, branched/chain, or cross-linked polymers. This classification is done based on the chemical structure of a polymer molecule. Then we have described about synthetic, semi-synthetic, and natural polymers. At the end of the unit different synthetic polymers are described in details.

3.8 Self-assessment questions

1. What are polymers?
2. How are polymers classified?
3. Write short notes on: Addition polymer, Condensation polymer, Copolymer.
4. What is thermoplastic and thermosetting polymer?
5. What is PVC?
6. What is the monomer of polythene? Write the synthesis and use of polythene.
7. What is the monomer of polyurethane? Write the synthesis and use of polyurethane.

3.9 References

1. P. K. Gangopadhyay, Application Oriented Chemistry; Book Syndicate (P) Limited.
2. M. S. Bhatnagar;A Textbook of Polymer Chemistry, S Chand Publisher.
3. K. K. Mandal, K. Basu, P. Dutta; Basic Concepts of Polymer Chemistry; Techno world Publisher.

Unit-4 ❑ Fuels

Structure

4.1 Objectives

After going through this unit, we will be able to know about

- different types of fuels
- Calorific Value, net Calorific Value, flash point
- principle, composition, manufacture and uses of producer gases
- principle, composition, manufacture and uses of water gases
- Liquefied petroleum gas and bio gas
- crude oil, gasoline and Diesel oil
- Octane number, cetane number and Antiknock compounds

4.2. Introduction

A fuel is a substance which on oxidation releases light and large amount of heat which can be used in domestic and industrial process. Commercial fuels are composed of carbon and hydrogen.

4.2.1 Type of fuels

Fuels are mainly three types like solid, liquid and gaseous. They are also natural and artificial.

Type	Natural/primary	Artificial/Secondary
Solid fuels	Firewood, charcoal, coal, peat, dung, sawdust,wheat, straw and other fibrous material.	Charcoal, coke.
Liquid fuels	Petroleum	Petrol, diesel, kerosene, fuel oil, coal tar, LPG, naphtha, ethanol.
Gaseous fuels	Natural gas	Water gas, producer gas, coal gas, blastfurnace gas, acetylene gas, coke oven gas, CNG, propane, methane, hydrogen.

4.3. Gaseous fuels

Gaseous fuels are obtained either naturally or by the treatment of solid or liquid fuel. Among the naturally occurring gaseous fuels, natural gas and liquefied petroleum gas are most important. These gases have high calorific value (CV).

CV: This value of gaseous fuel determines the thermal output of a heating appliance. It is defined as the amount of heat liberated when unit mass of fuel is completely burnt in air or oxygen. examples: High-volatile bituminous B calorific value 12130 Btu/lb or 28262 KJ/Kg, High-volatile bituminous C calorific value 10750 Btu/lb or 25047 KJ/Kg, Sub-bituminous B calorific value 9150 Btu/lb or 21319 KJ/Kg.

Gross or High Calorific Value (GCV): It is defined as the amount of heat liberated when unit mass of the fuel is burnt completely in air and the products of combustion are cooled to room temperature.

Net or Lower calorific Value (NCV or LCV): It is the total quantity of heat liberated when one unit of fuel is burnt completely and products of combustion has been permitted to escape.

LCV = HCV- Latent heat of water vapour formed. (Latent heat of steam = 587 cal/gm).

Flash Point (FP):The flash point of a flammable liquid is the lowest temperature at which there will be enough flammable vapour to ignite when an ignition source is applied.The lower the flash point, the easier it is to ignite the material.

Autoignition Temperature (AT) : The lowest temperature at which a substancespontaneously ignites without a source of ignition (such as a flame or spark).

Unlike flash points, the autoignition temperature does not use an ignition source. As a result, the autoignition temperature is higher than the flash point.Example Gasoline FP is 43°C and AIT is 280°C.

4.4. Producer gas

4.4.1 Principle

It is produced by passing air over white hot coke bed maintained at about 1000°C-1500°C. Exothermic reaction occurs between carbon and oxygen of air producing CO and CO_2. The excess heat is utilised for the endothermic reaction between carbon and steam to produce CO and H_2.The temperature of the fuel is maintained between 1000°C-1500°C (depending on the melting point of ash) and the reactions are given below.

$C + O_2 = CO_2 + 94.05$ Kcals.
$2C + O_2 = 2CO + 52.84$ Kcals.

$C + CO_2 = 2CO - 41.21$Kcals.
$C + H_2O = CO + H_2 - 41.9$Kcals
$CO + H_2O = CO_2 + H_2 - 0.7$Kcals

Composition : It is mainly a mixture of CO and N_2. Percentage $N_2 = 50\text{-}55\%$, $CO = 25\text{-}30\%$, $H_2=10\%$ $CO_2=5\%$ and rest $CH_4 = 2\text{-}3\%$.

The calorific value of producer gas is 900-1300 kcal/m_3 or 150 B.Th.U

4.4.2 Manufacture

Producer gases are made of cylindrical steel shells of about 10fts in diameter and 12ft high and can hold about one ton of coal. Steel shells are either water jacketed or refectory lined with steam and air inlets at the bottom. The gas outlet and coal charging door are at the top. Ash is taken out through the grate at the bottom. The sensible heat from the hot gas is utilised for preheating the incoming combustion air and raising steam in a boiler to be used in the producer. The volume of producer gas generated per kg of coal varies between 2 to 3.5 cubic meter.

4.4.3 Uses

Producer gas was used primarily as an industrial fuel for iron and steel manufacturing, such as firing coke ovens and blast furnaces, cement and ceramic kilns or for mechanical power through gas engines. It is also used as a reducing reagent in certain metallurgical operations.

4.5 Water Gas

4.5.1 Principle

Water gas is made by passing steam into a bed of white hot coal or coke at a temperature between 1000°C and 1400°C according to the reaction.

$C + H_2O = CO + H_2 - 41.9$ Kcal

As the reaction is endothermic, the temperature of the coke bed gradually falls. At lower temperature more CO_2 is produced according to the reaction.

$C + 2H_2O = CO_2 + 2H_2 - 42.6$ Kcal

The reaction is not wanted as CO_2 has no heating value. So, steam is stopped and the bed temperature is brought back to 1400°C by combustion of carbon by air blast producing CO_2 and heat. A proportion of CO2 reacts with red hot carbon to produce CO and rest escapes. Steaming is started again. The total cycle takes 4 to 6 minutes. About 50 to 60% coke is transformed to CO and rest produces heat by combustion.Water gas is also known as blue gas as it burns with a blue flame. To enhance the heating value of water gas, it is mixed with hydrocarbons obtained from cracked oil and the product is known as carburetted water gas having higher heating value. Oil gas is prepared in auxiliary plant called carburettor.

The calorific value of water gas is 300 B.Th.U or 2500-2800 Kcal/m3

Composition : Mainly it is a mixture of H_2 and CO. Percentage $H_2 = 48\%$, CO=42 %, $N_2=6\%$, $CO_2=3\%$ and $CH_4= 1\%$.

4.5.2 Manufacture

The gas generator is a refractory lined steel cylinder of 10 ft diameter and 15 ft length. It has a door at the top and another at the bottom for charging coke and removing ash. Air blast enters near the grate. There is arrangement for introducing steam from both top and bottom of the generator. Provisions are made for collecting gas from top and bottom. In order to use hot coke bed fully, the steaming of coke is divided into two parts, for half of the time from below and during the other half from above.

4.5.3. Uses

1. It is used to remove carbon monoxide from fuel cell applications.
2. Used in Fischer-Tropsch process.
3. Reaction with producer gas to produce fuel gas. It is used to gain pure hydrogen for synthesis of ammonia.

4.6 Liquefied petroleum gas

Liquefied petroleum gas is a mixture of butane and propane where butane content may vary from 50 to 100%. It is recovered either from natural gas or is derived from the refining of crude oil. Some LPG may be obtained as a by-product during the cracking of heavy oils.

LPG is recovered from natural gas by absorption or adsorption methods. In the absorption process, the natural gas is subjected to oil-absorption at a very low temperature (– 45°C). All the low molecular weight hydrocarbons are absorbed in the oil. LPG is then separated from the natural gas by fractional distillation.

In the absorption process, activated carbon, aluminium gel and silica gel are used as adsorbents. Latter the adsorbed gas is separated by heating. Subsequently the gas is cooled and compressed to obtain a liquid called LPG. It is bottled under pressure in gas cylinder and sold as LPG for domestic use as fuel under the trade name such as Indane. If the pressure is released it becomes a gas. Little mercaptan is mixed with LPG to detect any leakage. Ethyl mercaptan gives off characteristics bad smell.

The main use of LPG is as domestic and industrial fuel. It is also used as motor fuel. The antiknock property of LPG has been improved by the addition of tetramethyl lead. LPG is clean and highly efficient fuel. Under proper condition it burns without any smoke. Its heating value is much higher than coal gas.

4.7 Bio Gas

It is formed by the bacterial degradation of biomass under anaerobic condition(airtight digesters). Biogas mainly contains methane (50-70%), carbon dioxide andtrace amount of water, sulfur andhydrogen sulfide (H_2S), moisture and siloxanes. The gases methane, hydrogen, and carbon monoxide (CO) can be combusted or oxidized with oxygen.

4.7.1 Manufacture

Biogas can be produced from raw materials such as agricultural waste, manure, municipal waste, plant material, sewage, green waste or food waste. In our country "gobar gas" plants have become quite successful in rural area. The biogas generated by anaerobic digestion of organic waste in biogas plant (closed system). This closed system is called also called an anaerobic digester, biodigester or a bioreactor.Process mainly involves three steps: hydrolysis, acidformation and gas production.

Hydrolysis: In this step, macromolecule like fats, proteins, carbohydrates arebroken down through hydrolysis into fatty acids, amino acids and sugarsrespectively.

Acid formation: in this step, fatty acids, amino acids and sugars are fermented byacid producing bacteria under anaerobic condition into acetic acid, carbon dioxideand hydrogen.

Gas production: In this step, methanogenic bacteria produce methane either byfermenting acetic acid to form methane and carbon dioxide or by reduction ofcarbon dioxide into methane. These plants not only produce gas but also produce huge organic bio fertilizer. If bio gas content 50% methane then its calorific value is 4429 Kcal/m3.

Bovine dung is highly suitable for producing biogas. However, human excreata and paultry wastes can be used with cattle dung to reduce the water necessary to make the slurry for anaerobic decomposition. This energy release allows biogas to be used as a fuel and it is a renewable energy source.

4.7.2 Uses

It can be used for any heating purpose, such as cooking. It can also be used in a gas engine to convert the energy in the gas into electricity and heat.

4.8 Liquid fuels

Liquid fuels are those combustible or energy generating molecules that can be harnessed to create mechanical energy, usually producing kinetic energy.

4.8.1 Crude oil

Crude oil means a mixture of hydrocarbons that exists in liquid phase in natural underground reservoirs and remains liquid at atmospheric pressure after passing through surface separating facilities.

4.8.2 Gasoline

Gasoline or petrol is a transparent, petroleum-derived flammable liquid that is used primarily as a fuel in most spark-ignited internal combustion engines. It consists mostly of organic compounds obtained by the fractional distillation of petroleum, enhanced with a variety of additives.Petroleum refineries convert crude oil and other liquids into many petroleum products that people use every day.

4.8.3 Crude oil Purification

Petroleum can be separated into various types of fuel, by a process called refining, using fractional distillation. Petrol, Diesel and Kerosene are all products (or fractions) of the process of refining Petroleum. On an industrial scale, the different fractions of Petroleum are separated out by fractional distillation.Modern separation involves piping crude oil through hot furnaces. The resulting liquids and vapours are discharged into distillation units. The lightest fractions, including gasoline and liquefied refinery gases, vaporize and rise to the top of the distillation tower, where they condense back to liquids.

4.8.4 Diesel oil

Diesel fuel, is also known as diesel oil, combustible liquid used as fuel for diesel engines, ordinarily obtained from fractions of crude oil that are less volatile than the fractions used in gasoline.

4.9 Knocking

Knocking is a phenomenon that occurs in a gasoline engine when fuel burns unevenly in engine's cylinders. Knocking is the making sharp sounds due to uneven combustion of fuel in the cylinder of a vehicle engine. Knocking characteristics depend on the composition of the fuel. Branched chain hydrocarbon produces less knocking than long chain hydrocarbon molecules. Example like n-heptanes produce large knocking than 2,2,4-trimethyl pentane. In fuel engine mixture, these two compounds are used in balance proportions.

4.10 Octane number

The octane number (ON) is a measure of the knock resistance of gasoline. Octane number, also called Antiknock rating, measure of the ability of a fuel to resist knocking when ignited in a mixture with air in the cylinder of an internal-combustion engine. The Octane number of the fuel is the percentage of isooctane in a mixture of isooctane and n-heptane which match the knocking characteristics of the fuel under examination in a standard one cylinder engine.Regular fuel octane no generally 87 and Premium fuel hasthe highest octane no normally 91-94.

4.11 Cetane number

The suitability of diesel fuels are expressed in the terms of cetane number. It provides information about the ignition delay, i.e. the speed of self-ignition of diesel fuel when injected into hot air through the fuel injector. Cetane number describes the percentage of cetane in a mixture of cetane and 2-methyl naphthalene which has the same ignition characteristics as the diesel fuel under consideration. For high speed diesel engine this number is greater than 50 and for low speed it is around 35.

4.12 Antiknock compounds

An antiknock agent is a gasoline additive used to reduce engine knocking and increase the fuel's octane rating by raising the temperature and pressureat which auto-ignition occurs. TetraEthyl Lead is a colourless viscous liquid and is a well-known anti-knocking compound. Very small amount of TEL is used for raising the octane number of petrol that means the combustion occurs in a more smooth and improved way. Since TEL causes air pollution its use has been prevented. Methyl tertiary butyl ether (MTBE) is used as an anti knocking agent now a days.

4.13 Summary

In this unit we have discussed about fuels and its calorific value. Then we have described principle, manufacture and uses of different types of gases like producer gas, liquefied petroleum gas and bio gas. In the next part of this unit liquid fuels are described in details like crude oil, gasoline and diesel oil. At the end of this unit, we described about knocking, anti-knocking, octane number and cetane number.

4.14 Self-assessment questions

1. What is fuel? Give one example in each category?
2. What is GCV and LCV?
3. Write the reaction in preparation of producer gas?
4. What is Bio gas? Write advantage and disadvantage of Bio gas.
5. Write short notes on: Antiknock compound, Octane number and cetane number.
6. What is gasoline?
7. Why water gas is called blue gas?
8. What is carburetted water gas?

4.15 References

1. O. P. Gupta; Elements of Fuel and Combustion Technology; Khanna Publishing.
2. K. Bhaskararao; A Text on Petro Chemicals; Khanna Publishing.
3. P. K. Gangopadhyay, Application Oriented Chemistry; Book Syndicate (P) Limited.

Unit-5 ❑ Paints and Varnishes

Structure

5.1 Objectives

After going through this unit, we will be able to know about

- Constituents of paints in details
- Oil paint, latex paint and their advantages and disadvantages

- Varnishes and their compositions
- Formulation of paint and varnishes
- Applications paints and varnishes

5.2 Introduction

Paint is the general term for liquid that is used to add colour to the surface of an object by covering it with a pigmented (coloured) coating. It protects the surface against of atmospheric agencies like sunlight, rain, frost, fumes etc. It also prevents corrosion and enhancement of aesthetic appeal. Oily portion of the paint is called vehicle and resin is used in the paint which act as a binder.

5.3 Constituents

Primary Constituents of the oil based paints are as follows:

5.3.1 Pigments

Pigment is a powdered inorganic substances and organic dyes (toner) that are mixed with paint. It should be chemically inert, non toxic and opaque. It increases the strength of paint and protects it from UV rays. Example of colour pigments are given below

a) White (Titanium oxide, ZnO),

b) Black (Carbon black and graphite)

c) Red (Red lead, Pb_3O_4)

d) Blue (Ultramarine, Cobalt blue)

e) Green (Chromium oxide)

f) Yellow (Lead chromate, PbO)

5.3.2 Solvent

Organic solvent andwater are usedto reduce the viscosity of the paint. Water-borne paints are replacing some paints that use volatile organic compounds such as the hydrocarbons which are harmful to the atmosphere.

5.3.3 Binders

Binders are the film forming components of a paint as it dries and affects the flexibility, durability and gloss of the coating. Examples of common binders are polyurethanes, polyesters and acrylics. Now a day's acrylics, alkyd and epoxy polymers are extensively used.

5.3.4 Extenders

These are inert substances which increases the covering power of pigment and protects the paints from weathering. They act as a suspending agent and prevent settling of the pigment particles.

5.3.5 Drying Oil

Drying oil is fatty vegetable oil (linseed oil, tung oil/China wood oil, dehydrated castor oil) that is capable of chemically reacting with oxygen present in the air. Eventually, the oil hardens and dries. Chemically these are glycerides of palmitic, stearic, oleic and linoleic acid. These increases the elasticity of the paint so that it can tolerate the thermal expansion and construction of temperature change. These oils serve as the major component of varnishes, oil paints and other anti-corrosion coatings.

5.3.6 Thinners

A paint thinner is a solvent used by brushing and spraying to reduce thickness of oil-based paints or clean up after their use. Terpentine, mineral spirits, naphtha etc are examples of thinner.

5.4 Solvents for paints

The solvent is the medium in which all other components of the paint are dissolved and evaporates away as the paint dries and cures. there are two types of paints a) solvent-borne and b) water-borne paint. Solvent borne paints are organic solvents as the primary vehicle carrying the solid components in a paint formulation, whereas water borne paints use water as the continuous medium. common solvents used acetone, toluene, methyl ethyl ketone, turpentine, etc.

5.4.1 Oil paint

Oil based paint is a slow drying paint that consists of particles of pigment suspended in a drying oil commonly used linseed oil. Walnut oil, sunflower oil is also used as oils in paints. The viscosity of the oil based paints may be modified by the addition of turpentine solvent which increases the glossiness.

5.5 Latex Paint

It is a water based paints.In case of latex paints the film is formed by synthetic resin latex in water or oil emulsion. Water dispersion of a protective hydrophilic colloid and appropriate latex is used to prepare latex paints.

Advantages of latex paint: a) Easier to apply and touch up b) Cleans up with water. c) Non-flammable. d) Dries faster. e) Less fading, cracking or peeling.

Disadvantage of Latex Paint: a) Swells and cracks if painted on wood surfacesb) Takes a long time to cure and can crack on rough surfacesc) Won't Adhere to dirty wallsd)Not for use on things being touched or moved.

Difference between Latex and oil paints: Latex paints or acrylic paints are fast-drying water-based paints. Latex paints are generally better for the interior of homes and on large surfaces.Oil based paint is a slow drying paint made with oil usually turpentine.Its expels harmful vapour into atmosphere as it evaporates.

5.6 Varnishes

A varnish is a colloidal dispersion of natural or synthetic resins in oil or solvents.

Varnishes provide protective coatings for wooden surfaces, paintings and various decorative objects. Varnish protects and enhances the appearance of wooden floors, interior wood panelling and trim, and furniture.

5.6.1 Composition of Varnishes

The main constituents present in varnishes are resin, drying oil, drier and thinner.

a) Resin : Natural and synthetic resins are used in varnishes include amber, kauri gum, dammar, copal (fossil resin), pine resin. Shellac is also used as a resin in varnishes.

b) Drying oil : there are many types of drying oils, including linseed oil, tong oil and walnut oil. This contains high levels of polyunsaturated fatty acids.

c) Solvent : Generally turpentine was used as the thinner or solvent but now it has been replaced by several mineral based turpentine substitutes such as white spirit or mineral spirit.

d) Driers : These are the Pb, Co, Mn salt of linolates, resinates and naphthenates. Role of drier is to increase the rate of drying of oil and hardness of the varnish film.

5.7 Paint formulation

Pigments, extenders are mixed in a drying oil to produce paintswhere turpentine is used for film formation and for the reduction of viscosity. It actually depends on requirements and mode of use. These may have variation in weather resistance, washability, colour, lusture, anticorrosive property and method of application like brushing, spraying, dipping etc. the process of the paint formulation depends on the expertise of the formulator. A technique is used based on the pigment volume concentration (PVC) and the formula is as follows:

$$\%\,\text{PVC} = \frac{\text{Volume in pigment in paint}}{\text{volume of pigment in paint} + \text{volume of non volatile oil in paint}} \times 100$$

PVC values are given below to get an idea about the paint formulator -House paint: 28 to 36%, Wood primer 35 to 40 %, Metal primer 25 to 40.

5.8 Formulation of varnishes

Properties of the varnishes depend on the relative concentrations of oil and resin. When varnish dries, its solvent portion evaporates, and the remaining constituents oxidize or polymerize to form a durable transparent film. Varnish dries at faster rate with higher concentration and becomes more brittle. Classification is done on the number of gallons of oil used per 100lbs of resin. Furniture, exterior application and for general purpose 6 to 15, 35 to 60,20-to-30-gallon oil are used consecutively.

5.9 Summary

In this unit we have described about paint in details. Different components like pigment, binders, extenders, solvents are discussed. Then we have discussed about the water and oil paint. Advantage and disadvantage of the latex paints are elaborately described. Then composition and formulation of varnish are discussed.

Pigments

Pigments are fine, insoluble particles that provide color, opacity, and protection to paints. They can be natural or synthetic and are classified as organic or inorganic.

Solvent

Solvents dissolve binders and pigments, adjusting the viscosity of the paint for easy application. They evaporate after application, leaving behind a solid paint film.

Binders

Binders (or resins) hold the pigment particles together and form a continuous film on the painted surface. They determine the paint's adhesion, durability, and finish.

Extenders

Extenders are additives that improve paint properties like texture, durability, and coverage while reducing costs. Common examples include calcium carbonate and silica.

Drying Oil

Drying oils, such as linseed and tung oil, are used in oil-based paints. They undergo oxidation upon exposure to air, forming a hard, protective film.

Thinners

Thinners reduce the viscosity of paint for easier application. They help clean brushes and equipment and include substances like turpentine and mineral spirits.

Solvents for Paints

Solvents help dissolve paint components and control drying time. Different types are used depending on the paint formulation.

Oil Paint

Oil paints use organic solvents like turpentine or mineral spirits to dissolve binders and adjust consistency. These solvents evaporate, leaving the paint to dry through oxidation.

Latex Paint

Latex paints are water-based, using synthetic polymer binders such as acrylics or vinyl. They dry quickly, are environmentally friendly, and provide good durability and flexibility.

5.10. Self-assessment questions

Multiple Type questions

1. **What is the primary function of pigments in paint?**

   a) To dissolve binders

   b) To provide color and opacity

   c) To improve paint flow

d) To reduce drying time

Answer : b) To provide color and opacity

---

2. What is the role of solvents in paint?

a) To bind pigments together

b) To increase the thickness of paint

c) To dissolve binders and adjust viscosity

d) To accelerate oxidation

Answer : c) To dissolve binders and adjust viscosity

---

3. Which component in paint is responsible for adhesion and durability?

a) Pigments

b) Binders

c) Extenders

d) Solvents

Answer : b) Binders

---

4. What is the purpose of extenders in paint?

a) To dissolve pigments

b) To improve paint properties and reduce costs

c) To accelerate drying

d) To make the paint glossy

Answer : b) To improve paint properties and reduce costs

---

5. Which of the following is an example of a drying oil used in oil paints?

a) Water

b) Linseed oil

c) Acetone

d) Ethanol

Answer : b) Linseed oil

---

6. **What is the function of thinners in paint?**

a) To speed up oxidation

b) To reduce paint viscosity for easy application

c) To increase pigment concentration

d) To replace binders

Answer : b) To reduce paint viscosity for easy application

---

7. **Which solvent is commonly used in oil-based paints?**

a) Water

b) Turpentine

c) Latex

d) Silicone oil

Answer : b) Turpentine

---

8. **What is the main advantage of latex paint over oil-based paint?**

a) Longer drying time

b) More environmentally friendly and quick-drying

c) Requires toxic solvents

d) Contains high levels of lead

Answer : b) More environmentally friendly and quick-drying

---

9. What is the primary purpose of varnish?

a) To dissolve pigments

b) To provide a protective, transparent coating

c) To increase paint thickness

d) To speed up drying time

Answer : b) To provide a protective, transparent coating

---

10. Which of the following is NOT a component of varnish?

a) Resins

b) Drying oils

c) Pigments

d) Solvents

Answer : c) Pigments

Short Type Ques

1. What is the function of pigments in paint?
2. Why are solvents used in paint formulations?
3. Give one example of a binder used in paint.
4. What is the main purpose of thinners in paint?
5. Name two extenders commonly used in paints.
6. What is the function of drying oils in oil-based paints?
7. What solvent is commonly used in oil-based paints?
8. How does latex paint differ from oil-based paint in terms of drying?
9. What is varnish used for?
10. List two main components of varnish.

5.11 References

1. J. G. Bearn; The Chemistry of Paints, Pigments & Varnishes; E. Benn
2. P. K. Gangopadhyay, Application Oriented Chemistry; Book Syndicate (P) Limited.
3. A. Bahl, B. S. Bahl; 5000 Solved Problems in Organic Chemistry, S Chand Publisher.

Unit-6 ❑ Synthetic Dyes

Structure

6.0 Objectives

- Understand the synthesis process of methyl orange, Congo red, malachite green, and crystal violet.
- Explore the chemical structure and properties of these dyes.
- Learn the industrial and laboratory applications of each dye.
- Examine the environmental and health impacts associated with these dyes.
- Discuss the color-changing properties and pH sensitivity of certain dyes.
- Analyze the role of these dyes in biological and textile industries.

6.1 Introduction

Dyes are essential compounds widely used in various industries, including textiles, pharmaceuticals, food, and biological sciences. They are organic molecules capable of imparting colour to materials by selective absorption of light. Dyes can be classified based on their chemical structure, application, or mode of binding to substrates. Among the numerous synthetic dyes, methyl orange, Congo red, malachite green, and crystal violet hold significant importance due to their distinct properties and applications.

Methyl orange is a well-known pH indicator that changes colour in acidic and basic solutions. It is commonly used in titrations and analytical chemistry to determine acidity and alkalinity. The synthesis of methyl orange involves the diazotization of sulfanilic acid followed by coupling with dimethylaniline, forming an azo dye. Its ability to exhibit different colours in varying pH conditions makes it useful in laboratory experiments and industrial processes.

Congo red is another azo dye primarily used as a histological stain and in the detection of amyloidosis in medical research. Its ability to bind to amyloid fibrils and exhibit birefringence under polarized light makes it valuable in pathology. Additionally, Congo red has applications in textiles and as an acid-base indicator. However, due to its toxicity and environmental concerns, its usage has been restricted in some areas.

Malachite green, a triphenylmethane dye, is widely utilized in the aquaculture industry as an antifungal and antiparasitic agent. It is also used in microbiology for staining bacterial spores and in the textile industry for dyeing silk, wool, and paper. Despite its effectiveness, concerns over its toxicity have led to regulatory restrictions in several countries.

Crystal violet, another triphenylmethane dye, is extensively used as a biological stain, an antimicrobial agent, and in Gram staining to differentiate bacterial species. It is also applied in forensic science and textile dyeing. However, like other synthetic dyes, crystal violet raises environmental concerns due to its persistence and potential toxicity.

This study aims to explore the synthesis, properties, and applications of these four dyes, highlighting their significance and associated challenges. Understanding these dyes' chemical nature and their uses will provide insights into their role in scientific, medical, and industrial fields.

6.2 Dye

A dye is an organic compound, normally used in solution, which is capable of being fixed to a fabric. For a substance to act as a dye, certain conditions must be fulfilled.

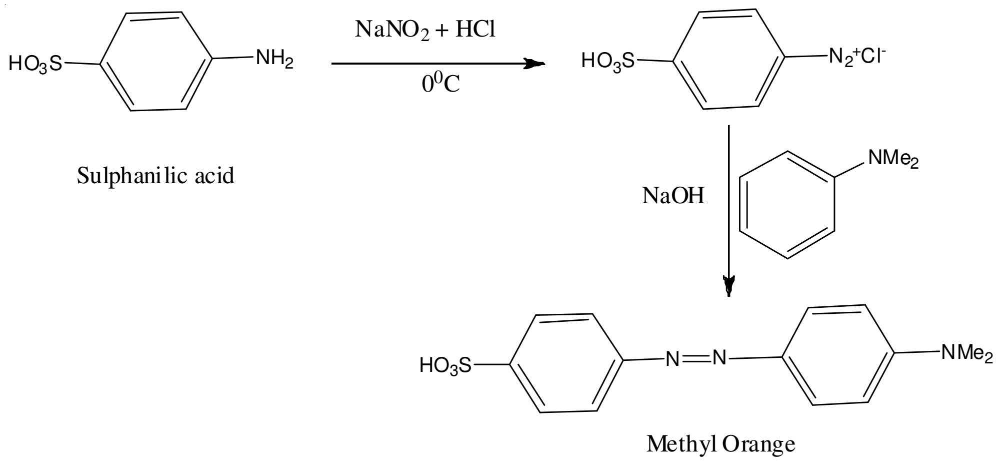
a) It must have a suitable colour.

b) It must be capable of being fixed to the fabric.

c) When fixed, it must be fast to light and it must be resistant to the action of water and to a certain extent, to dilute acids and alkalis, particularly the latter, on account of the alkaline nature of washing soda.

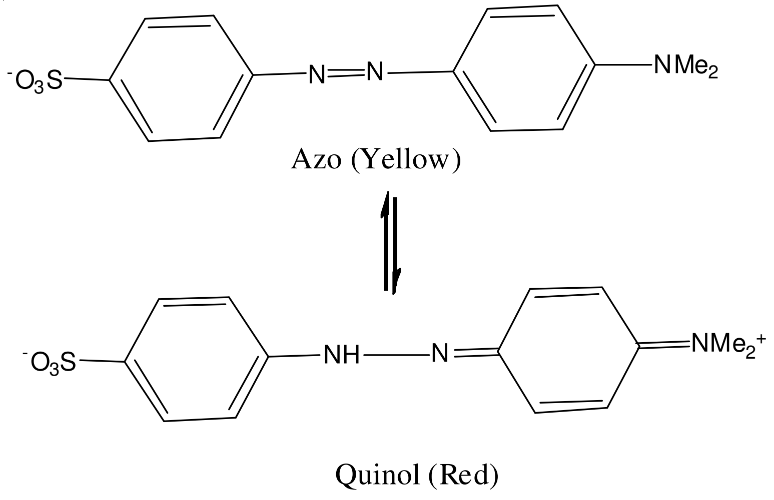
6.3. Synthesis of methyl orange

Methyl orange is synthesized by coupling diazotized sulphanilic acid with N,N-dimethyl aniline.



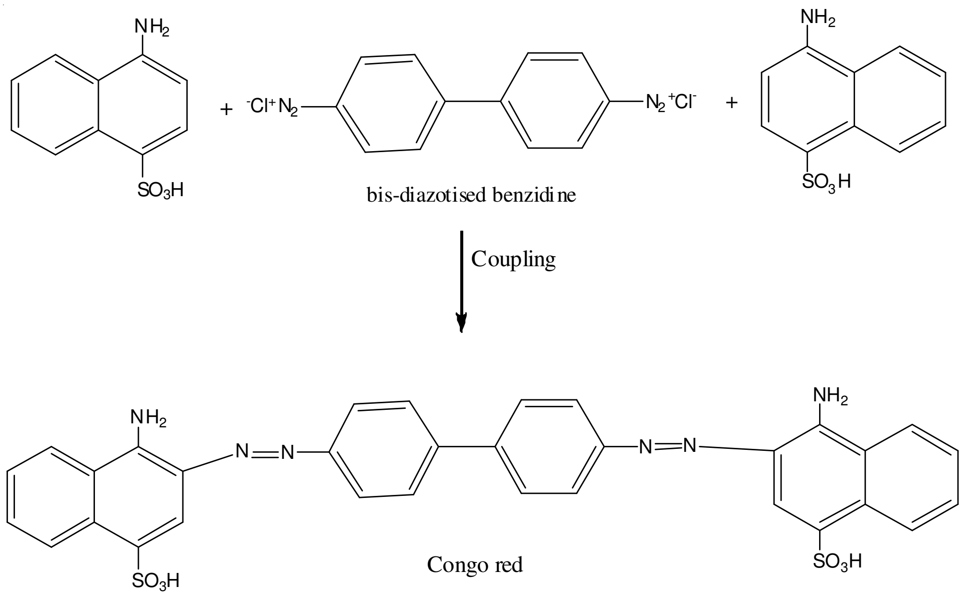
6.3.1. Uses

It is a valuable indicator for strong acid-Strong base titration because it gives yellow colour in basic solution and red colour in acid solution.



6.4. Congo red

It is synthesized by coupling, bis-diazotized benzidine (1 mol) with Naphthionic acid (1-naphthyl-amine-4-sulphonic acid) (2 mols).

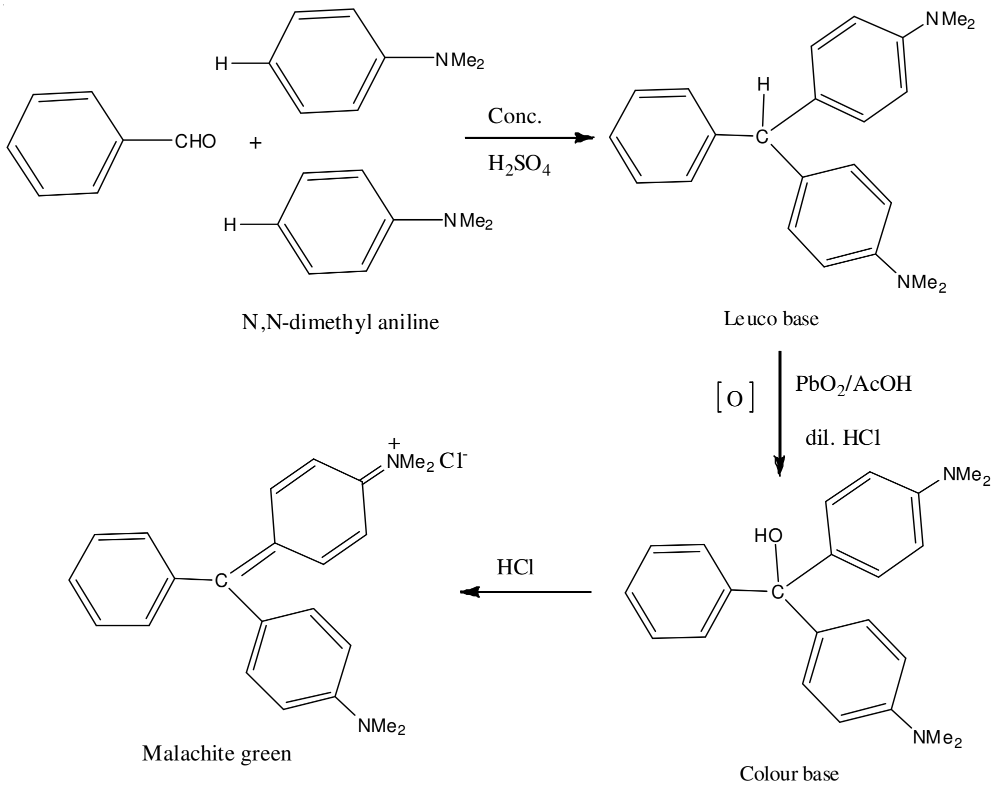


6.4.1. Uses

Congo red is a direct dye and its sodium salt dyes cotton a full red from aqueous solution. It is also used as an indicator being red in alkali and blue in acid solution.

6.5. Malachite green

It is synthesized by condensing N,N-dimethyl aniline (2 mols) with benzaldehyde (1 mol) at 1000C in presence of conc. sulphuric acid. The leuco-base produced is oxidised with PbO2 in a solution of acetic acid with a little hydrochloric acid, the resulting colour base gives Malachite green with excess hydrochloric acid.

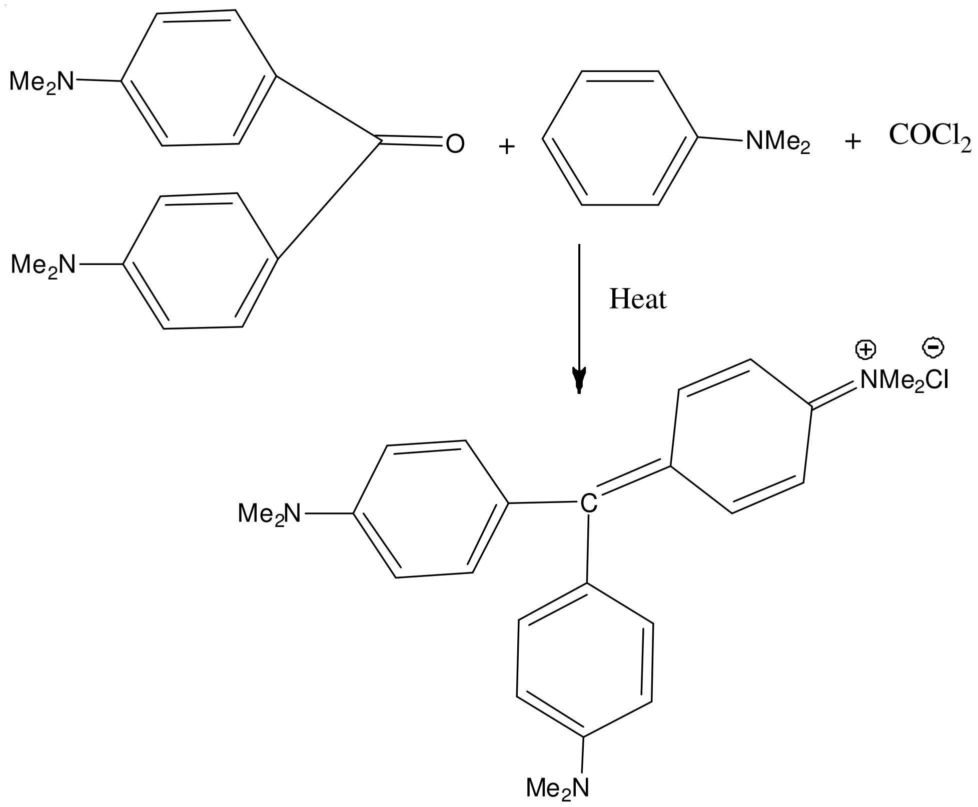


6.5.1 Uses

Malachite green is a deep green-blue colour. It dyes wool, cotton and silk directly with tannic acid to deep green. This dye is commonly used for colouring paper, ribbons. It is also an antiseptic.

6.6. Crystal violet

It is synthesized by heatingMichler's ketone, N,N-dimethyl aniline with carbonyl chloride. Colour of the crystal violet depends on PH. In weak acid solution crystal violet is purple and in strong acid solution it is green.



Crystal violet

6.6.1 Uses

Crystal violet is not only used as a textile dye, but it is also used to dye paper and as a component of navy blue, black inks for printing, ball-point pens and inkjet printers. It is also used to colourize diverse products such asleather, detergents, antifreezes and fertilizers.

6.7. Summary

Dyes are widely used in various industries, including textiles, medicine, and scientific research, due to their ability to impart color to materials. This study focuses on four important synthetic dyes-methyl orange, Congo red, malachite green, and crystal violet-covering their synthesis, properties, and applications.

Methyl orange is an azo dye commonly used as a pH indicator in acid-base titrations. Its color change from red in acidic solutions to yellow in basic solutions makes it a valuable analytical tool in chemistry. Congo red, another azo dye, is primarily used in medical research to detect amyloid fibrils in tissues. It is also applied in textile dyeing and as an acid-base indicator, though its toxicity has led to restricted usage.

Malachite green, a triphenylmethane dye, is widely used as an antimicrobial agent in aquaculture and as a biological stain in microbiology. Despite its effectiveness, concerns over its carcinogenicity and environmental impact have led to regulatory restrictions. Similarly, crystal violet, another triphenylmethane dye, is extensively used in Gram staining for bacterial classification, as well as in textile and forensic applications. However, its persistence in the environment raises toxicity concerns.

The synthesis of these dyes involves various chemical processes, including diazotization and coupling reactions for azo dyes and oxidation reactions for triphenylmethane dyes. While these dyes offer significant advantages in research, medicine, and industry, their environmental and health risks necessitate careful regulation and disposal.

This study highlights the importance of these dyes, their widespread applications, and the challenges associated with their use. Understanding their properties and potential hazards is crucial for developing safer alternatives and sustainable practices in dye usage.

6.8. Self-assessment questions

1. **What are dyes, and how are they classified?**

   Ans. Dyes are organic compounds that impart colour to materials by absorbing specific wavelengths of light. They can be classified based on their chemical structure (azo, triphenylmethane, etc.), application (textile, biological, pH indicator), or mode of binding (acidic, basic, direct, reactive).

2. **What is the chemical nature of methyl orange?**

   Ans. Methyl orange is an azo dye containing an azo (-N=N-) functional group, responsible for its color-changing properties in different pH conditions.

3. **What is the primary use of methyl orange?**

   Ans. Methyl orange is commonly used as a pH indicator in acid-base titrations due to its colour change from red in acidic solutions to yellow in basic solutions.

4. **How is methyl orange synthesized?**

   Ans. Methyl orange is synthesized through diazotization of sulfanilic acid followed by coupling with dimethylaniline, forming an azo linkage.

5. **What are the main applications of Congo red?**

   Ans. Congo red is used in medical research for detecting amyloid fibrils, as a textile dye, and as an acid-base indicator.

6. **Why has the use of Congo red been restricted?**

   Ans. Congo red is toxic and potentially carcinogenic, leading to environmental and health concerns that have restricted its usage.

7. **What is the chemical classification of malachite green?**

   Ans. Malachite green is a triphenylmethane dye, known for its vivid green color and antimicrobial properties.

8. **What are the industrial uses of malachite green?**

   Ans. It is used in aquaculture as an antifungal and antiparasitic agent, as well as in microbiology for staining bacterial spores and in textile dyeing.

9. **Why is malachite green considered hazardous?**

   Ans. It is potentially toxic and carcinogenic, with long-term environmental persistence, leading to bans in several countries.

10. **What type of dye is crystal violet?**

    Ans. Crystal violet is a triphenylmethane dye widely used in microbiology and forensic science.

11. **What is the primary application of crystal violet in microbiology?**

    Ans. It is used in Gram staining to differentiate bacterial species into Gram-positive (purple) and Gram-negative (pink).

12. **How is crystal violet synthesized?**

    Ans. Crystal violet is synthesized through the oxidation of triphenylmethane derivatives in the presence of an acid catalyst.

13. **What are the environmental concerns associated with synthetic dyes?**

    Ans. Many synthetic dyes are non-biodegradable, toxic, and carcinogenic, leading to water pollution and health hazards if improperly disposed of.

14. What alternatives exist to synthetic dyes for sustainable usage?

Ans. Natural dyes derived from plants, fungi, and microorganisms are eco-friendly alternatives to synthetic dyes.

15. Why is research on dye toxicity and biodegradability important?

Ans. Understanding dye toxicity helps in minimizing environmental damage and promoting safer alternatives for industrial and medical applications.

6.9 References

1. J. G. Bearn; The Chemistry of Paints, Pigments & Varnishes; E. Benn
2. P. K. Gangopadhyay, Application Oriented Chemistry; Book Syndicate (P) Limited.
3. A. Bahl, B. S. Bahl; 5000 Solved Problems in Organic Chemistry, S Chand Publisher.

Unit-7 ❑ Drug and Pharmaceuticals

Structure

7.1. Objectives

After going through this unit, we will be able to know about

- drugs and its function
- synthesis of different drugs and their uses
- synthesis of vitamins and their uses
- preparation of penicillin and their uses

7.2. Introduction

Pharmaceutical chemistry is the study of chemistry and pharmacology where properties, production, synthesis and purification of drugs are described briefly. It is also known as Medicinal Chemistry. When a drug is administered to a living organism, produces a biological effect. A pharmaceutical drug, also called a medication or medicine, is a chemical substance used to treat, cure, prevent, or diagnose a disease or to promote well-being. Traditionally drugs were obtained through extraction from medicinal plants, but more recently also by organic synthesis. Pharmaceutical drugs may be used for a limited duration, or on a regular basis for chronic disorders. Drugs are typically distinguished from food and substances that provide nutritional support. Consumption of drugs can be via inhalation, injection, smoking, ingestion, absorption via a patch on the skin, suppository, or dissolution under the tongue.

7.3 Drug

Drug is defined as the all chemical or natural substances capable of being used for therapeutic purpose that means to cure the diseases. So a drug is a chemical that interacts with proteins in the body to affect a physiological function. Once these chemicals are absorbed into the systemic circulation they bind with certain proteins and this changes the functioning of the cell slightly.

For example, anticancer drugs bind to proteins on the surface of cancer cells this stimulates the cells to die. In this case cell death is the physiological action of the drug.

The chemical in the drug that affects physiological functioning is the active ingredient of the drug. For most drugs, the amount of chemical needed to cause an effect is very small, often as small as 5 mg. Some inactive ingredients that have no effect on the functioning of cells, namely lactose, dyes and gluten also present with the drug. If the drug needs to be taken orally, the inactive ingredients work to bind the drug together and lubricate the drug so it is easy to swallow. So the inactive ingredients are the fillers, binders and lubricants of the drug whereas the active ingredient is the very small amount of chemical that reacts with the body to produce an effect.

7.3.1 Medicine

Medicine is defined as drugs for therapeutic purpose and it is safe for human body. All medicines are drugs but all drugs are not medicines.

7.3.2 Illegal drugs

Illegal drugs are those that are not prescribed by a doctor or brought at a drugstore. They are sometimes also called street drugs. Example: Heroin (opioid), Cocaine (A stimulant), Mescaline, Methamphetamine etc.

7.3.3. Prodrug

Prodrug is a precursor of a drug. A prodrug must undergo chemical conversion by metabolic processes before becoming an active pharmacological agent. For example, aspirin is a prodrug. It is not active in its ingested form. The ester group of aspirin is hydrolysed in the body. The active moiety appears to be the salicylate anion.

7.3.4. Function of drugs

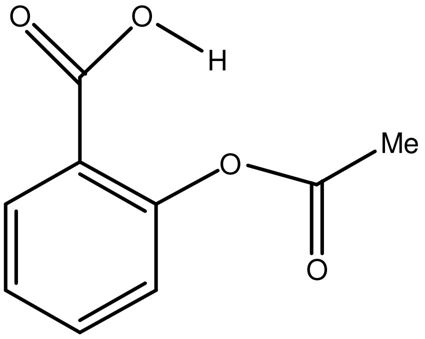
Our bodies are largely controlled by proteins. Proteins exist in many different forms in the body and have many different functions. Each protein has a specific function and is quite specific to the cell type that it acts on. For example, there are specific types of proteins called receptors. Receptors are embedded on the cell surfaces, there are different receptors for different types of cells. A liver cell will have different receptors than a cardiac cell. The receptor binds to other proteins and chemicals on the outside of the cell and this in turn creates a change in the functioning of the cell.

Proteins also act as drug targets. In order for a drug to exert an effect it needs to be bound to a protein. This can be thought of as a lock and key system; where the drugs are the key and the protein is the lock. Once the drug is bound in this lock and key mechanism it can have one of two main influences over the cell. It can produce a change in response or it can stop a normal response of the cell. Drugs that produce a change in the cell functioning are called agonists. Drugs that stop a normal function of the cell are called antagonists. Once the drug is bound to a protein it exerts a therapeutic effect on the body, this is the pharmacodynamics of a drug.

7.4. Aspirin

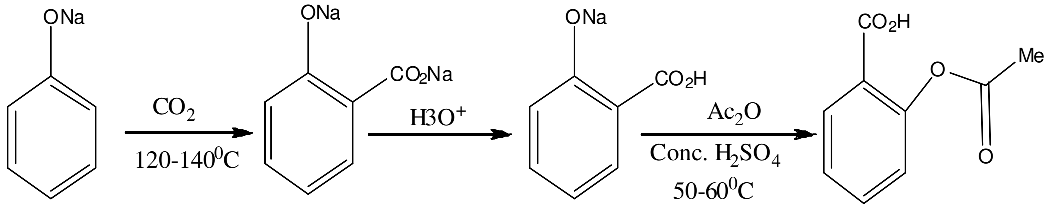
Aspirin:O-acetyl salicylic acid, IUPAC Name: 2-Acetoxybenzoic acid,

Trade name: Aspro, Anacin, Disprin, Coldarin, Codopyrine



Structure

7.4.1 Synthesis of Aspirin



Kolbe schmidt reaction **Salicyclic acid** **Aspirin**

7.4.2 Purification

The solid aspirin is collected by using vacuum filtration. The aspirin collected is then be purified by recrystallization process. In this purification method, the crude aspirin is dissolved in a small amount of warm ethanol. one to two drops of water is then be added and the solution is cooled slowly and then chilled.

7.4.3 Uses

It is used both as analgesic (pain killer0 and antipyretic (fever reducing) agent. It has the anticoagulant property and hence nowadays used in the heart-attack patients. It is also used for rheumatic fever and in a variety of conditions ranging from headache, discomfort and fever associated with cold and muscular pain.

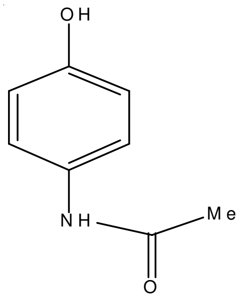
7.4.4 Mechanism of action

Aspirin in the gastrointestinal tract is hydrolysed into salicylic acid and absorb into blood stream. Salicylic acid is a metabolite of aspirin and inhibits the enzymatic activity of prostaglandin. This results in the controlled product of prostaglandin which is responsible for the sensation of pain. The result is that the impulses responsible for the pain are suppressed. Salicylic acid cannot be used as a drug directly. It is sour and causes severe intestinal bleeding, when taken orally. Aspirin does not cause such bleeding. this is the advantage of aspirin over salicylic acid as a drug. Aspirin is a prodrug.

7.5 Paracetamol

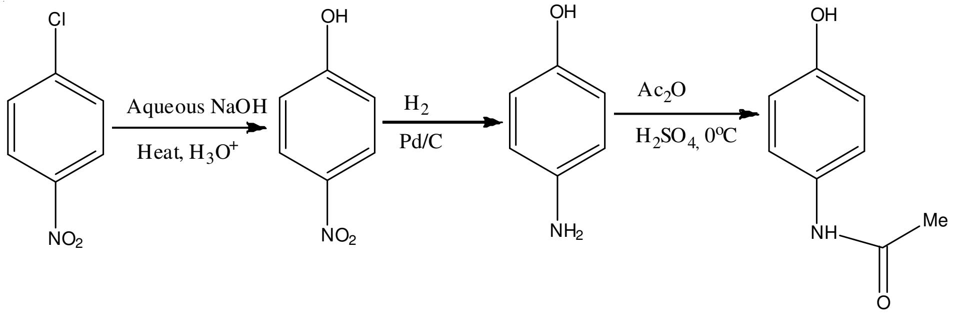
N-acetyl p-hydroxy aniline, IUPAC Name: 4-Hydroxy acetanilide

Trade name: Crocin, Calpol, Metacin



Structure

7.5.1 Synthesis of Paracetamol



7.5.2 Purification

The material can be purified by recrystallisation from water. This process relies on the fact that paracetamol is not very soluble in cold water (1.4 g/100 cm3) but very soluble in hot water (5 g/100 cm3). When the crude solid is heated in water it will dissolve and any insoluble impurities can be filtered off.

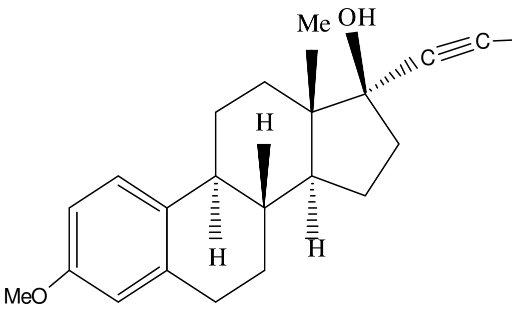
The solid paracetamol is filtered by using vacuum filtration. The paracetamol collected is then be purified by recrystallization process. In this method, the crude paracetamol is dissolved in a small amount of warm water then the solution is cooled slowly.

7.5.3 Uses

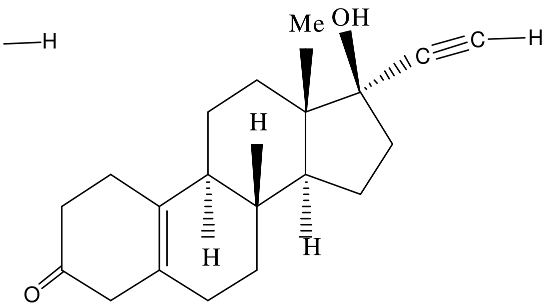
Paracetamol is used both as an analgesic and antipyretic agent. It acts on the hypothalamus to reduce temperature. Heat dissipation increases as a result of vasodilation and increased peripherial blood flow.

7.6 Envoid

Enovid is a combination of two synthetic steroidal hormones, Mestranol (Estrogen) and Norethynodrel (Progestrin).

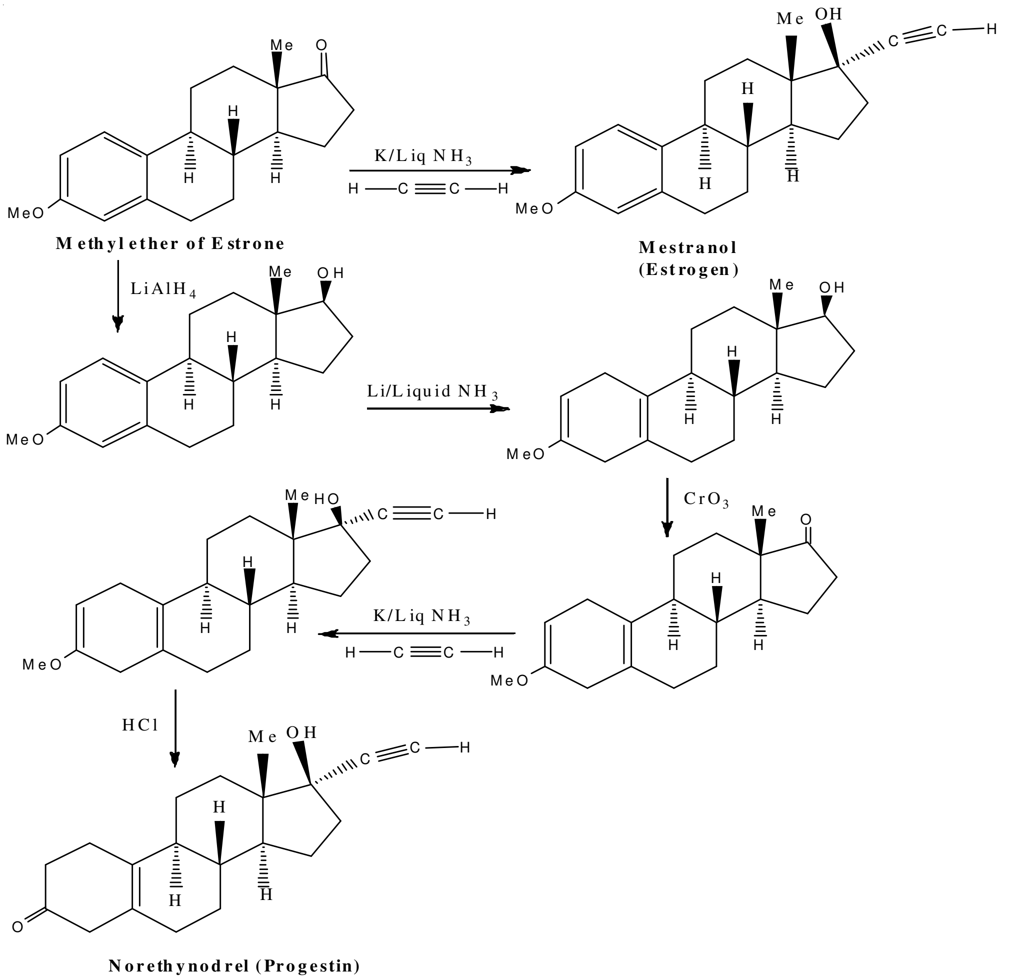


Mestranol (Estrogen)



Norethynodrel (Progestin)

7.6.1 Synthesis of Enovid (Mestranol and Norethynodrel)



7.6.2 Purification

The tools necessary for purification in multi-step reaction process is column chromatography. Enovid is purified in each step by column chromatography.

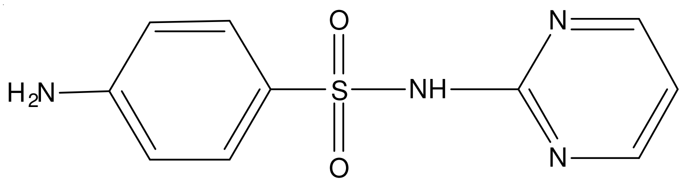
7.6.3 Uses

Estrogen and Progestron both are female sex hormones which are secreted under the influence of pituitary gland, mostly by the ovaries. Estrogen is known to induce reproductive activity during the period. Estrogen (Mestranol) and Progestin (Norethynodrel) together control the development of secondary sex characteristic in females. These two combined steroids control the growth and development of vagina, uterus and fallopian tube and also control the female sex characteristics, menstrual cycle and pregnancy. That is why they are used in the prevention of absorption and uterus bleeding.

7.7 Sulphadiazine

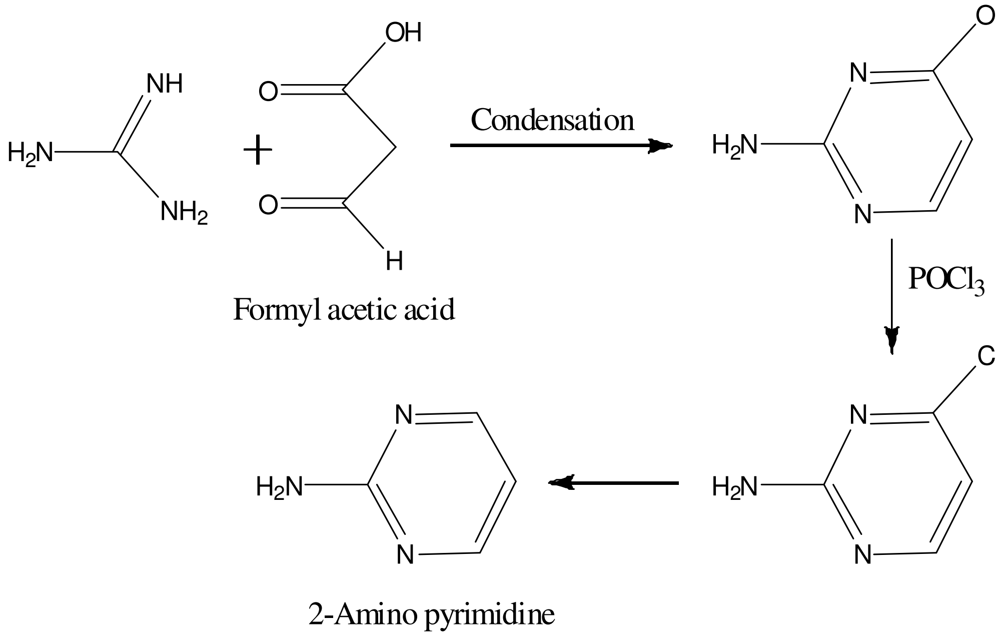
IUPAC Name: [(4-aminophenyl)sulfonyl](pyrimidin-2-yl)azanide

Trade name: codiazine, Coco-diazine, Diazyl

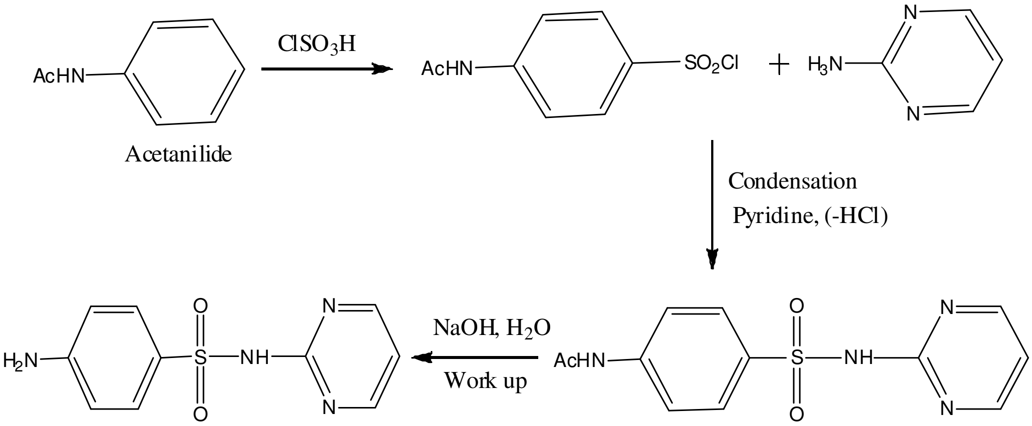


Structure

Preparation of starting material:



7.7.1 Synthesis of Sulphadiazine



7.7.2 Purification

Sulphadiazine is purified in each step by column chromatography

7.7.3 Uses

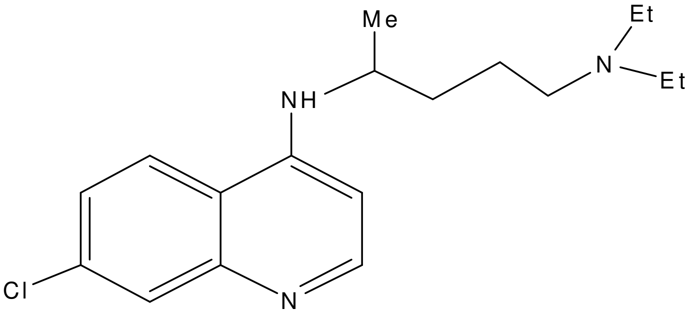
Sulphadiazine is ansulfonamide antibiotic. It is used to treat many different kinds of bacterial infections, like those of the brain, ears, and urinary tract. It is also used to prevent infections in people who are at risk. It will not work for colds, flu, or other viral infections.

7.8 Chloroquine

Chloroquine is an aminoquinoline that is quinoline which is substituted at position 4 by a [5-(diethylamino) pentan-2-yl]amino group at position 7 by chlorine.

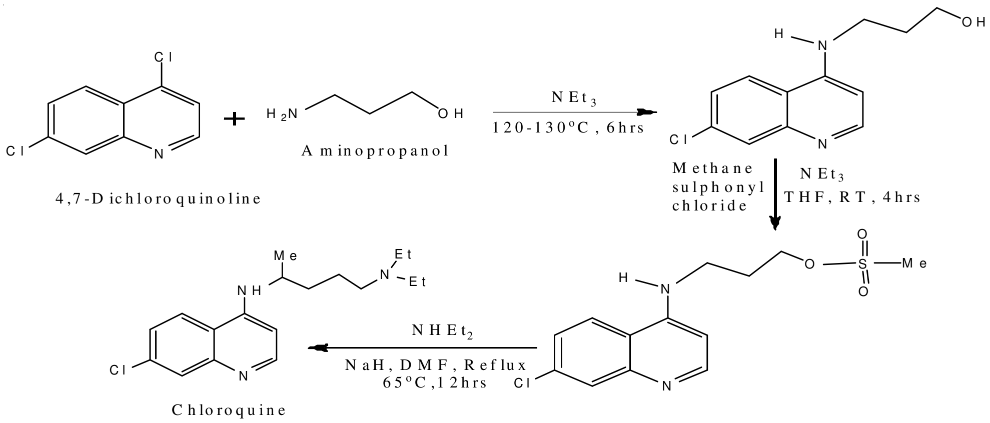
IUPAC Name: 4-N-(7-chloroquinolin-4-yl)-1-N,1-N-diethylpentane-1,4-diamine

Trade name : Anaquin, Nivaquine, Resochin



Structure

7.8.1 Synthesis of Chloroquine



7.8.2 Purification

In each step purification is carried out by column chromatography.

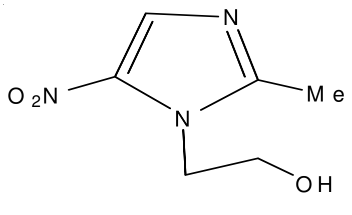
7.8.3 Uses

It is used as an anti malarial drug. Hydrochloride salt as injection and sulphate salt as tablets. It is also used for the disease like extra Intestinal amoebiases, Rheumatoid arthritis, Discoid lupus erythematousus, Infectious mononucleosis, Amoebic liver abcess, Visual abnormalities, Phorphyria, Hematologic disorders.

7.9 Metronidazole

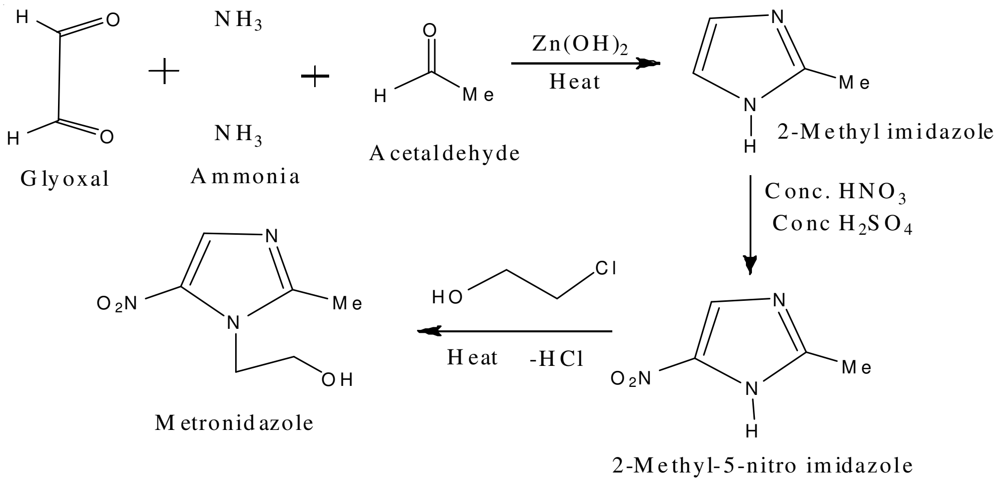
IUPAC Name: 2-(2-methyl-5-nitro-1H-imidazol-1-yl)ethan-1-ol

Trade Name: Flagyl, Unimezol, Metrogyl



Metronidazole

7.9.1 Synthesis



7.9.2 Purification

Column Chromatography is used in each step of purification process.

7.9.3 Uses

Metronidazole is an antibiotic. It is used as a drug to cure amoebic dysentery and diarrhoea in the case of bacterial infections. It's used to treat skin infections, rosacea and mouth infections (including infected gums and dental abscesses). It's used in the treatment of conditions such as bacterial vaginosis and pelvic inflammatory disease.

7.10 Vitamin B

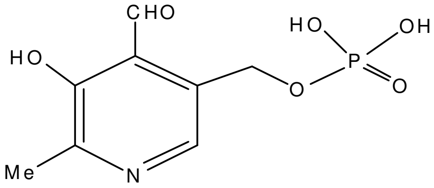
Vitamin B complex is composed of eight B vitamins: B-1 (Thiamine), B-2 (Riboflavin), B-3 (Niacin), B-5 (Pantothenic acid), B-6 (Pyridoxine), B-7 (Biotin), B-9 (Folic acid), B-12 (Cobalamin)

7.10.1 Introduction

Vitamin is an organic molecule that is an essential micronutrient which an organism needs in small quantities for the proper functioning of its metabolism. Essential nutrients cannot be synthesized in the organism, either at all or not in sufficient quantities, and therefore must be obtained through the diet.

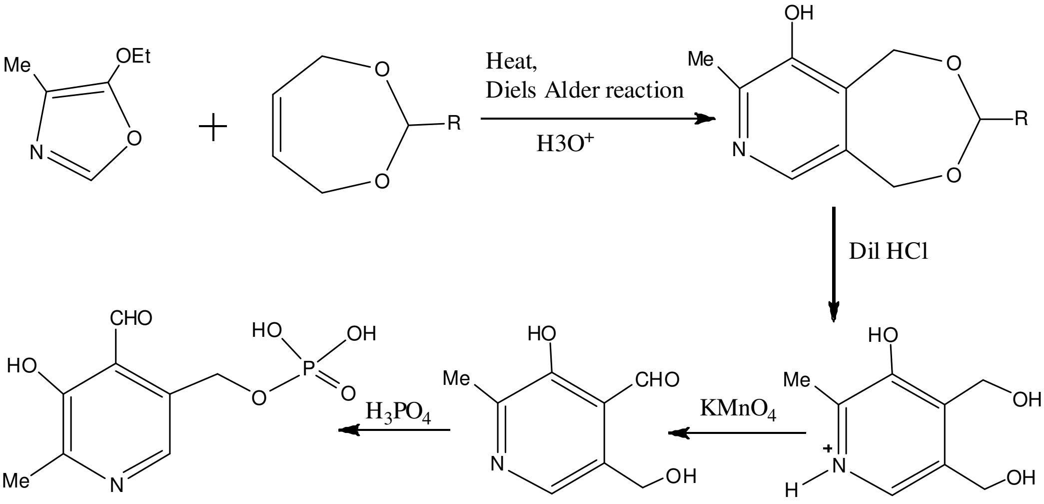
7.10.2 Source of Vitamin B6

Vitamin B-6 is one of the B vitamins, and thus an essential nutrient. The richest sources of vitamin B-6 include fish, beef liver and other organ meats, potatoes and some non-citrus fruits. Vitamin B-6 also present in fortified cereals, tuna, salmon, chickpeas, poultry and starchy vegetables. It is water and alcohol soluble vitamin and sensitive to light and alkali.



Structure Vitamin B6

7.10.3 Synthesis of Vitamin B6



7.10.4 Role of Vitamin B6

1. Assists in balance of sodium and potassium
2. Promotes the red blood cells production
3. Increases the oxygen carried by hemoglobin.
4. Essential for the nervous system.
5. Helps balance hormonal changes in woman.

6. Helps in immune system.
7. Helps to regulate blood glucose by converting stored nutrients into glucose.

7.10.5 Vitamin B6Deficiency

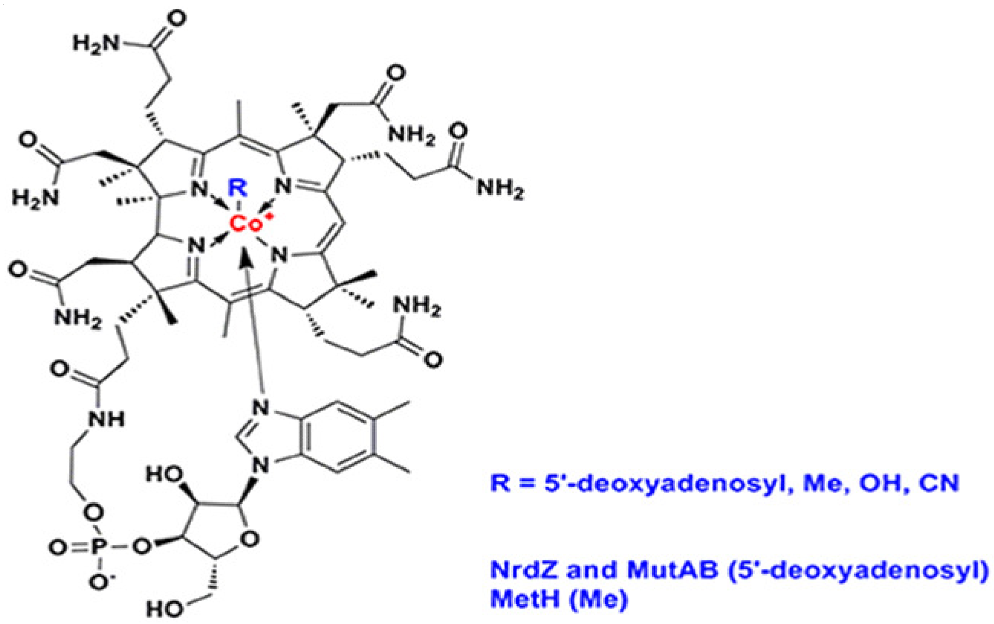
1. Depression 2. Nervousness 3. Mental confusion 4. Dizziness 5. Dermatitis 6. Sores in mouth 7. Convulsion.

7.11 Vitamin B12

Vitamin B12, also known as cobalamin, is a water-soluble vitamin involved in metabolism. It is one of eight B vitamins. It is a cofactor in DNA synthesis, in both fatty acid and amino acid metabolism.

7.11.1 Structure and Source

Vitamin B12 is naturally present in foods of animal origin, including fish, meat, poultry, eggs, and dairy products. Fortified breakfast cereals and fortified nutritional yeasts are readily available sources of vitamin B12 that have high bioavailability. In addition, clams, beef liver, salmon, trout, milk, yogurt are also the richest source of this vitamin.



R = 5'-deoxyadenosyl, Me, OH, CN

NrdZ and MutAB (5'-deoxyadenosyl)
MetH (Me)

Structure of Vitamin B12

7.11.2 Role of Vitamin B12

1. Metabolism of fatty acid and aliphatic acid.
2. It is a cofactor of synthesis of DNA
3. It is required for mylenation of nerves.
4. Methylation of homocystine to methionine.
5. It is a coenzyme and act as a prosthetic. It can bind several enzymes in the body.

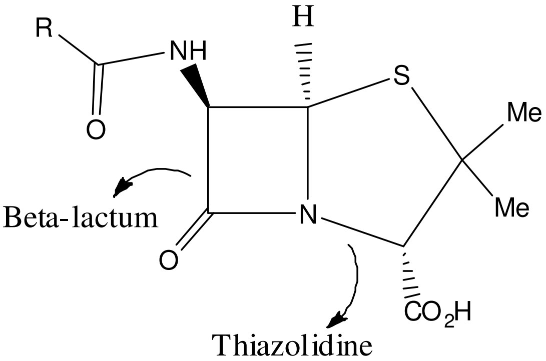
7.11.3 Vitamin B12 Deficiency

1. Chronic fatigue, 2. Muscle aches and weakness, 3.Joint pain, 4.shortness of breath, 5.Poor memory, 6.Feeling dizzy.

7.12 Penicillin

7.12.1 Introduction

Penicillin is a β-lactum antibiotic produced by microorganism (bacteria, fungus) that inhibits the growth of other organism. Antibiotics are medicines that help to stop infection caused by microorganism. Penicillin was discovered in 1928 by Dr Alexander Fleming during the Second World War and it became the first antibiotic to be used by doctors. Howard Florey and Ernst Chain helped in the production of penicillin on a large scale for the first time for human use in 1943. In 1945 Alexander Fleming, Florey and Chain were awarded the Nobel Prize in Physiology and medicine.



Structure of Penicillin

7.12.3 Preparation of Penicillin by fermentation process

Corn steep liquor, lactose, salts viz nitrate and phosphate and some ingredients are mixed together in a tank. The mixture is sterilized, cooled and pumped into fermenter. The mold penicillium Chrysogenum is added to fermenter and air (sterile) is passed through it at a temperature of 24°C. The pH varies between 5.5 and 7.5. The fermentation proceeds for more than 100 hrs without any harmful atmospheric contamination when maximum production is achieved.

7.12.4 Purification

Penicillin is extracted from the dilute fermented liquor. The mycelium is filtered by a rotatory filter. The pH is adjusted to 6.4 and penicillin is extracted with butyl alcohol as solvent. To this extract petrolium ether is added and stirred with NaHCO3 solution. The solution is then subjected to freeze, evaporation and subsequently vacuum drying to get white dry sodium salt of penicillin.

7.12.5 Uses

Penicillin is used to treat certain infections caused by bacteria such as pneumonia and other respiratory tract infections, scarlet fever, ear, skin, gum, mouth, and throat infections. It works by killing bacteria. It is also used to prevent rheumatic fever (a serious condition that may develop after a strep throat or scarlet fever infection and may cause swelling of the heart valves).

7.13 Summary

In this unit we have discussed about the basic difference about drugs and medicines. Then we have defined illegal and Prodrug. How drugs work in our body is described in details. We have discussed about the synthesis purification and uses of drugs aspirin, paracetamol, Envoid, Sulphadiazine, Chloroquine, Metronidazole. In the second part of this unit we have discussed about mainly the vitamin B complex. Source of Vitamin B-6, synthesis, role and deficiency are described in details. Then we have discussed structure, source, function and deficiency of another vitamin known as cobalamin. At the end of this unit we have discussed elaborately about the penicillin.

7.14 Self-assessment questions

1. What is the difference between drug and medicine?
2. How aspirin is synthesized?

3. Write the structure of paracetamol and its uses.
4. Write the function and structure of chloroquine.
5. What is the role of vitamin in our body?
6. Write the functions of vitamin B6 and B12 in our body?
7. What is the role of penicillin and write the purification process of the same?

7.15 References

1. D. Cairns; Essentials of Pharmaceutical Chemistry; Pharmaceutical Pres.
2. A. Tiwari, B. M. Sahoo, R. Shukla; Pharmaceutical Chemistry;Nirali Prakashan.
3. R. B. Silverman, M. W. Holladay;The Organic Chemistry of Drug Design and Drug Action; Academic press.
4. P. K. Gangopadhyay, Application Oriented Chemistry; Book Syndicate (P) Limited.

Unit-8 ❑ Domestic and Useful Materials

Structure

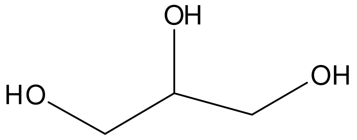
8.1 Objectives

After going through this unit, we will be able to know about

- Oils and fats
- Soap and detergents
- Cosmetics and perfumes

8.2 Introduction

Glycerides are the esters of glycerol with fatty acids, widely distributed in nature. Natural fats belong to animal fat category such as lard or fat of the pigs, tallow of the beef, mutton and sheep tallow and also butter fat from milk. Vegetable fats are all artificially made by hydrogenation of oils.



Glycerol

8.3 Oils and fats

Fats and oils have the same basic structure consists of glycerol and different straight chain organic acids that means they are esters known as glycerides. In organic monocarboxylic acid the hydrocarbon part may be saturated or unsaturated in nature. Saturated acids are palmitic, lauric, stearic acid and linoleic, linolenic acids are the example of unsaturated acids. These monocarboxylic acids are present in fat, so they are known as fatty acids. Fats contain more number of saturated acid at room temperature, so they are solid (m.p>200C). Oil contains greater proportion of unsaturated acids in glycerides, so at room temperature they are liquids.

$Me—(CH_2)_{14}COOH$ $Me—(CH_2)_{10}COOH$

Palmitic acid Lauric acid

8.3.1 Vegetable Oil

Vegetable oil is a group of fats that are derived from seeds, nuts, cereals grains and some fruits. These oils can be divided into two categories namely edible oil and inedible oil.

8.3.2 Edible oils

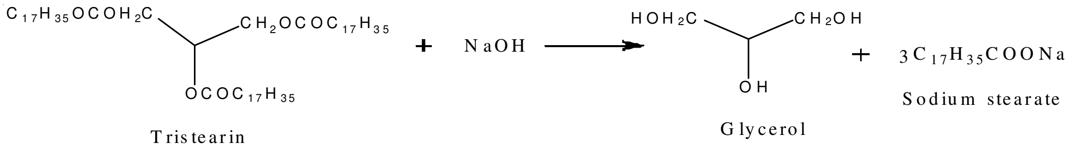
Edible oils are suitable for human consumption. These are olive oil, palm oil, soybean oil, canola oil, pumpkin seed oil, corn oil, sunflower oil, safflower oil, peanut oil, grape seed oil, sesame oil, argan oil and rice bran oil. Edible oil of superior grades are used for food purpose and lower grade edible oil are used for technical purposes such as lubricant, soap making, paints etc.

8.3.3 Inedible oils

Inedible oils are not suitable for human consumption. These are linseed, castor, tung oil etc.

8.4 Soap

Sodium or potassium salt of stearic, palmitic, oleic and other fatty acids are known as soap. Soap is made by the action of boiling caustic soda solution on a mixture of oils, tallow and greases when glycerol is also formed as a by-product. The saponification reaction is as follows:

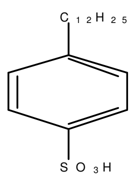


8.5 Detergent Powder

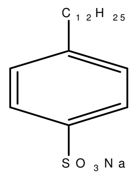
Detergent powders are materials that are used for cleaning. It consists of a surface active agent which is mixed with other constituents like fillers, boosters, builders etc. Mainly detergents are four types anionic, cationic, non-ionic and amphoteric but important among them are anionic and non-ionic detergents.

8.5.1 Anionic detergent

They consist of sulphonate or sulphate group present in the molecule. The important group among them are alkyl aryl sulphonates such as dodecyl benzene sulphonate. These molecules possess a hydrophilic group and also hydrophobic group. Examples are as follows:

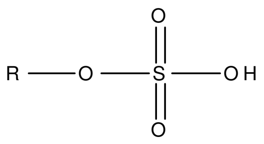


Dodecyl benzene sulphnic acid



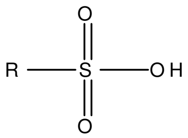
Na dodecylbenzene sulphonate

Here balance between the side chain and detergents are maintained to improve the detergent activity. In general length of the side chain on the aromatic nucleus increases, the solubility decreases. Other types of anionic detergents are long chain alcohol sulphates and alkane sulphonates having the following general formula:



$$\mathrm{R - O - \overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}} - OH}$$

Alkyl sulphate
R is alkyl group



$$\mathrm{R - \overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}} - OH}$$

Alkane sulphonate
R is alkyl group

8.5.2 Non-ionic detergents

Non-ionic detergents are formed by condensation between alcohol and ethylene oxide. Ethylene oxide may condense with fatty alcohol, amine or alkyl phenol etc. Detergent powders are generally diluted with sodium sulphate and then spray dried to give a dry free flowing powder. Very little carboxymethyl cellulose is added to reduce the foaming tendency of sodium sulphate. In many cases builders are required to enhance the activity of detergent. Phosphate, silicate and oxygen releasing materials are the examples of builders. Sodium perborates areadded to detergent powders because it forms hydrogen peroxide which acts as a bleaching agent and also NaBO2 maintain the alkali percentage of the detergent.

8.5.3. Enzyme based detergent

Enzymes are added in smallamount in the detergentto increase the activity of the detergent. It actually increases the strain removing capacity of detergent. An enzyme appears in the detergent as green or blue grains mixed with white detergent granules. Alkaline proteases enzyme is used to mainly to remove protein stain like blood stain by hydrolysis or splitting the peptide bonds of protein. Protease enzyme activity depends on the PH, temperature and other additives in the detergent powder like bleaching agent. The enzymes are mixed with fillers and binders to form small coloured granules of the same size with the main detergent powders. This is done to avoid segregation. Enzyme suppliers developed proteolytic enzymes that fulfil the requirements of the detergents. ?-Amylase enzyme is used in the detergent for the same purpose. In near future enzymes like cellulose and lipase will be used to get better result.

8.6 Liquid soaps

Potassium soaps with 15-20% fatty acid generally used in liquid soaps. The raw materials are coconut oil, olive oil and also other vegetable oils. Now synthetic detergents are replaced the liquid soaps for house hold uses. Alkyl benzene sulphonates and ether sulphates with alcohol amines are used as active materials. In the liquid soaps no cloudiness are present.

8.7 Cosmetics and perfumes

Fragrances are complex combinations of natural and man-made substances that are added to many consumer products to give them a distinctive smell. Perfume (Fragrance) is a mixture of essential oils or aroma compounds, used to give the human body "a pleasant scent".

8.8 Hair dyes

In our country it is used to change the colour of the hair like grey, golden, reddish, brownish greenish etc. Readymade hair dyes in the market are the mixture of several dyes to produce a particular colour. Concentration of the all the dyes together is only 5% because this dyes can affect the skin.

Side effect: 1. loss of hair strength 2. less ability for your hair to handle heat styling 3. reduced hair thickness 4. increased roughness of hair follicle.

8.9 Hair sprays

Hair spray is one of the most popular grooming products and is used by women and men to hold hairstyles in place. Hair spray can be described as fine mists of chemical compounds that are propelled from an aerosol. They can be applied to either wet or dry hair to help hold it in place in a particular look. Hair spray are a blend of polymers that provide structural support to hair. These frequently include copolymers of polyvinyl pyrrolidone (PVP) and polyvinyl acetate (PVAc). Vinyl acetate-crotonic acid copolymers give harder films.

Side effect: When used as directed, hairspray is minimally toxic. Unintentional eye contact, inhalation, or ingestion of small amounts of hairspray might produce minor irritating effects. Irritation should improve by rinsing the eyes or mouth or getting fresh air. Deliberate swallowing or inhaling hairspray can be very dangerous.

8.10 Creams

The creams are the emulsions of water-based and oil based phases. these are two phases' systems consisting of two incomplete miscible liquids in which the minor phase is dispersed as fine globules in the major phase which is continuous in nature. Cold cream may consist of beeswax, spermaceti, sweet almond oil, borax and water. The emulsifier is sodium cerotate formed by the reaction between borax and beeswax. Emulsion of stearic acid in a non-alkaline medium is present in the vanishing creams. It contains water, stearic acid, glycerol, potassium hydroxide and small amounts of preservatives and perfumes. Using a face cream is important because it keeps the moisture and elasticity in our skin, which can help reduce wrinkles, age spots and other fine lines. Face creams also act as a protective barrier for our skin.

Side effect:Excessive use is dangerous. Once the prescribed dosage is complete, many patients continue to get these creams from local chemists without prescription. This continued usage can lead to side effects such as skin redness, thinning of the skin, increased facial hair growth and even permanent damage.

8.11 Lipstick

In winter and in dry season the lip becomes dry and develops small cracks. In some cases small pieces of skins come out of the lip. So lip requires some protection by the application of greasy material. Necessary protection is given by lipstick as it contains oily and waxy chemicals. The lipstick has a decorative aspect to make it matching with the costume as well as attractive.

Side effect: Today's lipsticks may contain potentially harmful levels of chromium, lead, aluminium, cadmium as well as several other metals toxic to the human body. Heavy metals cause renal failure. Lead is harmful to the nervous system. Preservatives used in lipstick cause cancer. Lipstick increases toxin ingestion.

8.12 Face powder

Minor defects on skin can be masked by face powdered and oily patches can be suppressed so that the face appears to be smooth, beautiful and attractive. The face powder should possess desired covering powder, absorbing powder and brightness. titanium oxide and zinc oxide are frequently used because they have soothing effect on skin. ZnO is used in the treatment of skin irritation and it prevents sunburn to a greater extent. Kaolin and MnO are used as a covering agent.

Side effect: Inhaling of face powder can cause serious respiratory problems. If any child accidentally inhaled or swallowed face powder then poisoning arises. Symptoms of face powder poisoning include coughing, breathing trouble, eye irritation and a burning sensation in the throat.

8.13 Talcum powder

Baby powder is known as talcum powder. For dry and cooling effect this powder is used. It consists of starch and stearates of Zn and Mn. Starch possesses excellent moisture absorption properties and stearates give adhesion of the powder to the skin. Petroleum jelly and paraffin oil are used to improve adhesion properties of this powder.

Side effect: Talcum powder can cause significant harm if it's swallowed or inhaled. Talcum powder inhalation can cause wheezing, coughing, chest pain and difficulty breathing.

8.14 Tooth past

Ingredients of the tooth paste are cleansing agents, flavouring agent, fluorides, binders, sweeteners, fluorides and dyes. Toothpaste is used for brushing teeth with a toothbrush and is rinsed off later. Toothpaste is important to oral health because it fights off gum disease and contains fluoride, strengthening the tooth enamel and preventing tooth decay. The foam is produced by sodium laurial sulphate and active ingredients are added to control or suppress bacterial growth and may have beneficial effect on the tissues inside the mouth.

Side effect: Large amount of regular toothpaste may cause stomach pain and possible intestinal blockage. Another symptom convulsions and diarrhea occur when swallowing a large amount of toothpaste containing fluoride.

8.15 Nail polish

Nail polish is a lacquer that can be applied to the human fingernail or toenails to decorate and protect the nail plates. Basic components include film forming agents, resins and plasticizers, solvents and colouring agents. Nitrocellulose forms a thin film on the nail after evaporation of the solvent. Polymethyl acrylates and toluene sulphonamide and formaldehyde resins give lustre and also camphor, dibutyl phthalate are used as plasticizer.

Side effect: Constant exposure to toxic nail paints and other nail care products can produce minor health complaints like skin irritation, allergic reactions, nausea. Sometime produces serious troubles like respiratory problems, cancer and reproductive conditions.

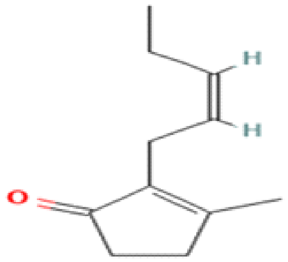
8.16 Shampoos

The main purpose of shampoo is to remove dirt and oil from the surface of the hair fibres and the scalp. Shampoo is generally made by combining a surfactant, most often sodium lauryl sulfate with a co-surfactant, most often cocamidopropyl betaine in water. The sulphate ingredient acts as a surfactant that makes it easier to trap oil and grease.

Side effect:It can make our hair dry and frizzy and also fades the texture and shine of hair.

8.17 Jasmone

Jasmone is an organic compound, which is a volatile portion of the oil from jasmine flowers. It is a colourless to pale yellow liquid. Structure of jasmone is



8.18 Amyl acetate

Amyl acetate is used as a flavouring agent in several countries. It is often blended with other esters to produce flavours that are more fruity and rounded. The compound is also used to flavour products such as food, solvent for lacquer and chewing gum.

Side effect:Exposure to high concentrations of amyl acetate can cause headache, drowsiness, weakness, dizziness and even unconsciousness. Prolonged or repeated skin contact can cause irritation, dryness and cracking. Amyl acetate may damage the liver.

8.19 Summary

In this unit we have discussed about the different glycerides and their formation. Then we have defined edible and inedible oils with examples. In details we have discussed about the ingredients of soap, detergent powder, and enzyme based detergents. In the second part of this unit we have discussed about mainly about the application and side effect of cosmetics and perfumes.

8.20 Self-assessmentquestions

1. What is soap and write the saponification reaction?
2. What is margarine and write its constituents?
3. Write the difference between fat and oils?
4. What are creams? How many types of creams are available?
5. What are the functions of hair spray?
6. Write the main constituents of shampoo?
7. What is the molecular formula of jasmone?

8.21 References

1. G. Jayshree; Fundamental Concepts Of Applied Chemistry; S Chand Publisher
2. P. K. Gangopadhyay, Application Oriented Chemistry; Book Syndicate (P) Limited.

Unit-9 ❑ Pesticides, Insecticides

Structure

9.1 Objectives

After going through this unit, we will be able to know about-

- different types of pesticides natural and synthetic
- synthesis of different pesticides, uses and their toxic effects

9.2 Introduction

A pest is adestructive plant or animal which directly or indirectly affects to human or human concerns including crops, livestock and forestry. Pesticides are substances or mixtures of substances that are mainly used in agriculture or in public health protection programs in order to protect plants from pests, weeds or diseases and humans from vector-borne diseases such as malaria, dengue fever.

9.3 TypesPesticides

On the basis of source pesticides are two types a) Natural pesticides b) Synthetic Pesticides

a) **Natural pesticides :** Pesticides that is made of natural ingredients such as minerals mined from the earth, bacterial extracts or plant extracts. Nicotine, pyrethrum, neemoil, boric acid etc.

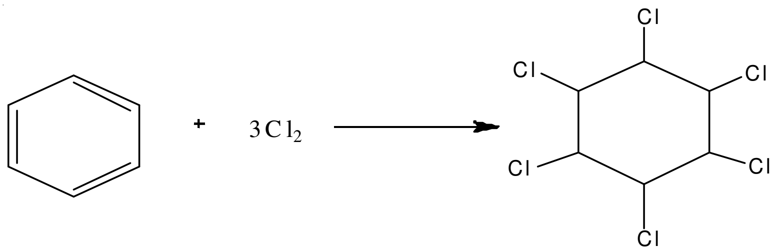
b) **Synthetic Pesticides :** These pesticides are synthesized in laboratory with the help of chemicals. They are also called man-made pesticides because of their low cost and effectiveness these synthetic pesticides are used widely.

9.4 Gammaxene

It is sometimes called benzene hexachloride. It is one the most widely studied pesticides with respect to its high effectiveness, low cost preparation, environmental fate and effects. As early as 1825, Faraday prepared the addition product of benzene and three molecules of chlorine formed in sunlight. The commercial name is gammaxene. It was introduced in world war II consists of a mixture of different isomers of hexachloro cyclohexane. In 1936 bender discovered the insecticidal properties of gammaxene.

9.4.1 Synthesis

Chlorine combines with benzene in presence of sunlight and in the absence of oxygen to form hexachloro cyclohexane.



9.4.2 Uses

Gammaxene is used as an insectide on crops, in forestry and for seed treatment.

9.4.3 Toxic effect

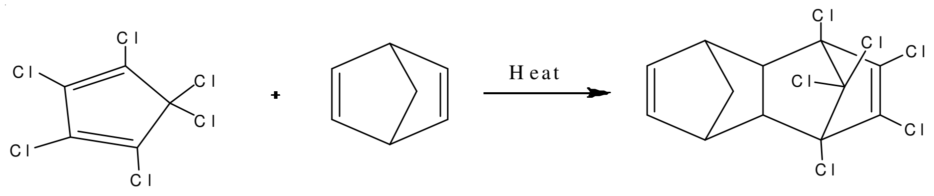
Toxic effects include seizures, ataxia, confusion and other central nervous system dysfunction.

9.5 Aldrin

Aldrin is chlorinated hydrocarbon and has long persistence.

9.5.1 Synthesis

It is synthesized by combining hexachlorocyclopentadiene with bicyclo [2.2.1] heptadiene (norbornadiene) in a Diels-Alder reaction to give the adduct.



Aldrin

9.5.2 Uses

Aldrin is used for killing harmful insects like termite, cockroach, grasshopper, fire ant and other insects.

9.5.3 Toxic effect

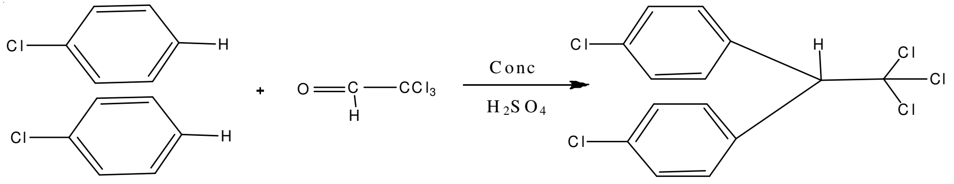
Aldrin is toxic to humans depends on concentration aldrin may cause headache, dizziness, nausea, general malaise and vomiting. It may damage other organs like liver, kidney etc.

9.6 DDT

It was first synthesized by German chemist Othmar Zeidler in 1874 and its insecticidal properties were discovered in 1939 by Paul Hermann Mullen Swiss Chemist.

9.6.1 Synthesis

Two moles of chlorobenzene is reacted with chloral in presence of conc. H2SO4 to give DDT.



9.6.2 Uses

DDT was used to control malaria, typhus, body lice, and bubonic plague.

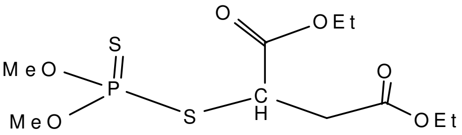
9.6.3 Toxic effects

High dose of DDT can cause vomiting, tremors or shakiness and seizures in human.

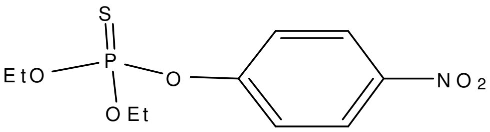
9.7 Organophosphates

Organophosphate compounds are a group of chemicals used in both domestic and industrial settings. This compound composed of carbon and phosphoric acid derivatives. Example: Malathion, Parathion etc.

9.7.1 Structure



Malathion



Parathion

9.7.2 Uses

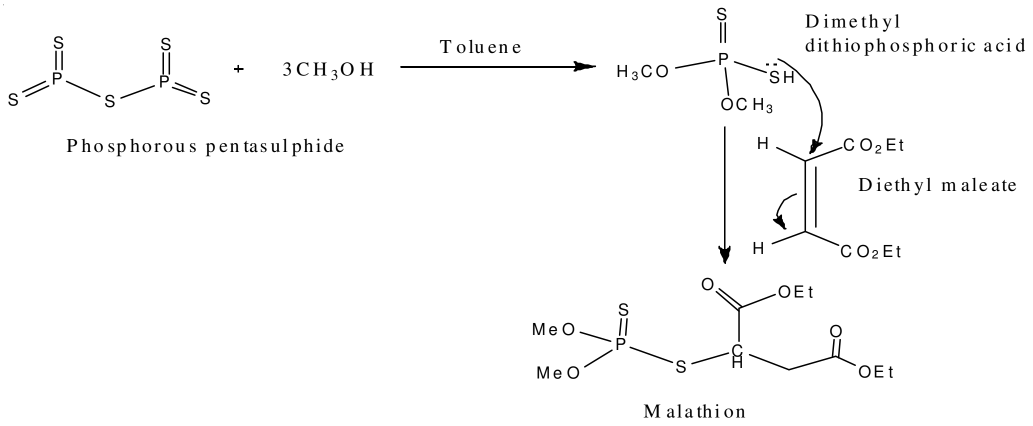
These are used as an insectide.

9.8 Malathion

It is an organo phosphate. It was introduced in 1950.

9.8.1 Synthesis

Phosphorus pentasulphide id treated with MeOH in a toluene solvent to produce dimethyl dithiophosphoric acid intermediate. This intermediate is isolated and reacted with diethyl maleate to produce malathion.



9.8.2 Uses

It is a non-systematic broad spectrum insectide, widely used in agriculture for nearly all fruits; all vegetables, field crops and house hold insects. It was also efficient against mosquito, flies and external parasites on lime stock. It is also used to treat lice in human and to kill locust in the initial stage.

9.8.3 Toxic effects

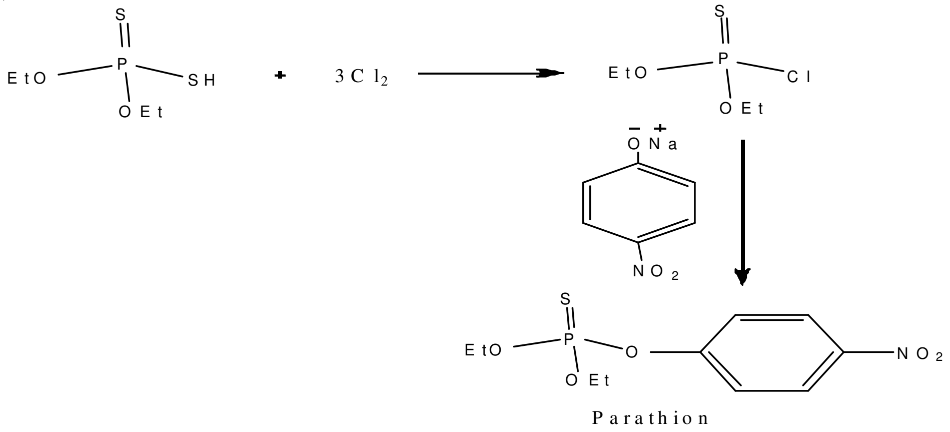
Symptoms occur when malathion is inhaled, swallowed or absorbed through the skin. Malathion can cause nausea, vomiting, stomach cramps and diarrhea, as well as confusion, blurred vision, sweating, muscle twitching, irregular heartbeat, convulsions and death of human.

9.9 Parathion

It was synthesized Scharader in 1944. Kukenthal and Unterstenhofer in 1948 shows insectide properties.

9.9.1 Synthesis

It is synthesized from diethyl dithiophosphoric acid by the chlorination which will give intermediate diethyl thiophosphoryl chloride. This intermediate is further reacted with sodium-4-nitro benzoate to give parathion.



9.9.2 Uses

It is a powerful insectide kills all harmful insects. Parathion shows its insectide action on about 400 insect pests. Parathion also kills the eggs of hibernating orchard pests hence it has also an ovicidal action.

9.9.3 Toxic effects

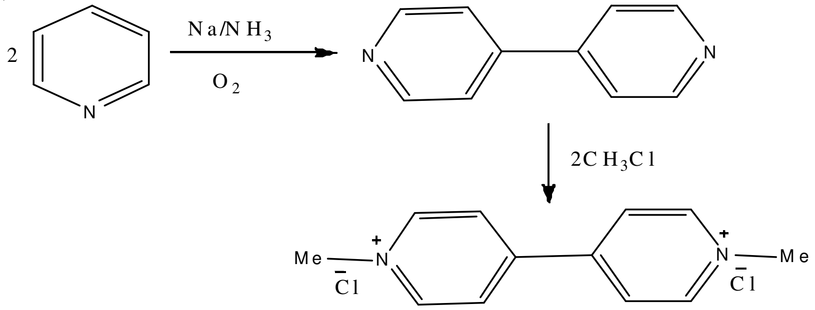
Parathion can cause nausea, vomiting, stomach cramps, and diarrhea, as well as confusion, blurred vision, sweating, muscle twitching, irregular heartbeat, convulsions, and death. Symptoms occur when parathion is inhaled, swallowed or absorbed through the skin.

9.10 Paraquat

It is a quaternary ammonium compound and it is available as dichloride.

9.10.1 Synthesis

4,4-bipyridil is obtained when pyridine is reacted with metallic sodium and liquid ammonia. Then in the second step it is reacted with methyl chloride to produce salt of bipyridile.



9.10.2 Uses

It is used as an aqueous solution so it shows quick action on harmful plant. so it acts as a herbicide. It is a very useful weed killer and is very effective on grass species. It is also effective in killing submerged aquatic weeds.

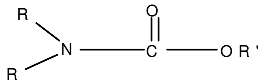
9.10.3 Toxic effects

Paraquat is not a skin irritant and but long term poisoning causes lung damage and kidney failure. Other long-term poisoning may also occur including heart failure and respiratory failure and liver failure.

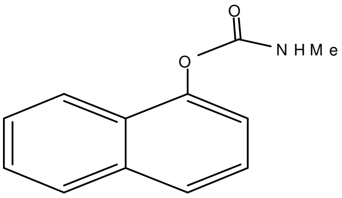
9.11 Carbamates

Carbamates are the group of insectides which are aryl or alkyl ester derivatives of carbamic acid. Carbamates pestisides were discovered in 1980 and first compound used is carbaryl. Carbamates are a class of pesticide structurally and mechanistically similar to organophosphates insectides. Example: Carbaryl, Carbofuran etc.

9.11.1 Structure



Substituted Carbamic ester



1-Naphthyl methyl carbamate (Carbaryl)

9.11.2 Uses

Carbamates are used as sprays or baits to kill insects by affecting their brains and nervous systems. They are used on crops and in the home to kill cockroaches, ants, fleas, crickets, aphids, scale, whitefly, lace bugs and mealy bugs. Some carbamates also control mosquitoes.

9.11.3 Toxic effects

The adverse effects of several carbamate pesticides include renal, hepatic, neurological, reproductive, immune, and metabolic functions in both humans and animals.

9.12 Summary

Pesticides are chemicals used to control pests affecting agriculture and public health. Different classes of pesticides have distinct chemical structures, uses, and toxic effects.

Gammaxene (Lindane) is synthesized from benzene and chlorine. It is widely used as an insecticide in agriculture and for treating lice and scabies. However, it is neurotoxic, leading to seizures and liver damage.

Aldrin is synthesized from cyclopentadiene and hexachlorocyclopentadiene. It was commonly used to control soil pests but is highly toxic, causing severe neurological and hepatic effects, leading to its ban in many countries.

DDT (Dichlorodiphenyltrichloroethane) is synthesized from chloral and chlorobenzene. It was historically used for mosquito control to combat malaria. However, its persistence in the environment and bioaccumulation in the food chain led to its prohibition due to ecological and health concerns.

Organophosphates contain phosphorus-based structures and function as insecticides by inhibiting acetylcholinesterase. They are highly effective but can cause acute neurotoxicity, leading to paralysis and respiratory failure.

Malathion, an organophosphate, is synthesized from phosphorus compounds and used in agriculture and public health programs. Though less toxic than other organophosphates, it can still cause nervous system disorders in high doses.

Parathion is another potent organophosphate synthesized from diethyl phosphorothioate. It is highly toxic to humans, causing severe cholinergic poisoning, necessitating strict regulation.

Paraquat is a non-selective herbicide synthesized from bipyridyl compounds. It is widely used to control weeds but is highly toxic, leading to fatal lung fibrosis if ingested.

Carbamates have a nitrogen-based structure and act similarly to organophosphates by inhibiting acetylcholinesterase. They are used as insecticides but pose moderate toxicity risks to humans and wildlife.

While pesticides play a crucial role in pest management, their toxic effects demand careful handling and regulation.

In this unit we have discussed about the different types of pesticides natural and synthetic. Then we have discussed the synthesis, use and toxic effects of pesticides gammaxene, aldrin, parathion, malathion, DDT, paraquat. Structure, use and toxic effects of organophosphorus and carbamates are described in details.

9.13 Self-assessmentquestions

1. What is the common name of Gammaxene?
2. Which pesticide was historically used to control malaria but is now banned in many countries?
3. Name one organophosphate pesticide.
4. What enzyme do organophosphates inhibit?
5. Which pesticide is known to cause lung fibrosis upon ingestion?
6. What is the primary use of Aldrin?
7. Which pesticide has a nitrogen-based structure and inhibits acetylcholinesterase?
8. Name one toxic effect of Parathion.

9. What makes DDT harmful to the environment?
10. Which pesticide is commonly used for treating lice and scabies?
11. What is the mode of action of carbamate pesticides?
12. Name one pesticide that has been banned due to its toxicity and environmental impact.
13. What type of pesticide is Paraquat?
14. Which pesticide is synthesized from bipyridyl compounds?
15. What is the main advantage of using Malathion compared to other organophosphates?
16. What is the difference between pesticides and insectide?

9.14 References

1. N. K. Roy; Chemistry of Pesticides; CBS Publishers & Distributors.
2. B. Srilakshmi; Food Science; New Age International Publishers.
3. P. K. Gangopadhyay, Application Oriented Chemistry; Book Syndicate (P) Limited.

Unit-10 ❑ Food additives

Structure

10.0 Objectives

After going through this unit, we will be able to know about

- food Additives, food flavours, food colour and food preservatives
- artificial sweeteners, MSG and its side effects
- edible emulsifiers and edible foaming agents

10.1 Introduction

Food additives are substances added to food to enhance its flavour, colour, texture, and shelf life. They play a crucial role in modern food processing, ensuring food remains appealing and safe for consumption. Food Flavors enhance taste and aroma, making food more palatable. Food colours improve visual appeal, making products more attractive.

Food preservatives prevent spoilage by inhibiting microbial growth, extending shelf life. Artificial sweeteners provide sweetness without added calories, making them popular in diet products. Monosodium glutamate (MSG) is a common flavour enhancer, though excessive consumption may have side effects like headaches and nausea. Edible emulsifiers stabilize mixtures of oil and water, ensuring uniform texture in products like mayonnaise. Edible foaming agents help maintain air bubbles in foods like whipped cream and baked goods. While food additives offer many benefits, their safety and health effects remain subjects of research and regulation.

10.2 Food Additives

Food additives may be defined as chemical substances which are deliberately added to foods, in known and regulated quantities, for the purpose of assisting in the processing of foods, preservation of foods or in improving the flavour and texture or appearance of foods. Food additives may be natural and also synthetic. Synthetic additives are synthetic substances that are manufactured in the laboratory. Natural additives are made from chemicals but these are found naturally. Synthetic additives are widespread in industrialized country and easy of availability but they have been linked in research studies to cancer, digestive issues and behavioural effects.

10.3 Food Flavour

Natural and synthetic flavouring materials are used as food flavour. Natural flavouring substances are spices, essential oils, herbs and plant extracts. Chillies, black pepper, cumin seed, cloves, cinnamon, mustard seed are used in our country as flavouring agent for the preparation of food. To increase the flavour sometimes spices are fried in oil.

Some synthetic flavouring agents are benzaldehyde (cherry flavour), vanillin (vanilla), amyl acetate (ripen banana), ethyl butyrate (pineapple), methyl anthranilate (grape).

10.4 Food colour

Food colours are any substancesthat are added to food or drink to change its colour for acceptability. During food processing, heating and cooking colour must be stable.

These are derived from artificial and natural sources in varied intensities. Pure synthetic dye stuffs are used in the industries. Soft drink, candies and gelatine are coloured with certified coal tar dyes. Colour used in the preparation of cakes and biscuits should be stable at high temperature and in carbon dioxide also. Brown colour obtained from burnt sugar is used as a caramel. Turmeric and saffron are used as natural colouring materials to produce yellow and orange colour of the food. In butter and cheese annatto (yellow) colour is used. In some cases very small coal tar dye powder is used to generate desired colour. For green colour fast green, blue colour indigotine, yellow colour sunset yellow and tartrazine, red colour erythrosine etc are used generally to attract the food.

10.5 Food preservatives

The chemical substances which are used to check or stop the growth of harmful microorganisms in food and prevent the spoiling of food are called food preservatives. Natural preservatives include rosemary and oregano extract, hops, salt, sugar, vinegar, alcohol, diatomaceous earth and castor oil. Artificial preservatives are Artificial benzoates, propionates and sorbates or inorganic salts such as sulphites and nitrites/nitrates.

Preservatives are required because i) inhibit the growth of microorganisms like bacteria and fungi ii) increase shelf life iii) preserve the appearance of food iv) preserve the food characteristics like odour, taste and food is preserved for a long time.

Partial preservation can be done by using drying, refrigeration, salting, pickling and smoking.

Drying is the oldest method of food preservation. In this process moisture is removed so that microorganism can't live. Dry salting is used for the preservation of fish, meat, raw mango pickles. Smoking is a method of drying that also imparts flavour to the food (usually meat and fish items) and smoke helps keep bacteria-carrying-insects away during the drying process. Pickling is the process of preserving edible products in an acid solution, usually vinegar or in salt solution (brine). In the latter case, the acid that does the preservative action mainly lactic acid is produced by fermentation. The process of pickling is also known as brining and the resulting foods as pickles.

Chemicals used as preservatives: a) Sorbic and propionic acid and their salts are permitted in cottage cheese, yogurt to prevent growth of moulds on their surface and increase their shell life. b) Added sugar acts as preservatives of sweetened condensed milk and making moisture unavailable to organisms. c) Sodium chloride in salted butter decrease the number of those who are not salt tolerant. d) Addition of hydrogen peroxide combined with a mild heat treatment has been used for pasteurization of milk for destroy certain kinds of bacteria. e) Sodium benzoate inhibits the growth of potentially harmful bacteria, mould and other microbes in food, thus deterring spoilage. Therefore, it's commonly used in foods, such as soda, bottled lemon juice, pickles, jelly, salad dressing, soy sauce and other condiments. f) Edible oils extracted from plants are commonly known as vegetable oils.These have pronounced antimicrobial and food preservative properties.

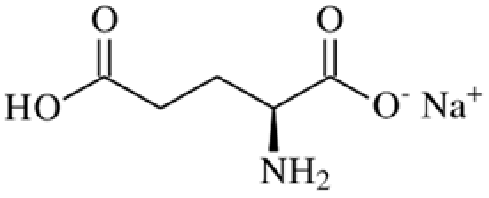
Disadvantage of the use of preservative:i) some nutrients are lost during processing like vitamin C ii) may contain more fat, sugar, sodium and calories. iii) Some modern synthetic preservatives have been shown to cause respiratory or other health problems.

10.6 Artificial sweeteners

Artificial sweeteners are synthetic sugar substitutes. Examples are given i) Saccharin used in many diet foods and drinks, ii) Aspartame mostly used to sweeten diet soft drinks, iii) Sucralose used in many diet foods and drinks. The side effects of artificial sweeteners include: headache, depression, increased risk of cancer, and weight gain due to increased appetite. In our country saccharine is used to a limited extent in food products.

10.7 MSG

Monosodium glutamate (MSG) is a flavour enhancer. It is commonly added to Chinese food, canned vegetables, soups and processed meats. MSG is made nowadays by fermenting starch, sugar beets, sugar cane, or molasses.



Structure of MSG

10.7.1 Side effects

It has several side effect such as MSG can excite brain cells to death, creates brain lesions, causes leptin insensitivity, contributes to obesity, linked to sudden cardiac death, implicated in strokes, promotes cancer cells growth.

10.8 Edible emulsifiers

Emulsifiers are used when food products contain oil in water or water in oil emulsions because these emulsifiers stabilised the food products. Lecithin is an emulsifier generally obtained from vegetable sources. It is also present in milk and egg. Mono and di-glycerides, disodium phosphate, polysorbates, carrageenan, guar gum are also used as an emulsifiers. Emulsifiers are used in pudding, salad dressing, ice-cream etc.

10.9 Edible foaming agents

A foaming agent is a surfactant, which when present in small amounts, facilitates the formation of foam or enhances its stability by inhibiting the coalescence of bubbles. Natural Food & Beverage foaming agent are food additives which are used maintain the uniform dispersion of gases in aerated foods. Foam is produced with the help of trapping the gas bubbles and it is offered either in form of solid or liquid. Major components of foam are protein, water and fats. Natural foaming agents are mostly used in carbonated soft drinks, syrups, frozen carbonated beverages, beer and juices.

10.10 Summary

In this unit we have discussed about the different types of pesticides natural and synthetic. Then we have discussed the synthesis, use and toxic effects of pesticides gammaxene, aldrin, parathion, malathion, DDT, paraquat. Structure, use and toxic effects of organophosphorus and carbamates are described in details. In the second part we have discussed the requirements of food additives, food flavour, food colours and food preservative and also their side effects in human body. Then we have discussed about artificial sweeteners and MSG. Emulsifiers and edible foaming agent are described at the end of this chapter.

10.11 Self-assessmentquestions

1. What are food additives?
2. Why are food Flavors added to food products?
3. How do food colours enhance food appeal?
4. What is the main purpose of food preservatives?
5. Name one commonly used artificial sweetener.
6. What does MSG stand for?
7. How does MSG enhance food taste?
8. Mention one possible side effect of MSG consumption.
9. What is the function of edible emulsifiers in food?

10. Name one food product that commonly contains edible emulsifiers.
11. What role do edible foaming agents play in food preparation?
12. Give an example of a food that contains edible foaming agents.
13. Why are artificial sweeteners preferred in diet products?
14. How do food preservatives help in food safety?
15. Name one commonly used food color additive.

10.12 References

1. N. K. Roy; Chemistry of Pesticides; CBS Publishers & Distributors.
2. B. Srilakshmi; Food Science; New Age International Publishers.
3. P. K. Gangopadhyay, Application Oriented Chemistry; Book Syndicate (P) Limited.

Unit-11 ❑ Cement and Electroplating

Structure

11.1 Objectives

After reading this unit we will be able to

- Understand the composition, manufacturing, quality and uses of cement.
- Understand the process of setting and hardening of cement.
- Explain the electroplating process and its importance.
- Describe the importance of galvanization and its uses.

11.2 Introduction

Concrete is the most widely used and important material in modern days. Concrete is produced by mixingcement with fine aggregateor with sand and gravel. So, cement is a binder, a substance used for construction that sets, hardens, and adheres to other materials to bind them together. So the quality of cement is an important factor. On the other hand protecting the metallic structures from corrosion of harsh weather and other factors coating with other stable elements is important. In this regard we will study the electroplating and galvanization in this unit.

11.3 Cement

Concrete is most widely used non-metallic material in construction of buildings,dams, bridges,high ways etc. In concrete, cement is the essential bonding material which binds sand and rock whenmixed with water.

Cement is a dirty greenish heavy powder and finds its importance as a building material. It canbe described as material possessing adhesive and cohesive properties and capable of bonding materialslike stones, bricks, building blocks etc. Cement has the property of setting and hardening in the presenceof water. So it is called as hydraulic cement. The essential constituents of cement used for constructionalpurposes are compounds of calcium (calcareous) and Al +Si (argillaceous).

Cement is classified into four types, based on the chemical composition: Natural cement, Puzzolona cement, Slag cement and Portland cement. Of these, Portland cement is the most widely used cement.is most widely used non-metallic material of construction. It is a mixture of calciumsilicates and calcium aluminates with small amount of gypsum.The name Portland cement is used because this powder on mixing with water gives a hard, stonelike mass which resembles Portland rock.

11.3.1 Composition of cement

A good sample of Portland cement contains

Calcium Oxide or lime (CaO): 60-70%

Silica (SiO_2): 20-24%

Alumina (Al_2O_3): 5-7.5%

Magnesia (MgO): 2-3%

Ferric Oxide (Fe_2O_3): 1-2.5%

Sulphur trioxide (SO_3): 1-1.5%

Sulphur Oxide (Na_2O): 1%

Potassium Oxide (K_2O): 1%

11.3.2 Manufacture of cement

At cement plant, according to different raw materials preparation methods, cement manufacturing can be divided into the dry process and wet process.

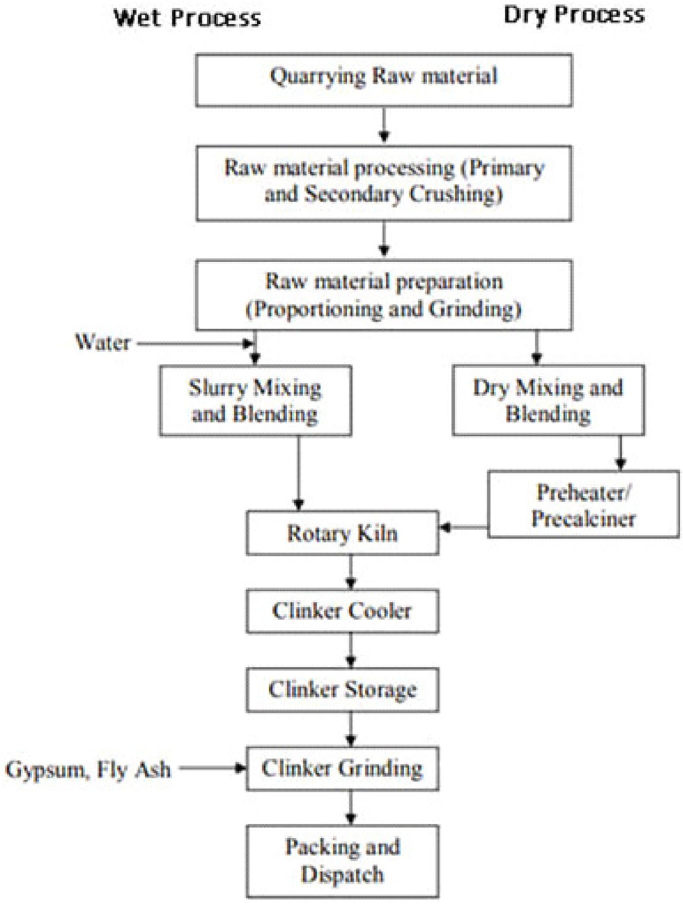


Figure 1. Flowchart of manufacturing of cement.

Wet Process

The wet process of cement manufacturing refers to grinding raw material into slurry after mixing with water and then feeding them into the wet process kiln for drying and calcination and finally forming clinker. The slurry's water content is usually between 32%-36%. In addition, the raw material slurry can also be dehydrated into raw material blocks and put into the kiln to calcine clinker. This method is called the semi-wet process, which still belongs to the cement wet process production.

Advantages: the wet process of cement production has the characteristics of simple operation, low dust and easy conveying. Because the slurry has fluidity so that its homogeneity is good and the quality of clinker is improved. What's more, the energy consumption of raw material grinding in the wet process is reduced by nearly 30%.

Disadvantages: the heat consumption of the wet process is too high, usually between 5234-6490 J/kg and the consumption of ball mill vulnerable parts is also large. Compared with other processing methods, the clinker manufactured by the wet process has a low temperature when it comes out of the kiln, so this method is not suitable to produce the clinker with a high silica rate and high aluminum-oxygen rate.

Dry Process

The dry process of cement manufacturing means that after raw materials with different particle sizes are dried, broken and ground into powders of certain fineness, they will be sent into the dry process kiln for calcining, finally forming clinker. Besides, the raw material powder can also be made into raw material balls by adding a proper amount of water and then be directly sent to the Lepol kiln for calcining. This method is called a semi-dry process, which belongs to the cement dry process production.

Advantages : as the dry process is to directly feed raw material powder into the rotary kiln for calcination, and the moisture content of raw materials is about 1% - 2%, it saves the heat consumption needed for the moisture evaporation. Therefore, this method has the advantages of energy-saving, high production efficiency and stable output, which can meet the production needs of large cement plants. At the same time, there is less sewage discharged in the dry process cement production. It is conducive to environmental protection.

Disadvantages : the disadvantages of dry process are the inhomogeneous composition of raw materials, high power consumption and the high dust content in the workshop.

11.3.3 Uses of Cement

At present, the cement is widely used across the world in the construction of various engineering structures. It has proved to be one of the leading engineering materials of modern times and has no rivals in production and applications. Cements may be used alone (i.e., "neat," as grouting materials), but the normal use is in mortar and concrete in which the cement is mixed with inert material known as aggregate to form a strong binding material. Following are various possible applications or uses of cement:

a. The most significant use of cement is production of concrete and mortar.

b. Cement mortar can be used for masonry work, plaster, pointing, etc.

c. Cement concrete can be used for laying floors, roofs, constructing lintels, beams, weather sheds, stairs, pillars, etc.

d. It can be used for construction of important engineering structures such as bridges, culvert, dams, tunnels, storage reservoirs, light houses, docks, etc.

e. It can also be used for construction of water tanks, tennis courts, septic tanks, lamp posts, roads, telephone cabins, etc.

f. It can be used for making joints for drains, pipes, etc.

g. It can be used for manufacturing precast pipes, garden seats, artistically designed urns, flower pots, dust bins, fencing posts, etc.

h. It can be used for preparation of foundations, watertight floors, footpaths, etc.

i. It can be used for creating fire-proof structures in the form of concrete. Also, it can be used for making acid-resistance and waterproof structures.

j. Coloured cement can be used for decorating or colouring the structures.

k. It can be used for concreting the tunnel or geological walls to strength the structure.

11.3.4 Setting of cement

Cement when mixed with water forms a plastic mass called cement paste. During hydrationreaction, gel and crystalline products are formed.

The inter-locking of the crystals binds the inert particles of the aggregates into a compact rocklike material.

This process of solidification comprises of

(i) setting and then

(ii) hardening

Setting is defined as stiffening of the original plastic mass due to initial gel formation. Hardeningis development of strength, due to crystallisation.

Due to the gradual progress of crystallisation in the interior mass of cement, hardening startsafter setting. The strength developed by cement paste at any time depends upon the amount of gelformed and the extent of crystallisation. The setting and hardening of cement is due to the formation ofinter locking crystals reinforced by rigid gels formed by the hydration and hydrolysis of theconstitutional compounds.

Reactions involved in setting and hardening of cement:-

When cement is mixed with water, the paste becomes rigid within a short time which is knownas initial setting. This is due to the hydration of tricalcium aluminate and gel formation of tetra calciumalumino ferrite.

$3CaO.Al_2O_3 + 6\,H_2O \rightarrow 3CaO.Al_2O_3.6\,H_2O + 880$ KJ/Kg

$C_3A + 6H_2O \rightarrow C_3A.6H_2O + 880$ KJ/Kg

tricalcium aluminate   hydrated tricalcium aluminate (crystalline)

$4CaO.Al_2O_3.Fe_2O_3 + 7H_2O \rightarrow 3CaO.Al_2O_3.6H_2O + CaO.Fe_2O_3.H_2O + 420$ KJ/Kg

$C_4AF + 7H_2O \rightarrow C_3A.\,6H_2O + CF.H_2O + 420$ KJ/Kg

tetracalciumalumino ferrite   (crystalline)   gel

Dicalcium silicate also hydrolyses to tobermonite gel which contributes to initial setting.

$2(2CaO.SiO_2) + 4H_2O \rightarrow 3CaO.2SiO_2.6H_2O + Ca(OH)_2 + 250$ KJ/Kg

$2C_2S + 4H_2O \rightarrow C_3S_2.6H_2O + Ca(OH)_2 + 250$ KJ/Kg

Dicalcium silicate   tobermonite gel

Final setting and hardening of cement paste is due to the formation of tobermonite gel andcrystallisation of calcium hydroxide and hydrated tricalcium aluminate.

$2(2CaO.SiO_2) + 6H_2O \rightarrow 3\,CaO.2SiO_2.3H_2O + 3Ca(OH)_2 + 500$ KJ/Kg

$2C_3S + 6H_2O \rightarrow C_3S_2.6H_2O + 3Ca(OH)_2 + 500$ KJ/Kg

tricalcium silicate   tobermonite gel   calcium hydroxide (crystalline)

During setting and hardening of cement, some amount of heat is liberated due to hydration andhydrolysis reactions. The quantity of heat evolved during complete hydration of cement is 500 KJ/Kg.

Sequence of chemical reactions during setting & hardening:

[redacted]

Function of gypsum in cement :

Tri calcium aluminate (C_3A) combines with water very rapidly.

$C_3A + 6H_2O \rightarrow C_3A \cdot 6H_2O$ + heat

After the initial setting, the paste becomes soft and the added gypsum retards the dissolution of C_3A by forming insoluble calcium sulpho aluminate.

$3\ CaO.Al_2O_3.\ x\ CaSO_4.7\ H_2O$

This reaction prevents the high concentration of alumina in the cement solution and hence retardsthe early initial setting of cement.

11.3.5 Determination of quality of cement

The quality of Cement is tested by performing various lab tests as well as on-site checks. In these tests properties of cement are tested, and the result is analyzed. Depending on the resulting quality of cement can be estimated.

Test done on cement in the laboratory are - Fineness Test of Cement, Consistency Test of Cement, Setting Time Test of Cement, Soundness Test of Cement, The Heat of Hydration Test, Specific Gravity Test of Cement, Tensile Strength Test, Chemical Composition Test.

11.4 Theories of electroplating

Electroplating is the process of plating one metal onto another by the process of electrolysis, most commonly for decorative purposes orto prevent corrosion of a metal. There are also specific types of electroplating such as copper plating, silver plating, andchromium plating. Electroplating allows manufacturers to use inexpensive metals such as steel or zinc for the majority ofthe product and then apply different metals on the outside to account for appearance, protection, and other propertiesdesired for the product. The surface can be a metal or even plastic.These types of products normally have a thin layer of gold, or silver applied so that it hasan attractive appeal to the consumer. Electroplating is widely used in industries such as automobile, airplanes, electronics,jewellery, and toys.

The article to be plated is made as cathode (substrate) and the metal to be plated upon cathode is made as anode. Electroplating is carried out in an electrolytic cell. Itconsists of two electrodes the metal to be coated is taken as cathode and connectedto negativeterminal of a DC power source. Anode is connected to positiveterminalof the power source and the electrodes are dipped in an ionic solution of themetal to be plated.During electroplating, cations move towards cathode and getreduced to metal atoms and deposited over cathode.

Cathode reaction:Mn+ + ne M

Anions present in the solution move towards anode and get oxidized at the anode surface if the anode is inert. But f the anode is dissolvable then the electrode itself gets oxidized.

Anode reaction: M Mn+ + ne

Hence, plating is a redox reaction, where oxidation occurs at anode and reduction at cathode.Commonly used coating metals are Zn, Cu, Cr, Ni, Ag, Pt, Au etc.In the figure below, the Ag ions are being drawn to the surfaceof the spoon and it eventually becomes plated. The process is undergone using silver as the anode, and a spoon as thecathode. The electrons are transferred from the anode to the cathode and this process underwent in a solution containing silver.

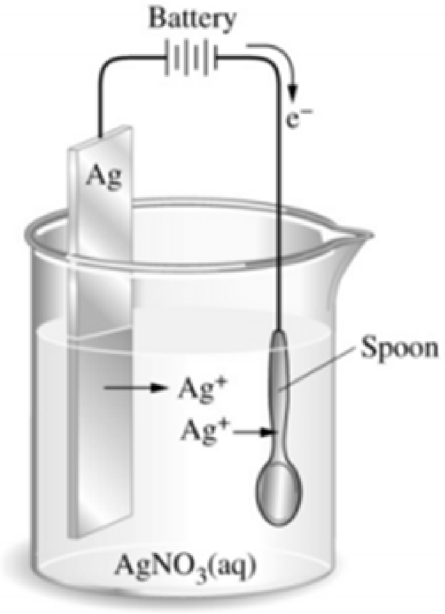


Figure 2. Electroplating of silver on a metal spoon.

Before the electroplating of any object, the surface of the object is prepared for electroplating. The purpose of preparing the surface before beginning to plate another metal onto it is to ensure that it is clean and free ofcontaminants, which may interfere with the bonding. Contamination often prevents deposition and lack of adhesion. Normally this is done in three steps: cleaning, treatment and rinsing. Cleaning usually consists of using certain solventssuch as alkaline cleaners, water, or acid cleaners in order to remove layers of oil on the surface. Treatment includes surfacemodification which is the hardening of the parts and applying metal layers. Rinsing leads to the final product and is thefinal touch to electroplating.Two certain methods of preparing the surface are physical cleaning and chemical cleaning.Chemical cleaning consists of using solvents that are either surface-active chemicals or chemicals which react with themetal/surface. In physical cleaning the mechanical energy is being applied in order to remove contaminants. Physicalcleaning includes brush abrasion and ultrasonic agitation.

11.5 Galvanization application and uses

Galvanization is one of the most widely used methods for protecting metal (mainly steel or iron) from corrosion. It involves applying a thin coating of zinc to a thicker base metal, helping to shield it from the surrounding environment.

Galvanizing can protect metal in a number of ways. Firstly, it creates a protective coating that shields the metal from the surrounding environment. The layer of zinc prevents water and moisture and other elements in the air from corroding the steel underneath. But if the zinc coating is scratched deep enough, the metal would become exposed and susceptible to corrosion.

Galvanizing can also protect metal through a process called "galvanic corrosion". Galvanic corrosion occurs when two metals of a different electrochemical make up are placed into contact with one another with an electrolyte present, such as salty water. Depending on the atomic structure of the two metals, one metal is the anode and the other is the cathode. The anode corrodes more rapidly than it would by itself and the cathode corrodes at a slower pace than it would by itself. The reason zinc is used for galvanizing is because it has an affinity towards being the anode when in contact with many different types of metals. Since the zinc coating in contact with the base metal is usually the anode, it slows the corrosion of the base metal, or the cathode. So in presence of deep scratch in the surface of galvanized iron the zinc layer protects iron from corrosion.

11.6 Summary

In this unit we have learned about chemical aspects of cement which is an important component of concrete. We have discussed about the composition, manufacturing and uses of cement. Beside this we have learned about the setting and hardening of cement which determines the quality of cement. Also we have discussed about other tests for determining the quality of cement. After that we have learned about theories of electroplating and galvanization and their uses.

11.7 Self-assessment questions

a) What are the compositions of Portland cement?

b) What is setting of cement?

c) What are the uses of cement?

d) What tests are done for determining the quality of cement?

e) What are the advantages of manufacturing cement in dry method?

f) What are the purposes of electroplating?

g) How does electroplating work?

h) Why is it important to prepare the surface before beginning electroplating?

i) What is galvanization?

j) How galvanization helps in preventing corrosion of iron?

11.8. References

1. Advances in Materials Science and Engineering, Volume 2018, Article ID 4158682, https://doi.org/10.1155/2018/4158682.
2. Engineering Materials Science: Properties, Uses, Degradation, Remediation, 2004,Elsevier. ISBN: 9781782420491.
3. Cement chemistry, H. F. W. Taylor, 1997, 2nd ed.
4. Electroplating, Anodizing and Galvanizing, K. K. Agarwal, 2018.

Unit-12 ❑ The atmosphere

Structure

12.1 Objectives

After going through this unit you would understand the following:

- Structure of atmosphere and role of ozone layer.
- Air pollution and origin of air pollutants.
- Importance of ozone layer and reason behind its depletion.

- Difference adverse effects on atmosphere due to air pollution.
- Effect of air pollution on living thing and the methods of prevention of air pollution.

12.2 Introduction

We all know that earth is a unique planet due to the presence of life. The air is one among the necessary conditions for the existence of life on this planet. The air is a mixture of several gases and it encompasses the earth from all sides. The air surrounding the earth is called the atmosphere.

The atmosphere contains life-giving gases like Oxygen for humans and animals and carbon dioxide for plants. It envelops the earth all round and is held in place by the gravity of the earth. It helps in stopping the ultraviolet rays harmful to the life and maintains the suitable temperature necessary for life. Generally, atmosphere extends up to about 1600 km from the earth's surface. However, 99 % of the total mass of the atmosphere is confined to the height of 32 km from the earth's surface.

The atmosphere is a mixture of many gases. In addition, it contains huge numbers of solid and liquid particles, collectively called 'aerosols'. Some of the gases may be regarded as permanent atmospheric components which remain in fixed proportion to the total gas volume. Other constituents vary in quantity from place to place and from time to time. If the suspended particles, water vapour and other variable gases were excluded from the atmosphere, then the dry air is very stable all over the earth up to an altitude of about 80 kilometres. The proportion of gases changes in the higher layers of the atmosphere in such a way that oxygen will be almost in negligible quantity at the height of 120 km. Similarly, carbon dioxide and water vapour are found only up to 90 km from the surface of the earth. Nitrogen and oxygen make up nearly 99% of the clean, dry air. The remaining gases are mostly inert and constitute about 1% of the atmosphere.Besides these gases, large quantities of water vapour and dust particles are also present in the atmosphere. These solid and liquid particles are of great climatic significance.

12.3 Structure of atmosphere

The atmosphere can be divided into five layers according to the diversity of temperature and density. They are:Troposphere, Stratosphere, Mesosphere, Thermosphere (Ionosphere), Exosphere.

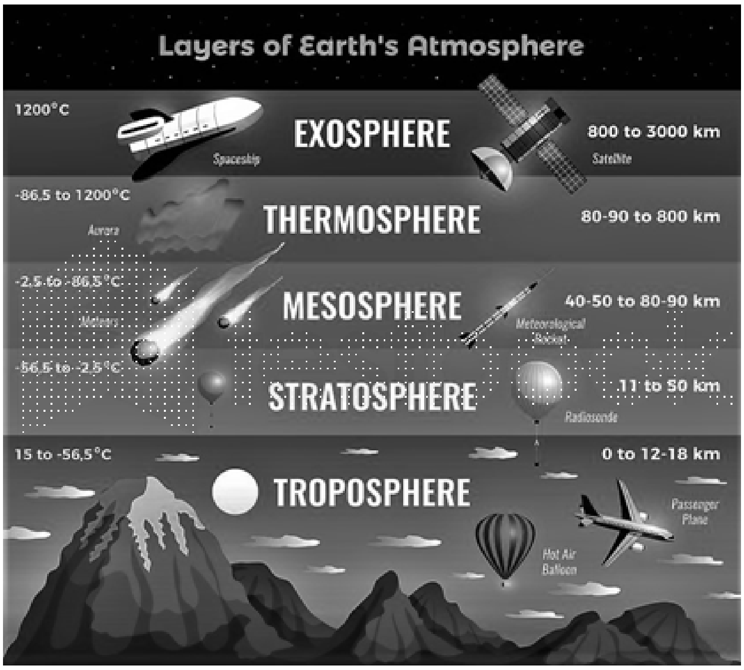


Figure 1. Structure of atmosphere.

Troposphere

Troposphere is the atmospheric layer between the earth's surface and an altitude of 8 km at the poles and 18 km at the equator.The thickness is greater at the equator, because the heated air rises to greater heights.The troposphere ends with the tropopause.Thetemperature in this layer, as one goes upwards, falls at the rate of 5°C per kilometer, and reaches -45°C at the poles and -80°C over the equator at tropopause (greater fall in temperature above equator is because of the greater thickness of troposphere - 18 km).The troposphere is marked by temperature inversion, turbulence and eddies.It is also meteorologically the most significant zone in the entire atmosphere. The troposphere is the theatre for weather because all cyclones, anticyclones, storms and precipitation occur here, as all water vapours and solid particles lie within this.The troposphere is influenced by seasons and jet streams.

Tropopause

Top most layer of troposphere is named as tropopause. It acts as a boundary between troposphere and stratosphere.This layer is marked by constant temperatures.

Stratosphere

Stratosphere lies beyond troposphere, up to an altitude of 50 km from the earth's surface.The temperature in this layer remains constant for some distance but then rises to reach a level of 0°C at 50 km altitude.This rise is due to the presence of ozone (harmful ultraviolet radiation is absorbed by ozone).This layer is almost free from clouds and associated weather phenomenon, making conditions most ideal for flying aeroplanes. So aeroplanes fly in lower stratosphere, sometimes in upper troposphere where weather is calm.Sometimes, cirrus clouds are present at lower levels in this layer.

Ozonosphere

Ozonosphere lies at an altitude between 30 km and 60 km from the earth's surface and spans the stratosphere and lower mesosphere.Because of the presence of ozone molecules, this layer reflects the harmful ultraviolet radiation.The ozonosphere is also called chemosphere because; a lot of chemical activity goes on here.The temperature rises at a rate of 5°C per kilometre through the ozonosphere.

Mesosphere

Mesosphere is an intermediate layer beyond the ozone layer and continues upto an altitude of 80 km from the earth's surface.The temperature gradually falls to -100°C at 80 km altitude.Meteorites burn up in this layer on entering from the space.

Thermosphere

Thermosphere temperature rises very rapidly with increasing height.Ionosphere is a part of this layer. It extends between 80-700 km.This layer helps in radio transmission. In fact, radio waves transmitted from the earth are reflected back to the earth by this layer. Any person would not feel warm in this layer because of the thermosphere's extremely low pressure.The International Space Station and satellites orbit in this layer. (Though temperature is high, the atmosphere is extremely rarefied- gas molecules are spaced hundreds of kilometres apart. Hence a person or an object in this layer doesn't feel the heat. Aurora's are observed in lower parts of this layer. This layer is also known as ionosphere.This layer is characterized by ionization of atoms.Because of the electric charge, radio waves transmitted from the earth are reflected back to the earth by this layer.Temperature again starts increasing with height because of radiation from the sun.

Exosphere

This is the uppermost layer of the atmosphere extending beyond the ionosphere above a height of about 700 km.The air is extremely rarefied and the temperature gradually increases through the layer.Light gases like helium and hydrogen float into the space from here.Temperature gradually increases through the layer (as it is exposed to direct sunlight). This layer coincides with space.

12.4 Ozone layer and its role

Earth's stratospheric ozone layer, which contains about 90 percent of the ozone in the atmosphere, makes the planet habitable by absorbing harmful solar ultraviolet (UV) radiation before it reaches the planet's surface. UV radiation damages cells and causes sunburn and premature skin aging in low doses. At higher levels, it can cause skin cancer and immune system suppression. Earth's stratospheric ozone layer absorbs 99 percent of incoming solar UV radiation.

Scientists have worked to understand the chemistry of the ozone layer since its discovery in the 1920s. In 1930 British geophysicist Sydney Chapman described a process in which strong UV photons photolyze oxygen molecules (O_2) into highly reactive oxygen atoms. These atoms rapidly combine with O_2 to form ozone (O_3). This process is still recognized as the only significant source of ozone to the stratosphere. Formation of ozone in the stratosphere is simple to understand, but the mechanisms for ozone loss are considerably more complicated. Ozone photolyzes to release O_2 and O, but this is not an actual sink since O_2 and O can just recombine to ozone. The main mechanism for ozone loss in the natural stratosphere is a catalytic cycle involving NO_x radicals, which speed up ozone loss by cycling between NO and NO_2 but are not consumed in the process. We will discuss in details about the depletion of ozone layer in details later.

Ozone levels in the stratosphere are 10 to 100 times higher than what one observes at Earth's surface in the worst smog events. Fortunately we are not there to breathe it, though exposure of passengers in jet aircraft to stratospheric ozone has emerged recently as a matter of public health concern as direct ozone environment is hazardous for the plants and animals.

12.5 Major air pollutants

Primary air pollutants are emitted directly into the air from sources. They can have effects both directly and as precursors of secondary air pollutants (chemicals formed through reactions in the atmosphere), which are discussed in the following section.

12.5.1 CO

Carbon monoxide (CO) is an odourless, colourless gas formed by incomplete combustion of carbon in fuel. The main source is motor vehicle exhaust, along with industrial processes and biomass burning. Carbon monoxide binds to haemoglobin in red blood cells, reducing their ability to transport and release oxygen throughout the body. Low exposures can aggravate cardiac ailments, while high exposures cause central nervous system impairment or death. It also plays a role in the generation of ground-level ozone.

12.5.2 SO_2

Sulphur dioxide (SO_2) is a gas formed when sulphur is exposed to oxygen at high temperatures during fossil fuel combustion, oil refining, or metal smelting. SO_2 is toxic at high concentrations, but its principal air pollution effects are associated with the formation of acid rain and aerosols. SO_2 dissolves in cloud droplets and oxidizes to form sulphuric acid (H_2SO_4), which can fall to Earth as acid rain or snow or form sulphate aerosol particles in the atmosphere.

12.5.3 NO_x

Nitrogen oxides (NO and NO_2, referred together as NO_x) are highly reactive gases formed when oxygen and nitrogen react at high temperatures during combustion or lightning strikes. Nitrogen present in fuel can also be emitted as NO_x during combustion. Emissions are dominated by fossil fuel combustion at northern mid-latitudes and by biomass burning in the tropics.

In the atmosphere NOx reacts with volatile organic compounds (VOC_s) and carbon monoxide to produce ground-level ozone through a complicated chain reaction mechanism. It is eventually oxidized to nitric acid (HNO_3). Like sulphuric acid, nitric acid contributes to acid deposition and to aerosol formation.

12.5.4 SPM

In addition to gases, the atmosphere contains solid and liquid particles that are suspended in the air. These particles are referred to as aerosols or suspended particulate matter (SPM). Aerosols in the atmosphere typically measure between 0.01 and 10 micrometers in diameter, a fraction of the width of a human hair. Most aerosols are found in the lower troposphere, where they have a residence time of a few days. They are removed when rain or snow carries them out of the atmosphere or when larger particles settle out of suspension due to gravity.

Large aerosol particles (usually 1 to 10 micrometers in diameter) are generated when winds blow sea salt, dust, and other debris into the atmosphere. Fine aerosol particles with diameters less than 1 micrometer are mainly produced when precursor gases condense in the atmosphere. Major components of fine aerosols are sulphate, nitrate, organic carbon, and elemental carbon. Sulphate,nitrate, and organic carbon particles are produced by atmospheric oxidation of SO_2, NOx, and VOCs as discussed above. Elemental carbon particles are emitted by combustion, which is also a major source of organic carbon particles. Light-absorbing carbon particles emitted by combustion are called black carbon or soot; they are important agents for climate change and are also suspected to be particularly hazardous for human health.

High concentrations of aerosols are a major cause of cardiovascular disease and are also suspected to cause cancer. Fine particles are especially serious threats because they are small enough to be absorbed deeply into the lungs, and sometimes even into the bloodstream.Aerosols also have important radiative effects in the atmosphere. Particles are said to scatter light when they alter the direction of radiation beams without absorbing radiation. This is the principal mechanism limiting visibility in the atmosphere, as it prevents us from distinguishing an object from the background.

12.6 Ozone layer depletion

The upper stratosphere consists ofconsiderable amount of ozone (O_3), whichprotects us from the harmful ultraviolet (UV) radiations (λ ~255 nm) coming from the sun.These radiations cause skin cancer(melanoma) in humans. Therefore, it is important to maintain the ozone shield. Ozone in the stratosphere is a product of UV radiations acting on dioxygen (O_2) molecules. The UV radiations split apart molecular oxygen into free oxygen (O) atoms. These oxygen atoms combine with the molecular oxygen to form ozone.

$$O_2\,(g) \xrightarrow{uv} O(g) + O(g)$$

$$O(g) + O_2\,(g) \overset{uv}{\leftrightarrow} O_3\,(g)$$

Ozone is thermodynamically unstable anddecomposes to molecular oxygen. Thus, adynamic equilibrium exists between theproduction and decomposition of ozonemolecules. In recent years, there have beenreports of the depletion of this protectiveozonelayer because of the presence of certainchemicals in the stratosphere. The mainreason of ozone layer depletion is believed tobe the release of chlorofluorocarbon compounds (CFCs), also known as freons.These compounds are nonreactive, nonflammable, non-toxic organic molecules andtherefore used in refrigerators, air conditioners,in the production of plastic foam and by theelectronic industry for cleaning computerparts etc. Once CFCs are released in theatmosphere, they mix with the normalatmospheric gases and eventually reach thestratosphere. In stratosphere, they get brokendown by powerful UV radiations, releasingchlorine free radical.

$$\mathrm{CF_2Cl_2\ (g)} \xrightarrow{uv} \dot{\mathrm{C}}\mathrm{l\ (g)} + \dot{\mathrm{C}}\mathrm{F_2Cl(g)} \qquad \text{(i)}$$

The chlorine radical then react withstratospheric ozone to form chlorine monoxideradicals and molecular oxygen.

$$\dot{\mathrm{C}}\mathrm{l\ (g)} + \mathrm{O_3\ (g)} \rightarrow \mathrm{Cl}\ \boxed{?}\ \mathrm{(g)} + \mathrm{O_2(g)} \qquad \text{(ii)}$$

Reaction of chlorine monoxide radical withatomic oxygen produces more chlorineradicals.

$$\mathrm{Cl}\ \boxed{?}\ \mathrm{(g)} + \mathrm{O\ (g)} \longrightarrow \dot{\mathrm{C}}\mathrm{l\ (g)} + \mathrm{O_2(g)} \qquad \text{(iii)}$$

The chlorine radicals are continuouslyregenerated and cause the breakdown ofozone. Thus, CFCs are transporting agents forcontinuously generating chlorine radicals intothe stratosphere and damaging the ozone layer.

The Ozone Hole

In 1980s atmospheric scientists working inAntarctica reported about depletion of ozonelayer commonly known as ozone hole over theSouth Pole. It was found that a unique set ofconditions was responsible for the ozone hole.In summer season, nitrogen dioxide andmethane react with chlorine monoxide(reaction iv) and chlorine atoms (reaction v) forming chlorine sinks, preventing much ozonedepletion, whereas in winter, special type ofclouds called polar stratospheric clouds areformed over Antarctica. These polarstratospheric clouds provide surface on whichchlorine nitrate formed (reaction iv) gets hydrolysed to form hypochlorous acid (reaction (vi)). It also reacts with hydrogen chloride produced as per reaction (v) to give molecular chlorine.

$$\mathrm{Cl}\ \boxed{?}\ \mathrm{(g)} + \mathrm{NO_2\ (g)} \rightarrow \mathrm{ClONO_2(g)} \qquad \text{(iv)}$$

$$\dot{\mathrm{C}}\mathrm{l\ (g)} + \mathrm{CH_4\ (g)} \rightarrow \dot{\mathrm{C}}\mathrm{H_3(g)} + \mathrm{HCl(g)} \qquad \text{(v)}$$

$$\mathrm{ClONO_2(g)} + \mathrm{H_2O(g)} \rightarrow \mathrm{HOCl\ (g)} + \mathrm{HNO_3\ (g)} \qquad \text{(vi)}$$

$$\mathrm{ClONO_2(g)} + \mathrm{HCl\ (g)} \rightarrow \mathrm{Cl_2\ (g)} + \mathrm{HNO_3\ (g)} \qquad \text{(vii)}$$

When sunlight returns to the Antarctica in the spring, the sun's warmth breaks up the clouds and HOCl and Cl2 are photolysis by sunlight, as given in reactions (viii) and (ix).

$$\mathrm{HOCl\ (g)} \xrightarrow{hv} \boxed{?}\ \mathrm{H\ (g)} + \dot{\mathrm{C}}\mathrm{l(g)} \qquad \text{(viii)}$$

$$\mathrm{Cl_2(g)} \xrightarrow{hv} 2\dot{\mathrm{C}}\mathrm{l(g)} \qquad \text{(ix)}$$

The chlorine radicals thus formed, initiate the chain reaction for ozone depletion as describedearlier. Effects of Depletion of the Ozone Layer With the depletion of ozone layer, more UV-radiation filters into troposphere. UV-radiations lead to ageing of skin, cataract, sunburn, skin cancer, killing of nanophytoplanktons, damage to fish productivity etc. It has also been reported that plant proteins get easily affected by UV radiations which leads to the harmful mutation of cells. It also increases evaporation of surface water through the stomata of the leaves and decreases the moisture content of the soil. Increase in UV radiations damage paints and fibres, causing them to fade faster.

12.7 Greenhouse effect

The greenhouse effect is the natural warming of the earth when gases in the atmosphere trap heat from the sun that would otherwise escape into space. Sunlight makes the earth habitable. While 30 percent of the solar energy that reaches our world is reflected back to space, approximately 70 percent passes through the atmosphere to the earth's surface, where it is absorbed by the land, oceans, and atmosphere, and heats the planet. This heat is then radiated back up in the form of invisible infrared light. While some of this infrared light continues on into space, the vast majority-indeed, some 90 percent- gets absorbed by atmospheric gases, known as greenhouse gases, and redirected back toward the earth, causing further warming. The main gases responsible for the greenhouse effect include carbon dioxide, methane, nitrous oxide, and water vapour (which all occur naturally), and fluorinated gases (which are synthetic).

According to the Intergovernmental Panel on Climate Change (IPCC), population size, economic activity, lifestyle, energy use, land use patterns, technology, and climate policy are the broad forcing factors that drives nearly all human-caused greenhouse gas emissions. Fuelled by man-made greenhouse gas emissions, global warming is altering the earth's climate systems in many ways. It is causing more frequent and/or intense extreme weather events, including heat waves, hurricanes, droughts, and floods. Also sea levels are raisings due to melting glaciers and sea ice and an increase in ocean temperatures (warmer water expands, which can contribute to sea level rise). These changes pose threats not only to plants and wildlife, but directly to people.

12.8. Acid rain

Acid rain, or acid deposition, is a broad term that includes any form of precipitation with acidic components, such as sulphuric or nitric acid that fall to the ground from the atmosphere in wet or dry forms. This can include rain, snow, fog, hail or even dust that is acidic.

Acid rain results when sulphur dioxide (SO_2) and nitrogen oxides (NO_X) are emitted into the atmosphere and transported by wind and air currents. The SO_2 and NO_x react with water, oxygen and other chemicals to form sulphuric and nitric acids. These then mix with water and other materials before falling to the ground.

While a small portion of the SO_2 and NO_x that cause acid rain is from natural sources such as volcanoes, most of it comes from the burning of fossil fuels. The major sources of SO_2 and NO_x in the atmosphere are:

a) Burning of fossil fuels to generate electricity. Two thirds of SO_2 and one fourth of NO_x in the atmosphere come from electric power generators.

b) Vehicles and heavy equipment.

c) Manufacturing, oil refineries and other industries.

Winds can blow SO_2 and NO_x over long distances and across borders making acid rain a problem for everyone and not just those who live close to these sources.

12.9 Smog

Smog is air pollution that reduces visibility. The term "smog" was first used in the early 1900s to describe a mix of smoke and fog. The smoke usually came from burning coal. Smog was common in industrial areas, and remains a familiar sight in cities today. Most of the smog we see now is photochemical smog. Photochemical smog is produced when sunlight reacts with nitrogen oxides and at least one volatile organic compound (VOC) in the atmosphere. Nitrogen oxides come from car exhaust, coal power plants, and factory emissions. VOCs are released from gasoline, paints, and many cleaning solvents. When sunlight hits these chemicals, they form airborne particles and ground-level ozoneor smog.Smog is unhealthy to humans and animals, and it can kill plants. Smog is also ugly. It makes the sky brown or gray. Smog is common in big cities with a lot of industry and traffic. Cities located in basins surrounded by mountains may have smog problems because the smog is trapped in the valley and cannot be carried away by wind.

12.10 Sulphurous smog

Sulphurous smog is also called "London smog," (first formed in London).Sulphurous smog results from a high concentration of sulphur oxides in the air and is caused by the use of sulphur-bearing fossil fuels, particularly coal (Coal was the mains source of power in London during nineteenth century. The effects of coal burning were observed in early twentieth century).This type of smog is aggravated by dampness and a high concentration of suspended particulate matter in the air.

12.11 Air pollution effect and methods of prevention

Air pollution is a significant risk factor for multiple health conditions including respiratory infections, heart disease, and lung cancer, according to the WHO. The health effects caused by air pollution may include difficulty in breathing, wheezing, coughing, asthma and aggravation of existing respiratory and cardiac conditions. These effects can result in increased medication use, increased doctor or emergency room visits, more hospital admissions and premature death. The human health effects of poor air quality are far-reaching, but principally affect the body's respiratory system and the cardiovascular system. Both indoor and outdoor air pollution have caused approximately 3.3million deaths worldwide. Children aged less than five years that live in developing

countries are the most vulnerable population in terms of total deaths attributable to indoor and outdoor air pollution. The World Health Organization states that 2.4 million people die each year from causes directly attributable to air pollution, with 1.5 million of these deaths attributable to indoor air pollution. Around the world, children living in cities with high exposure to air pollutants are at increased risk of developing asthma, pneumonia and other lower respiratory infections. Because children are outdoors more and have higher minute ventilation, they are more susceptible to the dangers of air pollution. Risks of low initial birth weight are also heightened in such cities.

Solution efforts on pollution are always a big problem. This is why prevention

interventions are always a better way of controlling air pollution. These prevention

methods can either come from government (laws) or by individual actions. In many big cities, monitoring equipment's have been installed at many points in the city. Authorities read them regularly to check the quality of air.

Government (or community) level prevention: Governments throughout the world have already taken action against air pollutionby introducing green energy. Some governments are investing in wind energy and solar energy, as well as other renewable energy, to minimize burning of fossil fuels, which cause heavy air pollution. Governments are also forcing companies to be more responsible with their manufacturing activities, so that even though they still cause pollution, they are a lot controlled. Companies are also building more energy efficient cars, which pollute less than before.

Individual Level Prevention: If we use the bus, train or bike when commuting, there will be fewer cars on road and less fumes. Similarly, if we use energy (light, water, boiler, kettle and fire woods) wisely, fewer amounts of fossil fuels will be burned to generate electricity, and so we can cut down the amount of pollution we create. Also, if we can recycle and re-use things then we can minimize the dependence of producing new things as manufacturing industries create a lot of pollution.

Control devices: Different control devices like mechanical collectors(dust cyclones, multi-cyclones), electrostatic precipitators or electrostatic air cleaner are commonly used as pollution control devices by industry or transportation devices. They can either destroy contaminants or remove them from an exhaust stream before it is emitted into the atmosphere.

12.12 Summary

In this unit we have learnt about the structure of atmosphere, different layers and their characteristics. We have discussed about the role of ozone layer for protecting the earth surface from harmful UV radiations. We have briefly discussed about different sources of air pollutants and their harmful effects like degradation of ozone layer, greenhouse effect, global warming, acid rain, smog, etc. Finally we have learnt about the effect of air pollution on plant and animal kingdom and different preventive measures of decreasing the air pollution for sustainable living of the mankind on the earth.

12.13 Self-assessment questions

1. What are the different layers of atmosphere?
2. What is the role of ozone layer for the existence of life on the earth?
3. What are the reasons behind the depletion of ozone layer?
4. What are the major air polluting agents?
5. Why acid rain occurs?
6. What is greenhouse effect?
7. What is the reason of formation of smog?
8. How air pollution can be prevented?

12.14 References

Air Pollution, M N Rao& H V N Rao, Tata McGraw-Hill, 2007.

Kaushik, A and Kaushik CP (2004) : Perspectives in Environmental Studies, New Age International Publishers, New Delhi.

NCERT, Environmental Chemistry, 2019-20.

Unit-13 ❑ The Hydrosphere-I

Structure

13.1 Objectives

After reading this unit, we will be able to:

- Become familiar with different sources of water pollutionand their characteristics and harmful effects.
- Know different water pollution control measures.
- Understand differentwater quality parameters.
- New technologies for purification of water.

13.2 Introduction

The hydrosphere is the total amount of water on a planet. The hydrosphere includes water thatis on the surface of the planet, underground, and in the air. A planet's hydrosphere canbe liquid, vapour, or ice.

On Earth, liquid water exists on the surface in the form of oceans, lakes and rivers. It also exists below ground- as groundwater, in wells and aquifers. Water vapour is most visible as clouds and fog.The frozen part of Earth's hydrosphere is made of ice: glaciers, ice caps and icebergs. The frozen part of the hydrosphere has its own name, the cryosphere.

Water moves through the hydrosphere in a cycle. Water collects in clouds, and then falls to Earth in the form of rain or snow. This water collects in rivers, lakes and oceans. Then it evaporates into the atmosphere to start the cycle all over again. This is called the water cycle or hydrological cycle.

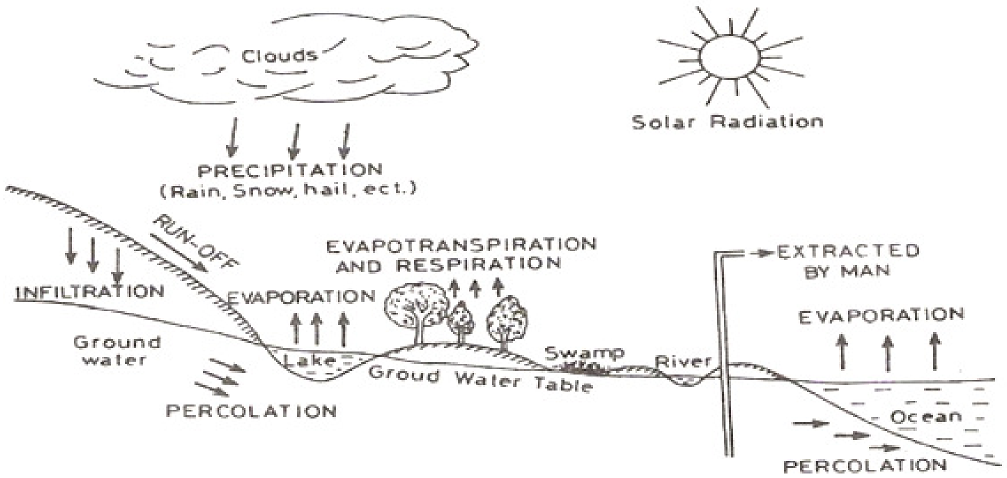


Figure 1. The hydrological cycle.

Water is essential for life. Without water there would be no life. 71% of the earth's surface is covered by water only a tiny fraction of this water is available to us as fresh water. About 97% of the total water available on earth is found in oceans and is too salty for drinking or irrigation. The remaining 3% is fresh water. Of this 2.997% is locked in ice caps or glaciers. Thus only 0.003% of the earth' total volume of water is easily available to us as soil moisture, groundwater, water vapour and water in lakes, streams, rivers and wetlands. Water that is found in streams, rivers, lakes, wetlands and artificial reservoirs is called surface water. Water that percolates into the ground and fills the pores in soil and rock is called groundwater. Porous water-saturated layers of sand, gravel or bedrock through which ground water flows are called aquifers. Most aquifers are replenished naturally by rainfall that percolates downward through the soil and rock. This process is called natural recharge. If the withdrawal rate of an aquifer exceeds its natural recharge rate, the water table is lowered. Any pollutant that is discharged onto the land above is also pulled into the aquifer and pollutes the groundwater resulting in polluted water in the nearby wells. When the quality or composition of water changes directly or indirectly as a result of man's activities such that it becomes unfit for any purpose it is said to be polluted. Any physical, biological or chemical change in water quality that adversely affects living organisms or makes water unsuitable for certain use is referred as water pollution.

We usually take water as granted for its purity, but we must ensure the quality of water. Pollution of water originates from human activities. Through different paths, pollution reaches surface or ground water. Easily identified source or place of pollution is called as point source. e.g., municipal and industrial discharge pipes where pollutants enter the water-source. Non point sources of pollutionare those where a source of pollution cannot be easily identified, e.g., agricultural runoff (from farm, animals and crop-lands), acid rain, storm-water drainage (from streets, parking lots and lawns), etc.

13.3 Water pollutants

The substances which cause pollution are known as pollutants. Pollutants may be defined as any substance that is released intentionally or unintentionally by man into the environment in such concentration that may cause adverse affect on environment health. The Indian Environment (Protection) Act, 1986 defines pollutant as any solid, liquid or gaseous substance present is such concentration as may be or tend to be injurious to environment. There are several classes of common water pollutants. The major sources of surface water contamination are construction, municipalities, agriculture, and industries. Some of these are discussed in the next part.

13.3.1 Action of soaps and detergents

The soaps are made from natural ingredients such as plant oils or the acids derived from animal fats. These all products are natural and are biodegradable in nature. On the other hand, the detergents are all synthetic in nature. These are potassium or sodium salts of long alkyl chains that end with a sulfonate group. These are all man-made; engineered to get the desired properties. The components of detergents are non- biodegradable in nature. So, when any detergent is used during washing; its components cannot be later disposed of and remain in water for long. This leads to heavy water pollution.

13.3.2 Phosphates

Inorganic plant nutrients can cause water pollution. These are water soluble nitrates and phosphates that cause excessive growth of algae and other aquatic plants. The excessive growth of algae and aquatic plants due to added nutrients is called eutrophication. They may interfere with the use of the water by clogging water intake pipes, changing the taste and odour of water and cause a build-up of organic matter. As the organic matter decays, oxygen levels decrease and fish and other aquatic species die.

13.3.3 Arsenic

Arsenic is a natural component of the earth's crust and is widely distributed throughout the environment in the air, water and land. It is highly toxic in its inorganic form. Arsenic is used industrially as an alloying agent, as well as in the processing of glass, pigments, textiles, paper, metal adhesives, wood preservatives and ammunition. Arsenic is also used in the hide tanning process and, to a limited extent, in pesticides, feed additives and pharmaceuticals. So from this industrial waste also water can be polluted by arsenic. People are exposed to elevated levels of inorganic arsenic through drinking contaminated water, using contaminated water in food preparation and irrigation of food crops, industrial processes, eating contaminated food and smoking tobacco. Long-term exposure to inorganic arsenic, mainly through drinking-water and food, can lead to chronic arsenic poisoning. Skin lesions and skin cancer are the most characteristic effects.

13.3.4 Industrial effluents

Industries produce a huge amount of waste which contains toxic chemicals and pollutants which can cause air pollution and damage to us and our environment. They contain pollutants such as lead, mercury, sulphur, asbestos, nitrates, and many other harmful chemicals. Many industries do not have a proper waste management system and drain the waste in the fresh water which goes into rivers, canals and later into the sea. The toxic chemicals have the capability to change the colour of water, increase the number of minerals, change the temperature of water and pose a serious hazard to water organisms. A variety of organic chemicals like oil, gasoline, plastics, pesticides, cleaning solvents, detergent and many other chemicals can cause serious water pollution. These are harmful to aquatic life and human health. They get into the water directly from industrial activity either from improper handling of the chemicals in industries and more often from improper and illegal disposal of chemical wastes.

13.3.5 Agriculture runoff

The quantity of fertilizers applied in a field is often many times more than is actually required by the plants. Also, when it rains, the chemicals mix up with rainwater and flow down into rivers and canals which pose serious damages for aquatic animals. The chemicals in fertilizers and pesticides pollute soil and water. While excess fertilizers cause eutrophication, pesticides cause bioaccumulation and biomagnification. Pesticides which enter water bodies are introduced into the aquatic food chain. They are then absorbed by the phytoplanktons and aquatic plants. These plants are eaten by the herbivorous fish which are in turn eaten by the carnivorous fish which are in turn eaten by the water birds. At each link in the food chain these chemicals which do not pass out of the body are accumulated and increasingly concentrated resulting in biomagnification of these harmful substances. One of the effects of accumulation of high levels of pesticides such as DDT is that birds lay eggs with shells that are much thinner than normal. This results in the premature breaking of these eggs, killing the chicks inside. Birds of prey such as hawks, eagles and other fish eating birds are affected by such pollution. Although DDT has been banned in India for agricultural use and is to be used only for malaria eradication, it is still used in the fields as it is cheap

13.3.6 Radioactive pollution

Nuclear energy is produced using nuclear fission or fusion. The element that is used in the production of nuclear energy is highly toxic chemical. Water soluble radioactive isotopesare yet another source of water pollution. These can be concentrated in various tissues and organs as they pass through food chains and food webs. Ionizing radiation emitted by such isotopes can cause birth defects, cancer and genetic damage. The nuclear waste that is produced by radioactive material needs to be disposed of to prevent any nuclear accident. Nuclear waste can have serious environmental hazards if not disposed of properly. Few major accidents have already taken place in Russia and Japan.

13.4 Effects of water pollution on animal and plants

Pollution of water affects both humans and aquatic life. Most water sources close tocities and urban centres are polluted by garbage and dumping of chemicals, legally orillegally. Below are some of the common as well as adverse effects of polluting waterbodies.

a) **Effects on Human Beings :** Life is a cycle, and humanity's irresponsible behaviour often comes back to haunt it. Adding contaminants to water bodies has affected the human family in several ways. According to a 2017 WHO report, 2.1 billion people do not have access to safe water. In 2019, it stated that 785 million people lack access to essential drinking water. One of the main effects of this is diseases. World Health Organisation notes that there are about 120,000 cholera-related deaths annually. Also, the Fukushima tragedy, for example, increased the prevalence of thyroid cancer in exposed infants by 70%.

b) **Death of Aquatic Life :** Animals and plants that depend on water for life are the most affected by polluted water. Statistics from the Centre for Biological Diversity on the effects of the Deep Horizon spill provides a useful glimpse of the impact of pollution on aquatic life.

c) **Food Chain Disruption :** Pollution disrupts the food chain by moving the toxins from one level in the chain to higher levels. In some cases, pollution can wipe out an entire part of the food chain. Such affect the other organisms by either causing excessive growth, in case the predator dies or death.

d) **Destruction of Ecosystems :** The introduction or elimination of certainmicroorganisms distorts the ecosystem. Nutrient pollution, for example, leads to an increase in algae, which depletes the water of oxygen, thereby leading to the death of fish and other aquatic life.

13.5 Water pollution control measures

Wastewater, or sewage, originates from human and home wastewaters, industrial wastes, animal wastes, rain runoff, and groundwater infiltration. The wastewater consists of 99.9% water by weight, wherethe remaining 0.1% is suspended or dissolved material. So the removal of these pollutants from the waste water is necessary before mixing with large water bodies for controlling the water pollution.

13.5.1 Waste water treatments

In urban areas of developed countries, municipal wastewater (or sewage) is typically treated by centralized sewage treatment plants. Well-designed and operated systems (i.e., with secondary treatment steps or more advanced treatment) can remove 90 percent or more of the pollutant load in sewage. Some plants have additional systems to remove nutrients and pathogens, but these more advanced treatment steps get progressively more expensive.

Some industrial facilities generate wastewater that is similar to domestic sewage and can be treated by sewage treatment plants. Industries that generate wastewater with high concentrations of organic matter (e.g. oil and grease), toxic pollutants (e.g. heavy metals, volatile organic compounds) or nutrients such as ammonia, need specialized treatment systems. Some industries install a pre-treatment system to remove some pollutants (e.g., toxic compounds), and then discharge the partially treated wastewater to the municipal sewer system. Industries generating large volumes of wastewater typically operate their own treatment systems. Some industries have been successful at redesigning their manufacturing processes to reduce or eliminate pollutants, through a process called pollution prevention.

13.5.2 Chemical treatments

Chemical treatment, using chemical materials will react with a portion of the undesired chemicals and heavy metals, but a portion of the polluting material will remain unaffected. The cost of chemical additives and the environmental problem of disposing large amounts of chemical sludge make this treatment process deficient. Chemical wastewater treatment processes include chemical precipitation (coagulation, flocculation), ion exchange, neutralization, adsorption, and disinfection (chlorination/dichlorination, ozone, UV light). Chemical processes can greatly reduce the level of water pollution.

13.5.3 Microbial treatment

The microbial treatment process implements naturally occurring microorganisms to transform the dissolved organic matter into a dense biomass that can be separated from the treated wastewater by the sedimentation process. Bioremediation is a system that utilizes microorganisms to degrade the pollutants present in wastewater and in soil environments with technological innovations. It is a technique that removes biodegradable complex toxic substances into harmless and acceptable end products, e.g., CO2 and H2O through cellular metabolisms.

13.6 Summary

Water Pollutants :

1. **Action of Soaps and Detergents :** These contain surfactants that reduce water surface tension, making it easier for contaminants to spread. Phosphates in detergents contribute to eutrophication, causing algal blooms and oxygen depletion.

2. **Phosphates :** Excessive phosphates, mainly from detergents and fertilizers, lead to algal overgrowth, disrupting aquatic ecosystems and causing oxygen depletion.
3. **Arsenic :** A toxic element found in groundwater due to natural leaching and industrial discharge, causing severe health issues such as cancer and neurological disorders.
4. **Industrial Effluents :** Factories release heavy metals, chemicals, and toxins into water bodies, harming aquatic life and contaminating drinking water sources.
5. **Agricultural Runoff :** Pesticides, herbicides, and fertilizers wash into water bodies, leading to toxicity, eutrophication, and bioaccumulation in aquatic organisms.
6. **Radioactive Pollution :** Nuclear waste and mining activities release radioactive materials into water, posing long-term ecological and health risks.

Effects of Water Pollution on Animals and Plants :

Pollution disrupts aquatic ecosystems, leading to loss of biodiversity, bioaccumulation of toxins, and destruction of habitats. Contaminated water affects plant growth and reduces oxygen levels, harming aquatic organisms.

Water Pollution Control Measures :

1. **Wastewater Treatments:** Includes primary, secondary, and tertiary treatment methods to remove physical, biological, and chemical contaminants before discharge.
2. **Chemical Treatments:** Uses coagulants, disinfectants, and activated carbon to neutralize pollutants and purify water.
3. **Microbial Treatment:** Utilizes bacteria and microorganisms to break down organic pollutants in water, making it a sustainable and eco-friendly solution.

13.7 Self-assessment questions

1. How do soaps and detergents contribute to water pollution?
2. What environmental problem is caused by excessive phosphates in water bodies?
3. What are the major sources of arsenic contamination in water?
4. How do industrial effluents affect aquatic life?
5. What pollutants are commonly found in agricultural runoff?
6. How does radioactive pollution enter water bodies?

7. What are the effects of water pollution on aquatic plants?
8. How does water pollution impact animals in an ecosystem?
9. What is the primary goal of wastewater treatment?
10. Name the three main stages of wastewater treatment.
11. How do chemical treatments help in water purification?
12. What role do microorganisms play in water treatment?
13. Why is microbial treatment considered an eco-friendly solution?
14. How can individuals help reduce water pollution?
15. What are some preventive measures to control industrial water pollution?

13.8 References

Aggarwal K C (1999). Environmental pollution. Agro Botanica, Bikaner.

Aggarwal S K (2002). Pollution management-II water pollution. APH Publishing Corporation, New Delhi.

Gaur D (2005). Water pollution and its management. Sarup & Sons, New Delhi.

Goel R P (1997). Water pollution: causes, effects and control. New Age International (Pvt.) Ltd, New Delhi.

Unit-14 ❑ The Hydrosphere-II

Structure

14.0 Objectives

W

14.1 Introduction

W

14.2 Water quality parameters

Water quality is a measure of the condition of water relative to the requirements of one or more biotic species and/or to any human need or purpose. There are three types of water quality parameters physical, chemical, and biological parameters. We will learn some of the important terms of quality parameters in the following part.

14.2.1 DO

Dissolved oxygen (DO) is considered to be one of the most important parameters of water quality in streams, rivers, and lakes. DO is the amount of oxygen that is present in water. Water bodies receive oxygen from the atmosphere and from aquatic plants. Running water, such as that of a swift moving stream, dissolves more oxygen than the still water of a pond or lake. It is a key test of water pollution. Oxygen is slightly soluble in water and very sensitive to temperature. For example, the saturation concentration at 20°C is about 9 mg/L and at 0°C is 14.6 mg/L. The actual amount of dissolved oxygen varies depending on pressure, temperature, and salinity of the water.

Low levels of oxygen (hypoxia) or no oxygen levels (anoxia) can occur when excess organic materials, such as large algal blooms, are decomposed by microorganisms. During this decomposition process, DO in the water is consumed. Low oxygen levels often occur in the bottom of the water column and affect organisms that live in the sediments. In some water bodies, DO levels fluctuate periodically, seasonally and even as part of the natural daily ecology of the aquatic resource. As DO levels drop, some sensitive animals may move away, decline in health or even die. Dissolved oxygen has no direct effect on public health, but drinking water with very little or no oxygen tastes unpalatable to some people.

14.2.2 BOD

Bacteria and other microorganisms use organic substances for food. As they metabolize organic material, they consume oxygen. The organics are broken down into simpler compounds, such as CO_2 and H_2O, and the microbes use the energy released for growth and reproduction.When this process occurs in water, the oxygen consumed is the DO in the water. If oxygen is not continuously replaced by natural or artificial means in the water, the DO concentration will reduce as the microbes decompose the organic materials. This need for oxygen is called the biochemical oxygen demand (BOD). So, BOD represents the amount of oxygen consumed by bacteria and other microorganisms while they decompose organic matter under aerobic (oxygen is present) conditions at a specified temperature. The more organic material there is in the water, the higher the BOD used by the microbes will be. BOD is used, often in wastewater-treatment plants, as an index of the degree of organic pollution in water.

14.2.3 COD

Chemical Oxygen Demand (COD) is a test that measures the amount of oxygen required to chemically oxidize the organic material and inorganic nutrients, such as ammonia or nitrate, present in water. COD is measured via a laboratory assay in which a sample is incubated with a strong chemical oxidant for a specified time interval and at constant temperature (usually 2 h at 150°C). The most commonly used oxidant is potassium dichromate, which is used in combination with boiling sulphuric acid. It is important to note that the chemical oxidant is not specific to organic or inorganic compounds; hence both these sources of oxygen demand are measured in a COD.

14.2.4 TDS

Total dissolved solids (TDS) refer to the amount of minerals, metals, organic material and salts that are dissolved in a certain water volume. It is directly associated with the quality and purity of water. Total dissolved solids are measured as parts per million (ppm), and standard drinking water recommends a limit of 500 ppm. The lower the TDS, the better the water quality. For drinking water and fountain beverages, a TDS of up to 500 is acceptable, but for boiler-based steam ovens, TDS should be kept very low i.e. less than 100 ppm.

14.3 Desalination of sea water

Water is very essential for all living beings. It covers nearly 70% of earth's surface. Even though the major portion of earth is covered by water, there is severe shortage of drinking water in most of the countries across the world. World Health Organization guidelines state that the permissible limits of salinity in drinking water are 500 ppm and in few cases it may extend up to 1000 ppm. Most of the water on earth has salinity ranging upto 10,000 ppm and for sea water it may be in the range of 35,000-45,000 ppm due to its dissolved salts. So, salt removal or desalination ofthe sea water is proven to be effective alternatives in a variety of situations.

Desalination is an artificial process by which saline water (generally sea water) is converted to fresh water. The most common desalination processes are distillation and reverse osmosis.

14.4 Reverse osmosis

Reverse Osmosis (RO) is a relatively a new process used for desalination. Reverse Osmosis works by using a high pressure pump to increase the pressure on the salt side of the RO and force the water across the semi-permeable RO membrane, leaving almost all (around 95% to 99%) of dissolved salts behind in the reject stream. The amount of pressure required depends on the salt concentration of the feed water. The more concentrated the feed water, the more pressure is required to overcome the osmotic pressure.

The desalinated water that is demineralized or deionized, is called permeate (or product) water. The water stream that carries the concentrated contaminants that did not pass through the RO membrane is called the reject (or concentrate) stream.

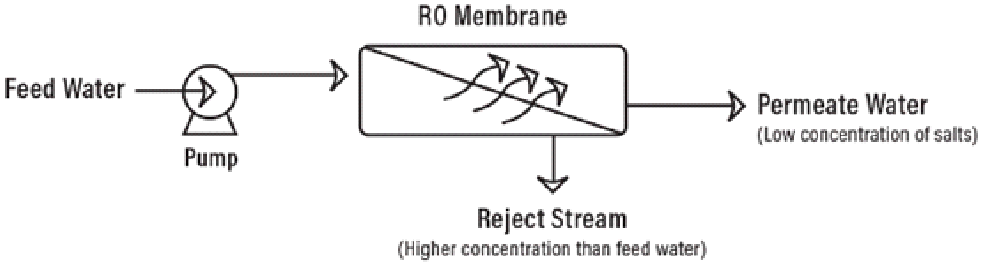


Figure 2. Reverse osmosis method for purification of water.

Reverse Osmosis is capable of removing up to 99% of the dissolved salts (ions), particles, colloids, organics, bacteria and pyrogens from the feed water (although an RO system should not be relied upon to remove 100% of bacteria and viruses). An RO membrane rejects contaminants based on their size and charge. Any contaminant that has a molecular weight greater than 200 is likely rejected by a properly running RO system (for comparison a water molecule has a MW of 18). Likewise, the greater the ionic charge of the contaminant, the more likely it will be unable to pass through the RO membrane. For example, a sodium ion has only one charge (monovalent) and is not rejected by the RO membrane as well as calcium for example, which has two charges. Likewise, this is why an RO system does not remove gases such as CO2 very well because they are not highly ionized (charged) while in solution and have a very low molecular weight.

14.5 Summary

In this unit we have learnt about different sources of water pollution and their aracteristics and harmful effects on animal and plants. We have discussed physical, chemical and microbial water pollution control treatments. Then we have learnt about different water quality parameters like DO, BOD, COD, TDS etc. which are important for testing the purity water. And finally we have learnt about the desalination of water and the reverse osmosis process for as a modern day water purification method.

14.6 Self-assessment questions

1. What are Pollutants? Give different type of water pollutants which lead to pollution of water.
2. Write the name of some diseases which occurs due to drinking of polluted water?
3. How can water pollution be prevented?

4. Why the DO level of water body falls when high-organic load discharged into it?
5. What is BOD and COD?
6. What is reverse osmosis process?

14.7 References

Gaur D (2005). Water pollution and its management. Sarup & Sons, New Delhi.

Goel R P (1997). Water pollution: causes, effects and control. New Age International (Pvt.) Ltd, New Delhi.