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INSTITUTE OF SCIENCE AND TECHNOLOGY
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School of Science and Humanities

Department of Chemistry

SCY1112

GENERAL CHEMISTRY II

Unit 1

Analytical Methods

Classification of analytical methods, advantages of instrumental methods - Qualitative Inorganic Analysis: Dry test, flame test, Cobalt nitrate test - Wet confirmatory tests for acid radicals - Interfering acid radicals- Theory of Interference- Elimination of Interfering acid radicals. Gravimetric analysis: mechanism of precipitation – solubility products –common ion effect – Types of precipitation – co-precipitation and post precipitation – homogeneous precipitation - General rules for precipitation Effect of digestion - washing of precipitates- Drying of precipitates Types, care and use of crucibles.

1. Introduction:

Analytical chemistry is the study of the separation, identification and quantification of the chemical components of natural and artificial materials. Analytical chemistry has applications in forensics, bioanalysis, clinical analysis, environmental analysis and materials analysis. Qualitative analysis is a method of analytical chemistry that deals with the determination of elemental composition of inorganic salts. It is mainly concerned with the detection of ions in an aqueous solution of the salt. For example, golden yellow in flame test shows the presence of sodium. Analytical methods can be separated into classical and instrumental.

1.1 Classical Methods:

- Separation are performed by precipitation, solvent extraction or distillation.
- Quantitative analysis performed by gravimetric and volumetric methods.
- Detection limits are in the ppm range.
- Precision can often be excellent.
- These methods are often labor intensive.

1.1.1 **Classification of Analytical Methods:**

The main techniques employed in quantitative analysis are based upon
(a) The quantitative performance of suitable chemical reactions and either measuring the amount of reagent needed to complete the reaction, or ascertaining the amount of reaction product obtained
(b) Appropriate electrical measurements (e.g. potentiometry)
(c) The measurement of certain optical properties (e.g. absorption spectra).

In some cases, a combination of optical or electrical measurements and quantitative chemical reaction (e.g. amperometric titration) may be used. The quantitative execution of chemical reactions is the basis of the traditional or 'classical' methods of chemical analysis: gravimetry, titrimetry and volumetry. In gravimetric analysis the substance being determined is converted into an insoluble precipitate which is collected and weighed, or in the special case of electrogravimetry electrolysis is carried out and the material deposited on one of the electrodes is weighed.

In titrimetric analysis, the substance to be determined is allowed to react with an appropriate reagent added as a standard solution, and the volume of solution needed for complete reaction is determined. The common types of reaction which are used in titrimetry are,

(a) Neutralization (acid-base) reactions
(b) Complex-forming reactions
(c) Precipitation reactions
(d) Oxidation-reduction reactions.

1.2 Instrumental Methods:

- Often these are semi to fully automated techniques that involve the manipulation of molecules, photons and electrons to provide simultaneous quantitative and qualitative analysis.
- Detection limit in the ppb range.
- Precision is dependent less on the operator and more on the instrument and sources of noise.

1.2.1 **Classification of Instrumental Methods:**

The methods dependent upon measurement of an electrical property, and those based upon determination of the extent to which radiation is absorbed or upon assessment of the intensity of emitted radiation, al1 require the use of a suitable instrument. e.g. polarograph, spectrophotometer, etc., and in consequence such methods are referred to as 'instrumental methods'.

Instrumental methods are usually much faster than purely chemical procedures, they are normally applicable at concentrations far too small to be amenable to determination by classical methods, and they find wide application in industry. In most cases a microcomputer can be interfaced to the instrument so that absorption curves, polarograms, titration curves, etc., can be plotted automatically by the incorporation of appropriate servo-mechanisms, the whole analytical process may, in suitable cases, be completely automated. Despite the advantages possessed by instrumental methods in many directions, their widespread adoption has not rendered the purely chemical or 'classical' methods obsolete; the situation is influenced by three main factors.

- The apparatus required for classical procedures is cheap and readily available in al1 laboratories, but many instruments are expensive and their use will only be justified if numerous samples have to be analyzed, or when dealing with the determination of substances present in minute quantities.
- With instrumental methods it is necessary to carry out a calibration operation using a sample of material of known composition as reference substance.
- Whilst an instrumental method is ideally suited to the performance of a large number of routine determinations, for an occasional, non-routine, analysis it is often simpler to use a classical method than to go to the trouble of preparing requisite standards and carrying out the calibration of an instrument.

Clearly, instrumental and classical methods must be regarded as supplementing each other. Electrical methods of analysis involve the measurement of current, voltage or resistance in relation to the concentration of a certain species in solution. Techniques which can be included under this general heading are

- (i) Voltammetry (measurement of current at a micro-electrode at a specified voltage)
- (ii) Coulometry (measurement of current and time needed to complete an electrochemical reaction or to generate sufficient material to react completely with a specified reagent)
- (iii) Potentiometry (measurement of the potential of an electrode in equilibrium with an ion to be determined)
- (iv) Conductometry (measurement of the electrical conductivity of a solution).

Optical methods of analysis are dependent either upon,

- (i) measurement of the amount of radiant energy of a particular wavelength absorbed by the sample, or
- (ii) the emission of radiant energy and measurement of the amount of energy of a particular wavelength emitted. Absorption methods are usually classified according to the wavelength involved as
  - (a) visible spectrophotometry (colorimetry),
  - (b) ultraviolet spectrophotometry, and
  - (c) infrared spectro- photometry.

Atomic absorption spectroscopy involves atomising the specimen, often by spraying a solution of the sample into a flame, and then studying the absorption of radiation from an electric lamp producing the spectrum of the element to be determined. Emission methods involve subjecting the sample to heat or electrical treatment so that atoms are raised to excited States causing them to emit energy: it is the intensity of this emitted energy which is measured. The common excitation techniques are:

(a) emission spectroscopy, where the sample is subjected to an electric arc or spark plasma and the light emitted (which may extend into the ultraviolet region) is examined;
(b) flame photometry, in which a solution of the sample is injected into a flame;
(c) fluorimetry, in which a suitable substance in solution (commonly a metal- fluorescent reagent complex) is excited by irradiation with visible or ultraviolet radiation.

Chromatography is a separation process employed for the separation of mixtures of substances. It is widely used for the identification of the components of mixtures, it is often possible to use the procedure to make quantitative determinations, particularly when using Gas Chromatography (GC) and High Performance Liquid Chromatography (HPLC).

1.3 OTHER TECHNIQUES:

In addition to the main general methods of analysis outlined above there are also certain specialized techniques which are applied in special circumstances. Among these are X-ray methods, methods based upon the measurement of radioactivity, mass spectrometry, the so-called kinetic methods, and thermal methods.

- X-ray methods. When high-speed electrons collide with a solid target (which can be the material under investigation), X-rays are produced. These are often referred to as primary X-rays, and arise because the electron beam may displace an electron from the inner electron shells of an atom in the target, and the electron lost is then replaced by one from an outer shell; in this process energy is emitted as X-rays. In the resultant X-ray emission it is possible to identify certain emission peaks which are characteristic of elements contained in the target. The wavelengths of the peaks can be related to the atomic number of the elements producing them, and thus provide a means of identifying elements present in the target sample. Further, under controlled conditions, the intensity of the peaks can be used to determine the amounts of the various elements present. This is the basis of electron probe microanalysis, in which a small target area of the sample is pinpointed for examination. This has important applications in metallurgical research, in the examination of geological samples, and in determining whether biological materials contain metallic elements.

- X-ray fluorescence analysis is a rapid process which finds application in metallurgical laboratories, in the processing of metallic ores, and in the cement industry.
- Mass spectrometry. In this technique, the material under examination is vapourised under a high vacuum and the vapour is bombarded by a high-energy electron beam. Many of the vapour molecules undergo fragmentation and produce ions of varying size. These ions can be distinguished by accelerating them in an electric field, and then deflecting them in a magnetic field where they follow paths dictated by their mass/charge ratio (m/e) to detection and recording equipment: each kind of ion gives a peak in the mass spectrum. Non-volatile inorganic materials can be examined by vapourising them by subjecting them to a high-voltage electric spark. Mass spectrometry can be used for gas analysis, for the analysis of petroleum products, and in examining semiconductors for impurities. It is also a very useful tool for establishing the structure of organic compounds.
- Thermal methods. Changes in weight, or changes in energy, recorded as a function of temperature (or of time) can provide valuable analytical data. Common techniques include the recording as a function of temperature or time of,
  (a) change in weight (Thermogravimetry, TG);
  (b) the difference in temperature between a test substance and an inert reference material (Differential Thermal Analysis, DTA);
  (c) the energy necessary to establish a zero temperature difference between a test substance and a reference material (Differential Scanning Calorimetry, DSC).

1.4 Advantages of Instrumental Methods:

- A small amount of a sample is needed for analysis.
- Determination by instrumental method is considerably fast.
- Complex mixture can be analyzed either with or without separation.
- Sufficient reliability and accuracy of results are obtained by instrumental method.

1.5 Limitation of Instrumental Methods:

- In general, instrumental methods are costly because of its cost, maintenance and trained personnel required for their handling.
- The sensitivity and accuracy depends upon the type of instrument.
- Specialized training for handling instrument is required.
- There is frequent need of checking results with other methods.

- In some cases, instrumental method may not be specific.

1.6 FACTORS AFFECTING THE CHOICE OF ANALYTICAL METHODS

The techniques have differing degrees of sophistication, of sensitivity, of selectivity, of cost and also of time requirements, and an important task for the analyst is the selection of the best procedure for a given determination. This will require careful consideration of the following criteria.

- The type of analysis required: elemental or molecular, routine or occasional.
- Problems arising from the nature of the material to be investigated, e.g. radioactive substances, corrosive substances, substances affected by water.
- Possible interference from components of the material other than those of interest.
- The concentration range which needs to be investigated.
- The accuracy required.
- The facilities available; this will refer particularly to the kinds of instrumentation which are at hand.
- The time required to complete the analysis; this will be particularly relevant when the analytical results are required quickly for the control of a manufacturing process. This may mean that accuracy has to be a secondary rather than a prime consideration, or it may require the use of expensive instrumentation.

1.7 Qualitative Inorganic Analysis:

The qualitative inorganic analysis is a method of analytical chemistry that seeks to find out the elemental composition of inorganic compounds through various reagents. It is mainly focused on detection of ions in an aqueous solution, so the substances in other states need to be converted into an aqueous solution before starting the experiment.

1.7.1 Dry test

This test is performed by heating a small amount of salt in a dry test tube. Quite valuable information can be gathered by carefully performing and noting the observations. On heating, some salts undergo decomposition, thus evolving the gases.

(a) Identification of Anions (Acid Radicals)

The identification of the radicals is first done on the basis of the preliminary tests. The Dry heating test is one of the preliminary tests performed earlier which may give some important information about the acid radical present. The other preliminary tests are based on the fact that:

- CO_3^{2-}, S^{2-}, NO_2^- and SO_3^{2-} react with dil. H_2SO_4 to give out CO_2, H_2S, NO_2 and SO_2 gases respectively. These gases on identification indicate the nature of the anion present in the salt.
- Cl^-,Br^-,I^-,NO_{3-} and $C_2O_4^{2-}$ and CH_3COO^- react with conc. H_2SO_4 but not with dil. H_2SO_4 to produce characteristic gases.
- SO_4^{2-} and PO_4^{3-} react neither with dil H_2SO_4 nor with conc. H_2SO_4. These are, therefore, identified by individual tests.

- Thus, these anions may be identified by performing the following tests below:

(b) Dil. H_2SO_4 Tests

Treat a pinch of the salt with dil. H_2SO_4 and identify the gas evolved.Dilute H_2SO_4 decomposes carbonates, sulphides, sulphites and nitrites in cold to give gases. These gases on identification indicate the nature of the anion present in the salt.

(i) Carbonate: On treating the solid carbonate, CO_2 is given off in the cold with brisk effervescence.

$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2O + CO_2\uparrow$$

(ii) Sulphide: Sulphides when treated with dil. H_2SO_4 give H_2S gas.

$$ZnS + H_2SO_4 \rightarrow ZnSO_4 + H_2S\uparrow$$

(iii) Sulphite: On heating solid sulphite with dil.H_2SO_4, SO_2 gas is evolved

$$Na_2SO_3 + H_2SO_4 \rightarrow Na_2SO_4 + H_2O + SO_2\uparrow$$

(iv) Nitrite: On treating solid nitrite with dil. H_2SO_4, nitric oxide (NO) gas is evolved which readly gives brown fumes of NO_2 with the oxygen of the air.

$$KNO_2 + H_2SO_4 \rightarrow KHSO_4 + HNO_2] \times 3$$

$$3HNO_2 \rightarrow HNO_3 + H_2O + 2NO$$

$$3KNO_2 + 3H_2SO_4 \rightarrow 3KHSO_4 + HON_3 + H_2O + 2NO$$

$$\underset{\text{(Colourless)}}{2NO + O_2} \rightarrow \underset{\text{(Brown fumes)}}{2NO_2}$$

(c) Conc. H_2SO_4 Test:

If no action takes place with dil. H_2SO_4, warm a pinch of the salt with conc. H_2SO_4 and identify the gas evolved. Chemical Reactions Involved in Conc. H_2SO_4 Test:

(i) Chlorides: Chloride salts react with conc. H_2SO_4 to evolve hydrogen chloride (HCl) gas.

$$NaCl + H_2SO_4 \rightarrow \underset{\text{Sodium bisulphate}}{NaHSO_4} + HCl\uparrow$$

(ii) Bromides: Bromide salts react with conc. H_2SO_4 to evolve bromine gas.

$$NaBr + H_2SO_4 \rightarrow \underset{\text{Sodium bisulphate}}{NaHSO_4} + HBr$$

$$H_2SO_4 + 2HBr \rightarrow SO_2 + Br_2\uparrow + 2H_2O$$

(iii) Iodides: Iodide salts react with conc. H_2SO_4 to evolve vapours of iodine.

$$KI + H_2SO_4 \rightarrow KHSO_4 + HI$$

$$H_2SO_4 + 2HI \rightarrow SO_2 + I_2\uparrow + 2H_2O$$

(iv) Nitrates: Upon reaction with conc.H_2SO_4 nitrates evolve NO_2 gas.

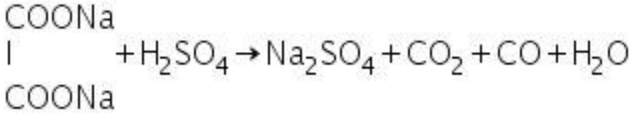
$$KNO_3 + H_2SO_4 \rightarrow KHSO_4 + HNO_3$$

$$4HNO_3 + \underset{\text{(Paper pellet)}}{C} \rightarrow 4NO_2\uparrow + CO_2 + 2H_2O$$

(v) Acetates: Acetates react with conc. H_2SO_4 to produce vapours of acetic acid.

$$CH_3COONa + H_2SO_4 \rightarrow NaHSO_4 + \underset{\text{Acetic acid}}{CH_3COOH}\uparrow$$

(vi) Oxalates: Oxalates salts react with conc. H_2SO_4 to evolve a mixture of carbon dioxide and carbon monoxide.



$$\begin{array}{l} COONa \\ | \\ COONa \end{array} + H_2SO_4 \rightarrow Na_2SO_4 + CO_2 + CO + H_2O$$

(d) Independent Group.

(SO_4^{2-} and PO_4^{3-}) Test:

If the salt does not react with dil H_2SO_4 as well as with conc. H_2SO_4 test for $SO_4^{2-}$and PO_4^{3-} by performing their individual tests.

(i)Potassium permanganate Test

This test is performed by using dilute sulphuric acid and potassium permanganate as reagents. This test helps in the detection of Cl^-, Br^-, I^- and $C_2O_4^{2-}$. Chemical reactions involved in Potassium permanganate test:

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

(a) Chlorides: $NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl$

$$2HCl + [O] \rightarrow H_2O + Cl_2\uparrow$$

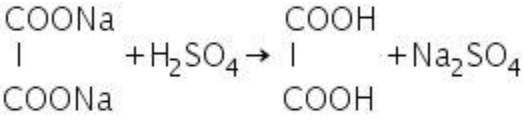
(b) Bromides: $NaBr + H_2SO_4 \rightarrow NaHSO_4 + HBr$

$$2HBr + [O] \rightarrow H_2O + Br_2\uparrow$$

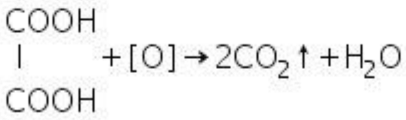
(c) Iodides: $NaI + H_2SO_4 \rightarrow NaHSO_4 + HI$

$$2HI + [O] \rightarrow H_2O + I_2\uparrow$$

(d) Oxalates:



$$\begin{array}{c} COONa \\ | \\ COONa \end{array} + H_2SO_4 \rightarrow \begin{array}{c} COOH \\ | \\ COOH \end{array} + Na_2SO_4$$



$$\begin{array}{c} COOH \\ | \\ COOH \end{array} + [O] \rightarrow 2CO_2\uparrow + H_2O$$

1.7.2 Wet Tests for Acid Radicals (Anions)

Let us discuss the chemical reactions involved in the confirmation of Anions:

(a) Confirmation of Carbonate (CO_3^{2-})

(i) Reaction with di.l HCl:

Carbonate on reaction with dil. HCl gives CO_2 gas that reacts with lime water to produce a white precipitate of calcium carbonate that turns lime water milky. In case of soluble carbonate, this test is performed with water extract and in case of insoluble carbonates, this test is performed with the solid salt.

$$\underset{\text{Calcium carbonate}}{CaCO_3} + 2HCl \rightarrow CaCl_2 + CO_2 + H_2O$$

$$\underset{\text{Lime water}}{Ca(OH)_2} + CO_2 \rightarrow \underset{\text{Milkness}}{CaCO_3\downarrow} + H_2O$$

(ii) Magnesium sulphate test:

This test is performed in the case of soluble carbonates only. Soluble carbonates react with the magnesium sulphate solution to form a white precipitate of magnesium carbonate.

$$\underset{\text{Sodium carbonate}}{Na_2CO_3} + MgSO_4 \rightarrow \underset{\text{White precipitate}}{MgCO_3\downarrow} + Na_2SO_4$$

(b) Confirmation of Sulphite (SO_3^{2-})

(i) Barium chloride test

Sulphites on reaction with barium chloride to form a white precipitate of barium sulphite. Barium sulphite dissolved in dil. HCl with the evolution of sulphur dioxide gas.

$$\underset{\text{Sodium carbonate}}{Na_2SO_3} + \underset{\text{Barium chloride}}{BaCl_2} \rightarrow 2NaCl + \underset{\substack{\text{Barium Sulphite}\\ \text{(White precipitate)}}}{BaSO_3\ (s)}$$

$$BaSO_3 + 2HCl \rightarrow BaCl_2 + SO_2\ (g) + H_2O$$

(ii) Potassium permanganate test

The colour of potassium permanganate is discharged when it reacts with sulphite. The reaction is given below.

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

$$Na_2SO_3 + [O] \rightarrow Na_2SO_4$$

(iii) Potassium dichromate test

A green colour is obtained when sulphites react with potassium dichromate solution.

$$K_2Cr_2O_7 + 4H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3[O]$$

$$Na_2SO_3 + [O] \rightarrow Na_2SO_4$$

(c) Confirmation of Sulphide (S^{2-})

(i) Sodium nitroprusside test

Sulphides give a violet or purple colouration with the sodium nitroprusside solution due to the formation of $Na_4[Fe(CN)_5NOS]$.

$$Na_2S + \underset{\text{Sodium nitroprusside}}{Na_2[Fe(CN)_5NO]} \rightarrow \underset{\text{(Violet or Purple colouration)}}{Na_4[Fe(CN)_5NOS]}$$

(ii) Lead acetate test

Sulphides react with lead acetate to form a black precipitate of lead sulphide.

$$Na_2S + (CH_3COO)_2Pb \rightarrow \underset{\text{Black precipitate}}{PbS\downarrow} + 2CH_3COONa$$

(iii) Cadmium carbonate test:

Sulphides react with a suspension of cadmium carbonate to form a yellow precipitate of cadmium sulphide.

$$Na_2S + CdCO_3 \rightarrow \underset{\substack{\text{Cadmium sulphide}\\ \text{(Yellow precipitate)}}}{CdS\downarrow} + Na_2CO_3$$

(d) Confirmation of Nitrite (NO_2^-)

(i) Ferrous sulphate test

Nitrites give a dark brown or black colouration in ferrous sulphate test due to the formation of $FeSO_4.NO$.

$$KNO_2 + CH_3COOH \rightarrow CH_3COOK + HNO_2$$

$$3HNO_2 \rightarrow HNO_3 + 2NO + H_2O$$

$$FeSO_4 + NO \rightarrow \underset{\text{(Dark brown or Black)}}{FeSO_4.NO}$$

(ii) Starch - Iodide test

Nitrites react with potassium iodide in the presence of dilute sulphuric acid to liberate iodine. Iodine forms a blue-black complex with starch.

$$2KI + 2H_2SO_4 + 2HNO_2 \rightarrow 2KHSO_4 + \underset{\text{Iodine}}{I_2} + 2NO + 2H_2O$$

$$I_2 + \text{Starch} \rightarrow \text{Blue-black complex}$$

(iii) Diphenylamine test

In the presence of nitrites, diphenylamine is oxidised, giving a blue colouration.

(e) Confirmation of Nitrate (NO_3^-)

(i) Diphenylamine test

In the presence of nitrates, diphenylamine is oxidised, giving a blue colouration.

(ii) Copper turnings test

In this reaction copper turnings reduces nitrates to reddish brown NO_2 gas.

(iii) Brown-ring test

This test can be performed by adding a solution of iron (II) sulphate to a solution of nitrate, followed by the slow addition of concentrated sulphuric acid, such that the sulphuric acid forms a layer below the aqueous solution. The formation of a brown ring at the junction of two layers indicates the presence of nitrate. The overall reaction is the reduction of nitrate ion by iron (II) which reduced to iron (I) and formation of a nitrosonium complex where nitric oxide is oxidised to NO^+.

$$KNO_3 + H_2SO_4 \rightarrow KHSO_4 + HNO_3$$

$$6FeSO_4 + 3H_2SO_4 + 2HNO_3 \rightarrow 3Fe_2(SO_4)_3 + 4H_2O + 2NO$$

$$FeSO_4 + NO + 5H_2O \rightarrow \underset{\text{Brown ring}}{[Fe(NO)(H_2O)_5SO_4}$$

(e) Confirmation of Chloride (Cl^-)

(i) Silver nitrate test

Chlorides on reaction with silver nitrate solution to form a white precipitate of silver chloride which is soluble in ammonium hydroxide.

$$NaCl + AgNO_3 \rightarrow \underset{\text{White precipitate}}{AgCl\downarrow} + NaNO_3$$

$$AgCl + 2NH_4OH \rightarrow \underset{\text{Soluble Complex}}{[Ag(NH_3)_2]Cl} + 2H_2O$$

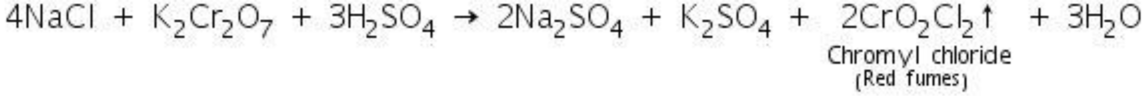
(ii) Manganese dioxide test

When chloride salts react with manganese dioxide and concentrated sulphuric acid, chlorine gas is liberated.

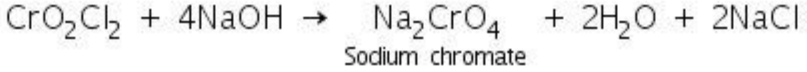
$$2NaCl + MnO_2 + 3H_2SO_4 \rightarrow 2NaHSO_4 + MnSO_4 + 2H_2O + Cl_2\uparrow$$

(iii) Chromyl chloride test

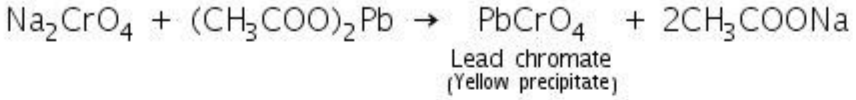
When chloride salts react with potassium dichromate and conc. sulphuric acid red fumes of chromyl chloride is formed which reacts with sodium hydroxide to form yellow solution of sodium chromate. Sodium chromate reacts with lead acetate in presence of dil. acetic acid to form yellow precipitate of lead chromate.



$$4NaCl + K_2Cr_2O_7 + 3H_2SO_4 \rightarrow 2Na_2SO_4 + K_2SO_4 + \underset{\substack{\text{Chromyl chloride}\\ \text{(Red fumes)}}}{2CrO_2Cl_2\uparrow} + 3H_2O$$



$$CrO_2Cl_2 + 4NaOH \rightarrow \underset{\text{Sodium chromate}}{Na_2CrO_4} + 2H_2O + 2NaCl$$

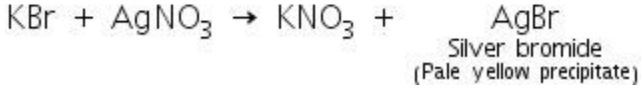


$$Na_2CrO_4 + (CH_3COO)_2Pb \rightarrow \underset{\substack{\text{Lead chromate}\\ \text{(Yellow precipitate)}}}{PbCrO_4} + 2CH_3COONa$$

(f) Confirmation of Bromide (Br^-)

(i) Silver nitrate test

Bromides on reaction with silver nitrate solution forms a pale yellow precipitate of silver bromide which is sparingly soluble in ammonium hydroxide.



$$KBr + AgNO_3 \rightarrow KNO_3 + \underset{\substack{\text{Silver bromide}\\ \text{(Pale yellow precipitate)}}}{AgBr}$$

(ii) Manganese dioxide test

When bromide salts react with manganese dioxide and concentrated sulphuric acid, bromine gas is liberated.

$$2KBr + MnO_2 + 3H_2SO_4 \rightarrow 2KHSO_4 + MnSO_4 + 2H_2O + Br_2\uparrow$$

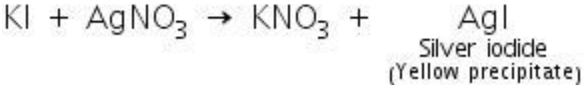
(iii) Chlorine water test

Bromine liberated in this test being soluble in carbon disulphide imparts an orange colour to the carbon disulphide layer.

$$2KBr + Cl_2 \rightarrow 2KCl + Br_2$$

(iv) Silver nitrate test

Iodides on reaction with silver nitrate solution forms an yellow precipitate of silver iodide which is insoluble in ammonium hydroxide.



$$KI + AgNO_3 \rightarrow KNO_3 + \underset{\substack{\text{Silver iodide}\\ \text{(Yellow precipitate)}}}{AgI}$$

(v) Manganese dioxide test:

When iodide salts react with manganese dioxide and concentrated sulphuric acid, iodine gas is liberated.

$$2KI + MnO_2 + 3H_2SO_4 \rightarrow 2KHSO_4 + MnSO_4 + 2H_2O + I_2\uparrow$$

(vi) Chlorine water test

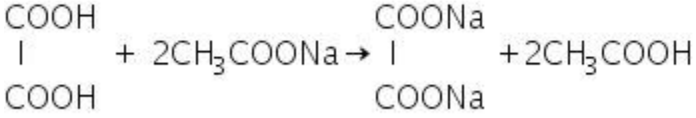
Iodine liberated in this test being soluble in carbon disulphide imparts a violet colour to the carbon disulphide layer.

$$2KI + Cl_2 \rightarrow 2KCl + I_2$$

(g) Confirmation of Acetate (CH_3COO^-)

(i) Oxalic acid test

Oxalic acid reacts with acetate salt to form acetic acid which has a characteristic vinegar like smell.



$$\begin{matrix} COOH \\ | \\ COOH \end{matrix} + 2CH_3COONa \rightarrow \begin{matrix} COONa \\ | \\ COONa \end{matrix} + 2CH_3COOH$$

(ii) Ester test

Acetate salts react with conc. sulphuric acid and ethyl alcohol to form the ester, ethyl acetate which has a fruity smell.

$$2CH_3COONa + H_2SO_4 \rightarrow Na_2SO_4 + 2CH_3COOH$$

$$CH_3COOH + C_2H_5OH \rightarrow \underset{\substack{\text{Ethyl acetate} \\ \text{(Fruity smell)}}}{CH_3COOC_2H_5} + H_2O$$

(iii) Ferric chloride test

The reaction takes place in the ferric chloride test is given by the following equations.

$$3CH_3COONa + FeCl_3 \rightarrow (CH_3COO)_3Fe + 3NaCl$$

$$(CH_3COO)_3Fe + 2H_2O \rightarrow \underset{\text{Reddish brown precipitate}}{(CH_3COO)(OH)_2Fe\downarrow} + 2CH_3COOH$$

(h) Confirmation of Oxalate ($C_2O_4^{2-}$)

(i) Calcium chloride test

Oxalate salts react with calcium chloride to form white precipitate of calcium oxalate.

$$(NH_4)_2C_2O_4 + CaCl_2 \rightarrow \underset{\text{White precipitate}}{CaC_2O_4\downarrow} + 2NH_4Cl$$

(ii) Potassium permanganate test

In this test, the pink colour of potassium permanganate is decolourised with the evolution of carbon dioxide gas.

$$2KMnO_4 + 3H_2SO_4 + \underset{\text{Oxalic acid}}{5H_2C_2O_4} \rightarrow K_2SO_4 + 2MnSO_4 + 10CO_2\uparrow + 8H_2O$$

(i) Confirmation of Sulphate (SO_4^{2-})

(i) Barium chloride test

Sulphates react with barium chloride to form white precipitate of barium sulphate.

$$Na_2SO_4 + BaCl_2 \rightarrow \underset{\text{White precipitate}}{BaSO_4\downarrow} + 2NaCl$$

(ii) Match stick test
Violet streaks are produced during this test.

(iii) Lead acetate test
Sulphates react with lead acetate to form white precipitate of lead sulphate.

$$Na_2SO_4 + (CH_3COO)_2Pb \rightarrow \underset{\text{White precipitate}}{PbSO_4\downarrow} + 2CH_3COONa$$

(j) Confirmation of Phosphate (PO_4^{3-})
(i) Ammonium molybdate test
Phosphate salts react with ammonium molybdate solution to form a deep yellow precipitate of ammonium phosphate molybdate. The chemical reaction is as follows:

$$K_3PO_4 + \underset{\text{Ammonium Molybdate}}{3(NH_4)_2MoO_4} \rightarrow 2(NH_4)_3PO_4 + \underset{\text{Potassium molybdate}}{3K_2MoO_4}$$

$$K_2MoO_4 + 2HNO_3 \rightarrow \underset{\text{Molybdic acid}}{H_2MoO_4} + 2KNO_3$$

$$H_2MoO_4 \rightarrow MoO_3 + H_2O$$

$$(NH_4)_3PO_4 + 12MoO_3 + 6H_2O \rightarrow \underset{\substack{\text{Ammonium phosphate molybdate} \\ \text{(Yellow precipitate)}}}{(NH_4)_3PO_4.12MoO_3.6H_2O}$$

(ii) Magnesia mixture test
Phosphate salts react with magnesia mixture to form white precipitate of magnesium ammonium phosphate.

$$\underset{\text{Disodium hydrogen phoisphate}}{Na_2HPO_4} + MgCl_2 + NH_4OH \rightarrow \underset{\substack{\text{Magnesium ammonium phosphate} \\ \text{(White precipitate)}}}{Mg(NH_4)PO_4\downarrow} + 2NaCl + H_2O$$

1.8 Gravimetric analysis:

1.8.1 Mechanism of precipitation:

In precipitation gravimetry an insoluble compound forms when we add a precipitating reagent, or **precipitant**, to a solution that contains our analyte. In most cases the precipitate is the product of a simple metathesis reaction between the analyte and the precipitant; however, any reaction that generates a precipitate potentially can serve as a gravimetric method. All precipitation gravimetric analyses share two important attributes. First, the precipitate must be of low solubility, of high purity, and of known composition if its mass is to reflect accurately the analyte's mass. Second, it must be easy to separate the precipitate from the reaction mixture.

Avoiding Impurities:

In addition to having a low solubility, a precipitate must be free from impurities. Because precipitation usually occurs in a solution that is rich in dissolved solids, the initial precipitate often is impure.

One common impurity is an **inclusion**, in which a potential interferent, whose size and charge is similar to a lattice ion, can substitute into the lattice structure if the interferent precipitates with the same crystal structure (Figure 8.2.48.2.4a). The probability of forming an inclusion is greatest when the interfering ion's concentration is substantially greater than the lattice ion's concentration. An inclusion does not decrease the amount of analyte that precipitates, provided that the precipitant is present in sufficient excess. Thus, the precipitate's mass always is larger than expected.

An inclusion is difficult to remove since it is chemically part of the precipitate's lattice. The only way to remove an inclusion is through **reprecipitation** in which we isolate the precipitate from its supernatant solution, dissolve the precipitate by heating in a small portion of a suitable solvent, and then reform the precipitate by allowing the solution to cool. Because the interferent's concentration after dissolving the precipitate is less than that in the original solution, the amount of included material decreases upon reprecipitation. We can repeat the process of reprecipitation until the inclusion's mass is insignificant. The loss of analyte during reprecipitation, however, is a potential source of determinate error.

An **occlusion** forms when an interfering ions is trapped within the growing precipitate. Unlike an inclusion, which is randomly dispersed within the precipitate, an occlusion is localized, either along flaws within the precipitate's lattice structure or within aggregates of individual precipitate particles. An occlusion usually increases a precipitate's mass; however, the precipitate's mass is smaller if the occlusion includes the analyte in a lower molecular weight form than that of the precipitate.

We can minimize an occlusion by maintaining the precipitate in equilibrium with its supernatant solution for an extended time, a process called digestion. During a **digestion**, the dynamic nature of the solubility–precipitation equilibria, in which the precipitate dissolves and reforms, ensures that the occlusion eventually is reexposed to the supernatant solution. Because the rates of dissolution and reprecipitation are slow, there is less opportunity for forming new occlusions.

After precipitation is complete the surface continues to attract ions from solution these **surface adsorbates** comprise a third type of impurity. We can minimize surface adsorption by decreasing the precipitate's available surface area. One benefit of digestion is that it increases a precipitate's average particle size. Because the probability that a particle will dissolve completely is inversely proportional to its size, during digestion larger particles increase in size at the expense of smaller particles. One consequence of forming a smaller number of larger particles is an overall decrease in the precipitate's surface area. We also can remove surface adsorbates by washing the precipitate, although we cannot ignore the potential loss of analyte.

Inclusions, occlusions, and surface adsorbates are examples of **coprecipitates**—otherwise soluble species that form along with the precipitate that contains the analyte. Another type of impurity is an interferent that forms an independent precipitate under the conditions of the analysis. For example, the precipitation of nickel dimethylglyoxime requires a slightly basic pH. Under these conditions any Fe^{3+} in the sample will precipitate as $Fe(OH)_3$. In addition, because most precipitants rarely are selective toward a single analyte, there is a risk that the precipitant will react with both the analyte and an interferent. In addition to forming a precipitate with Ni^{2+}, dimethylglyoxime also forms precipitates with Pd^{2+} and Pt^{2+}. These cations are potential interferents in an analysis for nickel.

We can minimize the formation of additional precipitates by controlling solution conditions. If an interferent forms a precipitate that is less soluble than the analyte's precipitate, we can precipitate the interferent and remove it by filtration, leaving the analyte behind in solution. Alternatively, we can mask the analyte or the interferent to prevent its precipitation. Both of the approaches outline above are illustrated in Fresenius' analytical method for the determination of Ni in ores that contain Pb^{2+}, Cu^{2+}, and Fe^{3+}. Dissolving the ore in the presence of H_2SO_4 selectively precipitates Pb^{2+} as $PbSO_4$. Treating the resulting supernatant with H_2S precipitates Cu^{2+} as CuS. After removing the CuS by filtration, ammonia is added to precipitate Fe^{3+} as $Fe(OH)_3$. Nickel, which forms a soluble amine complex, remains in solution.

Controlling Particle Size:

Size matters when it comes to forming a precipitate. Larger particles are easier to filter and, as noted earlier, a smaller surface area means there is less opportunity for surface adsorbates to form. By controlling the reaction conditions we can significantly increase a precipitate's average particle size. The formation of a precipitate consists of two distinct events: nucleation, the initial formation of smaller, stable particles of the precipitate, and particle growth. Larger particles form when the rate of particle growth exceeds the rate of nucleation. Understanding the conditions that favor particle growth is important when we design a gravimetric method of analysis.
We define a solute's **relative supersaturation**, *RSS*, as,

$$\mathrm{RSS} = \mathrm{Q}-\mathrm{S}/\mathrm{S}$$

Where,
Q is the solute's actual concentration and *S* is the solute's concentration at equilibrium

The numerator of equation $Q - S$, is a measure of the solute's supersaturation. A solution with a large, positive value of *RSS* has a high rate of nucleation and produces a precipitate with many small particles. When the *RSS* is small, precipitation is more likely to occur by particle growth than by nucleation. A supersaturated solution is one that contains more dissolved solute than that predicted by equilibrium chemistry. A supersaturated solution is inherently unstable and precipitates solute to reach its equilibrium position. How quickly precipitation occurs depends, in part, on the value of *RSS*.
A visible precipitate takes longer to form when *RSS* is small both because there is a slow rate of nucleation and because there is a steady decrease in *RSS* as the precipitate forms. One solution to the latter problem is to generate the precipitant *in situ* as the product of a slow chemical reaction, which effectively maintains a constant *RSS*. Because the precipitate forms under conditions of low *RSS*, initial nucleation produces a small number of particles. As additional precipitant forms, particle growth supersedes nucleation, which results in larger particles of precipitate. This process

is called a **homogeneous precipitation**. Two general methods are used for homogeneous precipitation. If the precipitate's solubility is pH-dependent, then we can mix the analyte and the precipitant under conditions where precipitation does not occur, and then increase or decrease the pH by chemically generating OH^- or H_3O^+. For example, the hydrolysis of urea, $CO(NH_2)_2$, is a source of OH^- because of the following two reactions.

$CO(NH_2)_{2(aq)} + H_2O_{(l)} \rightleftharpoons 2NH_{3(aq)} + CO_{2(g)}$ -------- (1)
$CO(NH_2)_{2(aq)} + H2O_{(l)} \rightleftharpoons 2NH_{3(aq)} + CO_{2(g)}$ -------- (2)
$NH_{3(aq)} + H_2O_{(l)} \rightleftharpoons OH^-_{(aq)} + NH_4^+{}_{(aq)}$ -------- (3)
$NH_3(aq) + H_2O_{(l)} \rightleftharpoons OH^-_{(aq)} + NH_4^+{}_{(aq)}$ -------- (4)

Because the hydrolysis of urea is temperature-dependent—the rate is negligible at room temperature. we can use temperature to control the rate of hydrolysis and the rate of precipitate formation.

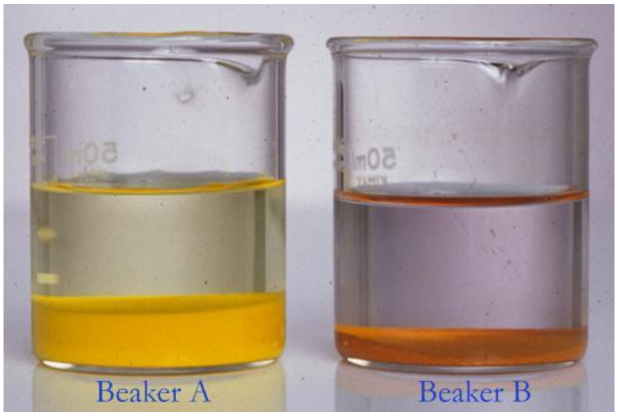


Fig.1. Homogeneous Precipitation

A homogeneous precipitation produces large particles of precipitate that are relatively free from impurities. These advantages, however, are offset by the increased time needed to produce the precipitate and by a tendency for the precipitate to deposit as a thin film on the container's walls. The latter problem is particularly severe for hydroxide precipitates generated using urea. An additional method for increasing particle size deserves mention. When a precipitate's particles are electrically neutral they tend to coagulate into larger particles that are easier to filter. Surface adsorption of excess lattice ions, however, provides the precipitate's particles with a net positive or a net negative surface charge. Electrostatic repulsion between particles of similar charge prevents them from coagulating into larger particles.

The precipitation of AgCl from a solution of $AgNO_3$ using NaCl as a precipitant to illustrate this effect. Early in the precipitation, when NaCl is the limiting reagent, excess Ag^+ ions chemically adsorb to the AgCl particles, forming a positively charged primary adsorption layer The solution outside the secondary adsorption layer remains electrically neutral. **Coagulation** cannot occur if the secondary adsorption layer is too thick because the individual particles of AgCl are unable to approach each other closely enough.

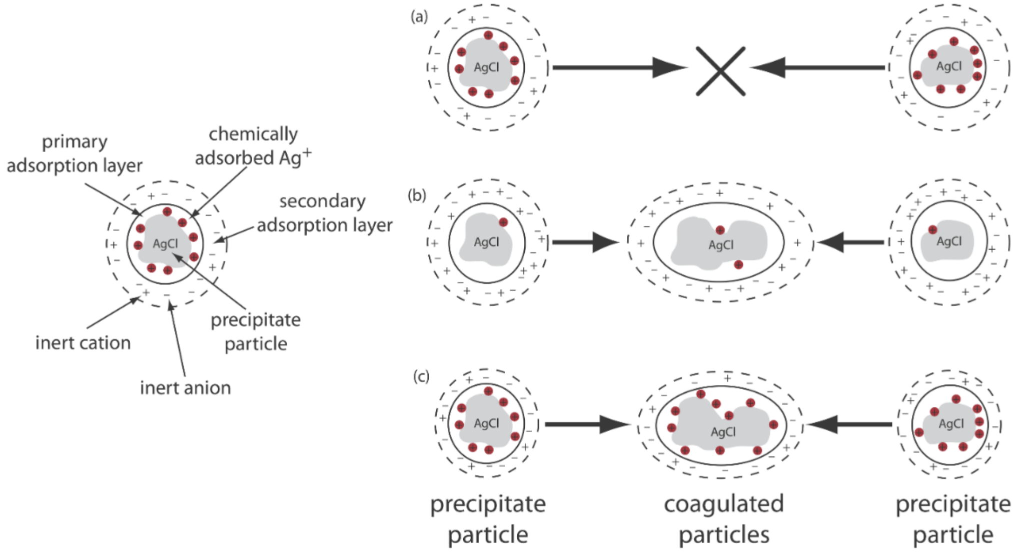


Fig. 2. Example for Coagulation

We can induce coagulation in three ways: by decreasing the number of chemically adsorbed Ag^+ ions, by increasing the concentration of inert ions, or by heating the solution. As we add additional NaCl, precipitating more of the excess Ag^+, the number of chemically adsorbed silver ions decreases and coagulation occurs. Adding too much NaCl, however, creates a primary adsorption layer of excess $Cl^–$ with a loss of coagulation.

A second way to induce coagulation is to add an inert electrolyte, which increases the concentration of ions in the secondary adsorption layer. With more ions available, the thickness of the secondary absorption layer decreases. Particles of precipitate may now approach each other more closely, which allows the precipitate to coagulate. The amount of electrolyte needed to cause spontaneous coagulation is called the critical coagulation concentration. Heating the solution and the precipitate provides a third way to induce coagulation. As the temperature increases, the number of ions in the primary adsorption layer decreases, which lowers the precipitate's surface charge. In addition, heating increases the particles' kinetic energy, allowing them to overcome the electrostatic repulsion that prevents coagulation at lower temperatures.

Filtering the Precipitate

After precipitating and digesting a precipitate, we separate it from solution by filtering. The most common filtration method uses filter paper, which is classified according to its speed, its size, and its ash content on ignition. Speed, or how quickly the supernatant passes through the filter paper, is a function of the paper's pore size. A larger pore size allows the supernatant to pass more quickly through the filter paper, but does not retain small particles of precipitate. Filter paper is rated as fast (retains particles larger than 20–25 μm), medium–fast (retains particles larger than 16 μm), medium (retains particles larger than 8 μm), and slow (retains particles larger than 2–3 μm). The proper choice of filtering speed is important. If the filtering speed is too fast, we may fail to retain some of the precipitate, which causes a negative determinate error. On the other hand, the precipitate may clog the pores if we use a filter paper that is too slow.

A filter paper's size is just its diameter. Filter paper comes in many sizes, including 4.25 cm, 7.0 cm, 11.0 cm, 12.5 cm, 15.0 cm, and 27.0 cm. Choose a size that fits comfortably into your funnel. or a typical 65-mm long-stem funnel, 11.0 cm and 12.5 cm filter paper are good choices. Because filter paper is hygroscopic, it is not easy to dry it to a constant weight. When accuracy is important, the filter paper is removed before we determine the precipitate's mass. After transferring the precipitate and filter paper to a covered crucible, we heat the crucible to a temperature that coverts the paper to $CO_2(g)$ and $H_2O(g)$, a process called ignition. Igniting a poor quality filter paper leaves behind a residue of inorganic ash. For quantitative work, use a low-ash filter paper. This grade of filter paper is pretreated with a mixture of HCl and HF to remove inorganic materials. Quantitative filter paper typically has an ash content of less than 0.010% w/w.

Gravity filtration is accomplished by folding the filter paper into a cone and placing it in a long-stem funnel. To form a tight seal between the filter cone and the funnel, we dampen the paper with water or supernatant and press the paper to the wall of the funnel. When prepared properly, the funnel's stem fills with the supernatant, increasing the rate of filtration.

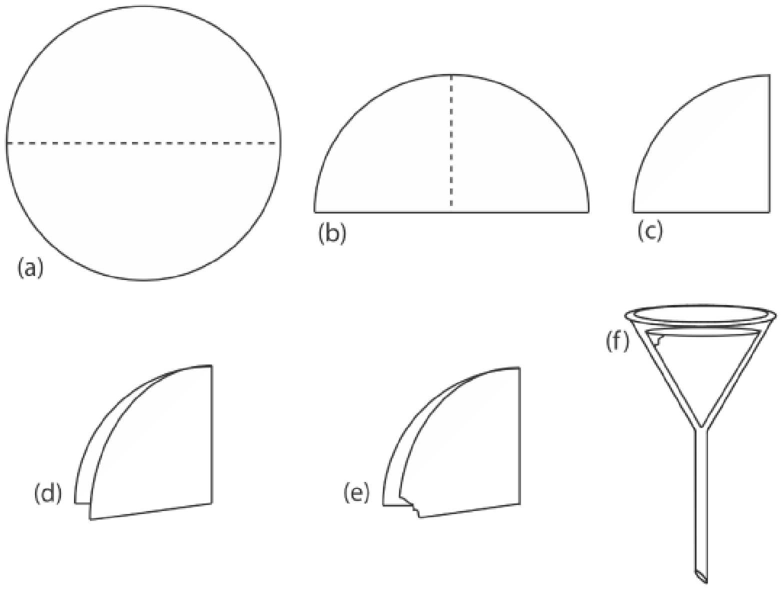


Fig. 3 Preparation of filter paper

The precipitate is transferred to the filter in several steps. The first step is to decant the majority of the supernatant through the filter paper without transferring the precipitate. This prevents the filter paper from clogging at the beginning of the filtration process. The precipitate is rinsed while it remains in its beaker, with the rinsing decanted through the filter paper. Finally, the precipitate is transferred onto the filter paper using a stream of rinse solution. Any precipitate that clings to the walls of the beaker is transferred using a rubber policeman. Figure 8.2.88.2.8. Proper procedure for transferring the supernatant to the filter paper cone. The glass stirring rod allows the supernatant to trickle into the funnel without splashing.

An alternative method for filtering a precipitate is to use a filtering crucible. The most common option is a fritted-glass crucible that contains a porous glass disk filter. Fritted-glass crucibles are classified by their porosity: coarse (retaining particles larger than 40–60 μm), medium (retaining particles greater than 10–15 μm), and fine (retaining particles greater than 4–5.5 μm). Another type of filtering crucible is the Gooch crucible, which is a porcelain crucible with a perforated bottom. A glass fiber mat is placed in the crucible to retain the precipitate. For both types of crucibles, the precipitate is transferred in the same manner described earlier for filter paper. Instead of using gravity, the supernatant is drawn through the crucible with the assistance of suction from a vacuum aspirator or pump.

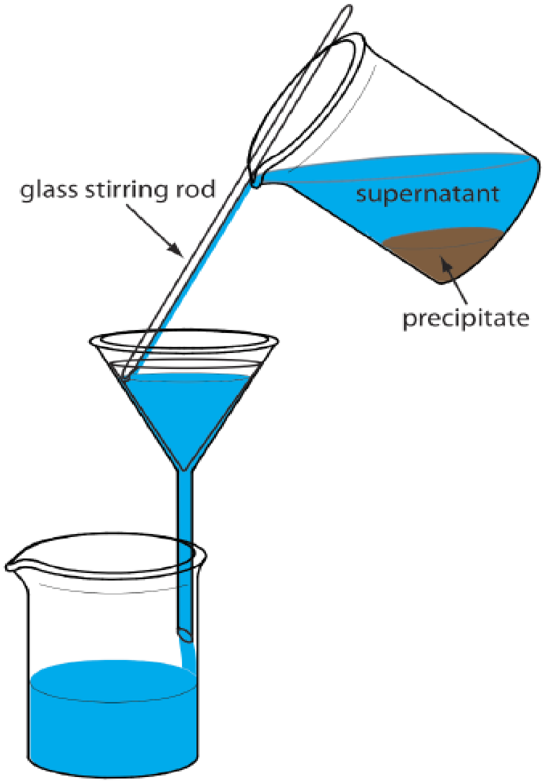


Fig. 4. Diagramatic representation of Filteration process

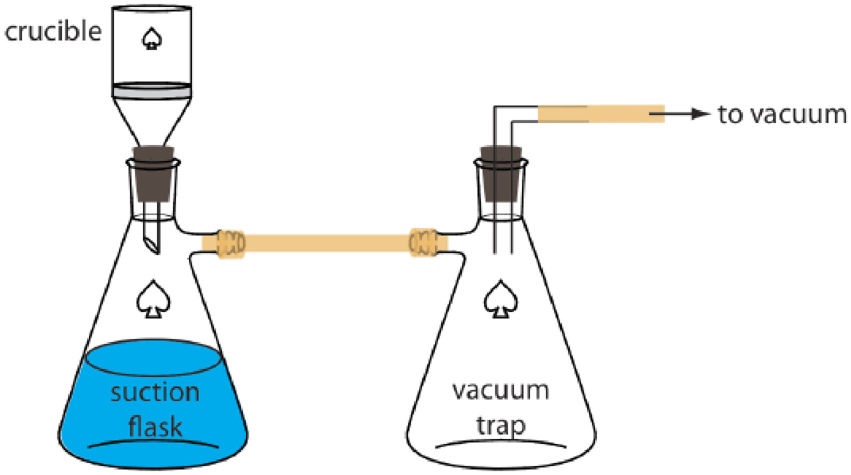


Fig.5. Procedure for filtering a precipitate through a filtering crucible.

Rinsing the Precipitate:

Because the supernatant is rich with dissolved inert ions, we must remove residual traces of supernatant without incurring loss of analyte due to solubility. In many cases this simply involves the use of cold solvents or rinse solutions that contain organic solvents such as ethanol. The pH of the rinse solution is critical if the precipitate contains an acidic or a basic ion. When coagulation plays an important role in determining particle size, adding a volatile inert electrolyte to the rinse solution prevents the precipitate from reverting into smaller particles that might pass through the filter. This process of reverting to smaller particles is called peptization. The volatile electrolyte is removed when drying the precipitate. In general, we can minimize the loss of analyte if we use several small portions of rinse solution instead of a single large volume. Testing the used rinse solution for the presence of an impurity is another way to guard against over-rinsing the precipitate. For example, if Cl^- is a residual ion in the supernatant, we can test for its presence using $AgNO_3$. After we collect a small portion of the rinse solution, we add a few drops of $AgNO_3$ and look for the presence or absence of a precipitate of AgCl. If a precipitate forms, then we know Cl^- is present and continue to rinse the precipitate. Additional rinsing is not needed if the $AgNO_3$ does not produce a precipitate.

Drying the Precipitate:

After separating the precipitate from its supernatant solution, it has to be dried to remove residual traces of rinse solution and to remove any volatile impurities. The temperature and method of drying depend on the method of filtration and the precipitate's desired chemical form. Placing the precipitate in a laboratory oven and heating to a temperature of 110^{o}C is sufficient to remove water and other easily volatilized impurities. Higher temperatures require a muffle furnace, a Bunsen burner is required to decompose the precipitate before its weight is determined.

Because filter paper absorbs moisture, and it should be removed before weighing. This is accomplished by folding the filter paper over the precipitate and transferring both the filter paper and the precipitate to a porcelain or platinum crucible. Gentle heating first dries and then chars the filter paper. Once the paper begins to char, we slowly increase the temperature until there is no trace of the filter paper and any remaining carbon is oxidized to CO_2. Fritted-glass crucibles cannot withstand high temperatures and are dried in an oven at a temperature below $200^{o}C$. The glass fiber mats used in Gooch crucibles can be heated to a maximum temperature of approximately $500^{o}C$.

Part A:

1. What are the limitations of instrumental method?
2. Mention any on confirmatory test for sulphate.
3. Explain Copper turnings test.
4. Give the principle of cobalt nitrate test.
5. Write a note on flame test for cations.
6. Suggest any one test for carbonates and bicarbonates.
7. Explain barium chloride test for sulphates.
8. Write a note on chromyl chloride test.
9. Explain brown ring test for nitrate ion.
10. Describe the ammonium molybdate test for phosphates.
11. What is meant by precipitant?
12. Write a note on zirconyl nitrate test.

Part B:

1. Discuss the mechanism of precipitation.
2. Explain the procedure for the elimination of interfering radicals.
3. Discuss the role of solubility product and common ion effect in precipitation reaction.
4. Explain the various types of precipitation reaction.
5. Describe the coprecipitation method and its effect for minimizing coprecipitation.

Reference Books:

1. Textbook of Analytical Chemistry by Vogel.

2. R. Gopalan, P. S. Subramanian and K. Rengarajan, Elements of Analytical Chemistry, Sultan Chand, New Delhi, 2007.

3.https://chem.libretexts.org/Bookshelves/Analytical_Chemistry/Book%3A_Analytical_Chemistry_2.1_(Harvey)/08%3A_Gravimetric_Methods/8.02%3A_Precipitation_Gravimetry

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UNIT – 2 – PERIODIC TABLE AND PERIODIC PROPERTIES – SCY1112

Introduction

Periodicity is one of the most fundamental aspects of the periodic table of the elements.

What Is Periodicity?

- Periodicity refers to the recurring trends that are seen in the element properties.
- These trends became apparent to Russian chemist Dmitri Mendeleev (1834–1907) when he arranged the elements in a table in order of increasing mass. Based on the properties that were displayed by the known elements, Mendeleev was able to predict where there were "holes" in his table, or elements yet to be discovered.
- The modern periodic table is very similar to Mendeleev's table, but elements today are ordered by increasing atomic number, which reflects the number of protons in an atom. There aren't any "undiscovered" elements, although new elements can be created that have even higher numbers of protons.

Periodic Properties

- The periodic properties are:
- **Ionization energy:** The energy required to remove an electron from an ion or gaseous atom
- **Atomic radius:** Half the distance between the centers of two atoms that are touching each other
- **Electronegativity:** The measure of the ability of an atom to attract a bonding pair of electrons towards itself.
- **Electron affinity:** It is the amount of energy released when an electron is attached to a neutral atom or molecule.

Trends or Periodicity

The periodicity of the properties follows trends as you move across a **row or period** of the periodic table or down a **column or group**:

Moving Left → Right (along the period)

- Ionization Energy - Increases
- Electronegativity - Increases
- Atomic Radius - Decreases

Moving Top → Bottom (Down the group)

- Ionization Energy - Decreases
- Electronegativity - Decreases
- Atomic Radius - Increases

Periodic Law

- Atomic numbers, not weights, determine the factor of chemical properties. Argon weighs more than potassium (39.9 vs. 39.1, respectively), yet argon is in front of potassium. Thus, we can see that elements are arranged based on their atomic number.
- The periodic law is found to help determine many patterns of many different properties of elements; melting and boiling points, densities, electrical conductivity, reactivity, acidic, basic, valance, polarity, and solubility.
- The table below shows that elements increase from left to right accordingly to their atomic number. The vertical columns have similar properties within their group for example Lithium is similar to sodium, beryllium is similar to magnesium, and so on.

Periodic Table

Periodic table or periodic table of the elements, in chemistry, the organized array of all the chemical elements in order of increasing atomic number—i.e., the total number of protons in the atomic nucleus.

When the chemical elements are thus arranged, there is a recurring pattern called the “periodic law” in their properties, in which elements in the same column (group) have similar properties.

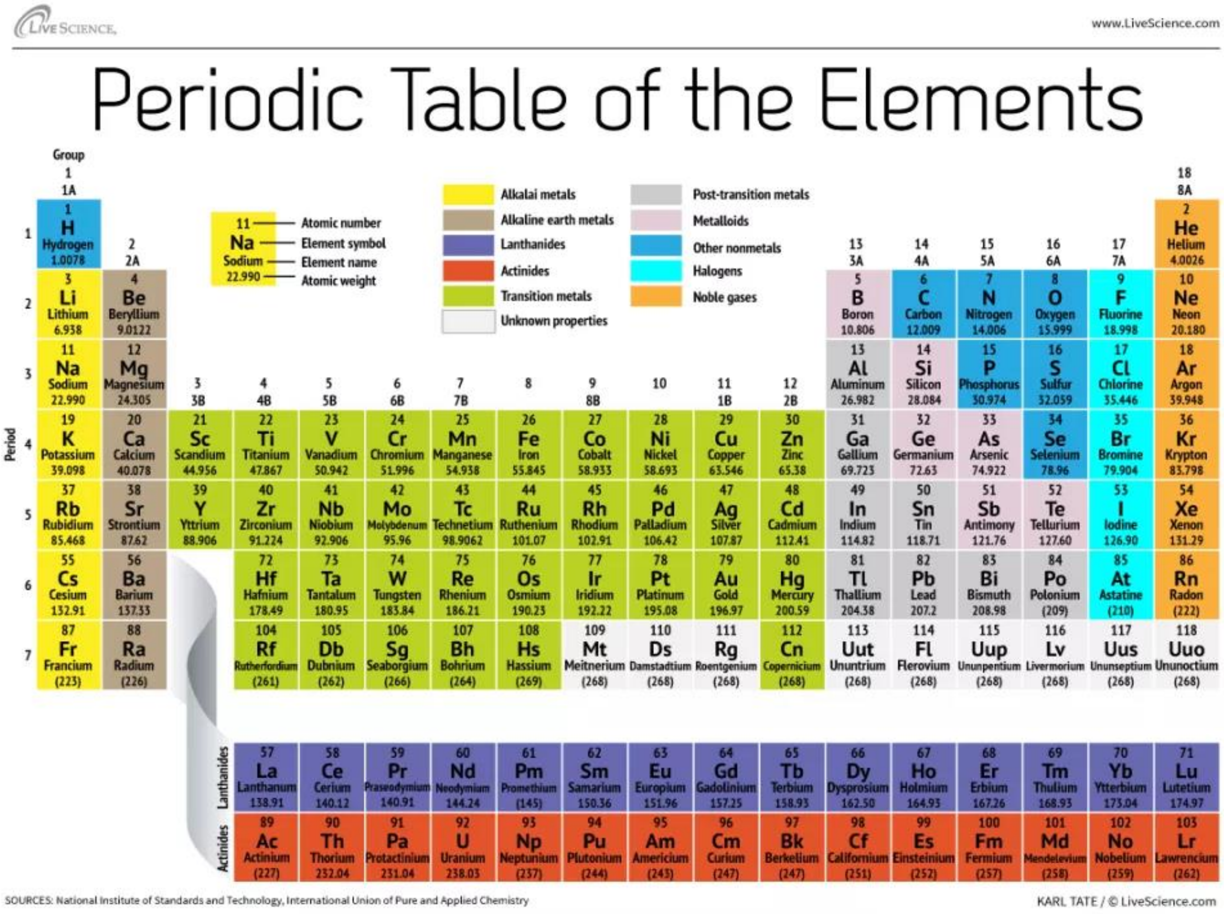
Periodic Table - Long form

In the long form, each period correlates to the building up of electronic shell.

First two groups (1-2) (s-block) and the last 6 groups (13-18) (p-block) make up the main-group elements and the groups (3-12) in between the s and p blocks are called the transition metals.

Group 18 elements are called noble gases, and group 17 are called halogens.

The f-block elements, called inner transition metals, which are at the bottom of the periodic table (periods 8 and 9); the 15 elements after barium (atomic number 56) are called lanthanides and the 15 elements after radium (atomic number 88) are called actinides.



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Periodic Table of the Elements

11 — Atomic number
Na — Element symbol
Sodium — Element name
22.990 — Atomic weight

🟨	Alkalai metals
🟫	Alkaline earth metals
🟪	Lanthanides
🟥	Actinides
🟩	Transition metals
⬜	Unknown properties
⬜	Post-transition metals
⬜	Metalloids
🟦	Other nonmetals
🟦	Halogens
🟧	Noble gases

Period	Group 1 1A	2 2A	3 3B	4 4B	5 5B	6 6B	7 7B	8	9 8B	10	11 1B	12 2B	13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
1	1 H Hydrogen 1.0078																	2 He Helium 4.0026
2	3 Li Lithium 6.938	4 Be Beryllium 9.0122											5 B Boron 10.806	6 C Carbon 12.009	7 N Nitrogen 14.006	8 O Oxygen 15.999	9 F Fluorine 18.998	10 Ne Neon 20.180
3	11 Na Sodium 22.990	12 Mg Magnesium 24.305											13 Al Aluminum 26.982	14 Si Silicon 28.084	15 P Phosphorus 30.974	16 S Sulfur 32.059	17 Cl Chlorine 35.446	18 Ar Argon 39.948
4	19 K Potassium 39.098	20 Ca Calcium 40.078	21 Sc Scandium 44.956	22 Ti Titanium 47.867	23 V Vanadium 50.942	24 Cr Chromium 51.996	25 Mn Manganese 54.938	26 Fe Iron 55.845	27 Co Cobalt 58.933	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.38	31 Ga Gallium 69.723	32 Ge Germanium 72.63	33 As Arsenic 74.922	34 Se Selenium 78.96	35 Br Bromine 79.904	36 Kr Krypton 83.798
5	37 Rb Rubidium 85.468	38 Sr Strontium 87.62	39 Y Yttrium 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.96	43 Tc Technetium 98.9062	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.91	46 Pd Palladium 106.42	47 Ag Silver 107.87	48 Cd Cadmium 112.41	49 In Indium 114.82	50 Sn Tin 118.71	51 Sb Antimony 121.76	52 Te Tellurium 127.60	53 I Iodine 126.90	54 Xe Xenon 131.29
6	55 Cs Cesium 132.91	56 Ba Barium 137.33		72 Hf Hafnium 178.49	73 Ta Tantalum 180.95	74 W Tungsten 183.84	75 Re Rhenium 186.21	76 Os Osmium 190.23	77 Ir Iridium 192.22	78 Pt Platinum 195.08	79 Au Gold 196.97	80 Hg Mercury 200.59	81 Tl Thallium 204.38	82 Pb Lead 207.2	83 Bi Bismuth 208.98	84 Po Polonium (209)	85 At Astatine (210)	86 Rn Radon (222)
7	87 Fr Francium (223)	88 Ra Radium (226)		104 Rf Rutherfordium (261)	105 Db Dubnium (262)	106 Sg Seaborgium (266)	107 Bh Bohrium (264)	108 Hs Hassium (269)	109 Mt Meitnerium (268)	110 Ds Damstadtium (268)	111 Rg Roentgenium (268)	112 Cn Copernicium (268)	113 Uut Ununtrium (268)	114 Fl Flerovium (268)	115 Uup Ununpentium (268)	116 Lv Livermorium (268)	117 Uus Ununseptium (268)	118 Uuo Ununoctium (268)

Lanthanides	57 La Lanthanum 138.91	58 Ce Cerium 140.12	59 Pr Praseodymium 140.91	60 Nd Neodymium 144.24	61 Pm Promethium (145)	62 Sm Samarium 150.36	63 Eu Europium 151.96	64 Gd Gadolinium 157.25	65 Tb Terbium 158.93	66 Dy Dysprosium 162.50	67 Ho Holmium 164.93	68 Er Erbium 167.26	69 Tm Thulium 168.93	70 Yb Ytterbium 173.04	71 Lu Lutetium 174.97
Actinides	89 Ac Actinium (227)	90 Th Thorium 232.04	91 Pa Protactinium 231.04	92 U Uranium 238.03	93 Np Neptunium (237)	94 Pu Plutonium (244)	95 Am Americium (243)	96 Cm Curium (247)	97 Bk Berkelium (247)	98 Cf Californium (251)	99 Es Einsteinium (252)	100 Fm Fermium (257)	101 Md Mendelevium (258)	102 No Nobelium (259)	103 Lr Lawrencium (262)

SOURCES: National Institute of Standards and Technology, International Union of Pure and Applied Chemistry

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Periodic Table : ROWS (Periods) & COLUMNS (Groups)

- The Periodic table has 7 rows and 18 columns. Each row represents one period; the period number of an element indicates how many of its energy levels house electrons.
- Sodium, for instance, sits in the third period, which means a sodium atom typically has electrons in the first three energy levels.

Moving down the table, periods are longer because it takes more electrons to fill the larger and more complex outer levels.

The columns of the table represent groups, or families, of elements. The elements in a group often behave similarly, because they have the same number of electrons in their outermost shell. Group 18 elements, on the far right side of the table, for example, have completely full outer shells and rarely participate in chemical reactions.

- **Alkali metals:** The alkali metals make up most of Group 1, the table's first column, start with lithium (Li) and end with francium (Fr).

- Shiny and soft enough to cut with a knife, they are also extremely reactive and will burst into flame or even explode on contact with water, so chemists store them in oils or inert gases. Hydrogen, with its single electron, also lives in Group 1, but the gas is considered a nonmetal.
- H is not an alkali metal. All other metals have ONE electron in the valence shell.
- Li – [He]$2s^1$
- Na – [Ne]$3s^1$
- K – [Ar]$4s^1$
- Rb – [Kr]$5s^1$
- Cs – [Xe]$6s^1$
- Fr – [Rn]$7s^1$
- **Alkaline-earth metals:** The alkaline-earth metals make up Group 2 of the periodic table, from beryllium (Be) through radium (Ra).
- Each of these elements has two electrons in its outermost energy level, which makes the alkaline earths reactive enough that they're rarely found alone in nature. They are not as reactive as the alkali metals. Their chemical reactions typically occur more slowly and produce less heat compared to the alkali metals.

Be – $2s^2$

Mg – $3s^2$

- **Lanthanides:** The third group is much too long to fit into the third column, so it is broken out and flipped sideways at the bottom of the table. This is the lanthanides, elements 57 through 71 —lanthanum (La) to lutetium (Lu). The elements in this group have a silvery white color and tarnish on contact with air.
- **Actinides:** The actinides line the bottom row of the island and comprise elements 89, actinium (Ac), through 103, lawrencium (Lr). Of these elements, only thorium (Th) and uranium (U) occur naturally on Earth in substantial amounts. All are radioactive. The actinides and the lanthanides together form a group called the inner transition metals.
- **Transition metals:** Groups 3 through 12 represent the rest of the transition metals. Hard but malleable, shiny, and possessing good conductivity, these elements are what called as metal. Many of the greatest hits of the metal world — including gold, silver, iron and platinum.

- **Post-transition metals:** The post-transition metals are aluminum (Al), gallium (Ga), indium (In), thallium (Tl), tin (Sn), lead (Pb) and bismuth (Bi), and they span Group 13 to Group 17. These elements have some of the classic characteristics of the transition metals, but they tend to be softer and conduct more poorly than other transition metals. Many periodic tables will feature a bolded "staircase" line below the diagonal connecting boron with astatine. The post-transition metals cluster to the lower left of this line.

- **Metalloids:** The metalloids are boron (B), silicon (Si), germanium (Ge), arsenic (As), antimony (Sb), tellurium (Te) and polonium (Po). They form the staircase that represents the gradual transition from metals to nonmetals. These elements sometimes behave as semiconductors (B, Si, Ge) rather than as conductors. Metalloids are also called "semimetals" or "poor metals."

- **Nonmetals:** Everything else to the upper right of the staircase along with hydrogen (H), are nonmetals. They are carbon (C), nitrogen (N), phosphorus (P), oxygen (O), sulfur (S) and selenium (Se).

- **Halogens:** The top four elements of Group 17, from fluorine (F) through astatine (At), represent one of two subsets of the nonmetals. The halogens are quite chemically reactive and tend to pair up with alkali metals to produce various types of salt.

- **Noble gases:** They are colorless, odorless and almost non-reactive. They are inert, or noble gases in Group 18. Many chemists expect oganesson, one of the four newly named elements, to share these characteristics; however, because this element has a half-life measuring in the milliseconds, no one has been able to test it directly. Oganesson completes the seventh period of the periodic table, so if anyone manages to synthesize element 119, it will loop around to start row eight in the alkali metal column.

Atomic Radii

Along a period there is a decrease from left to right in the periodic table.

The decrease is more significant for the s and p block elements compared to the d block elements.

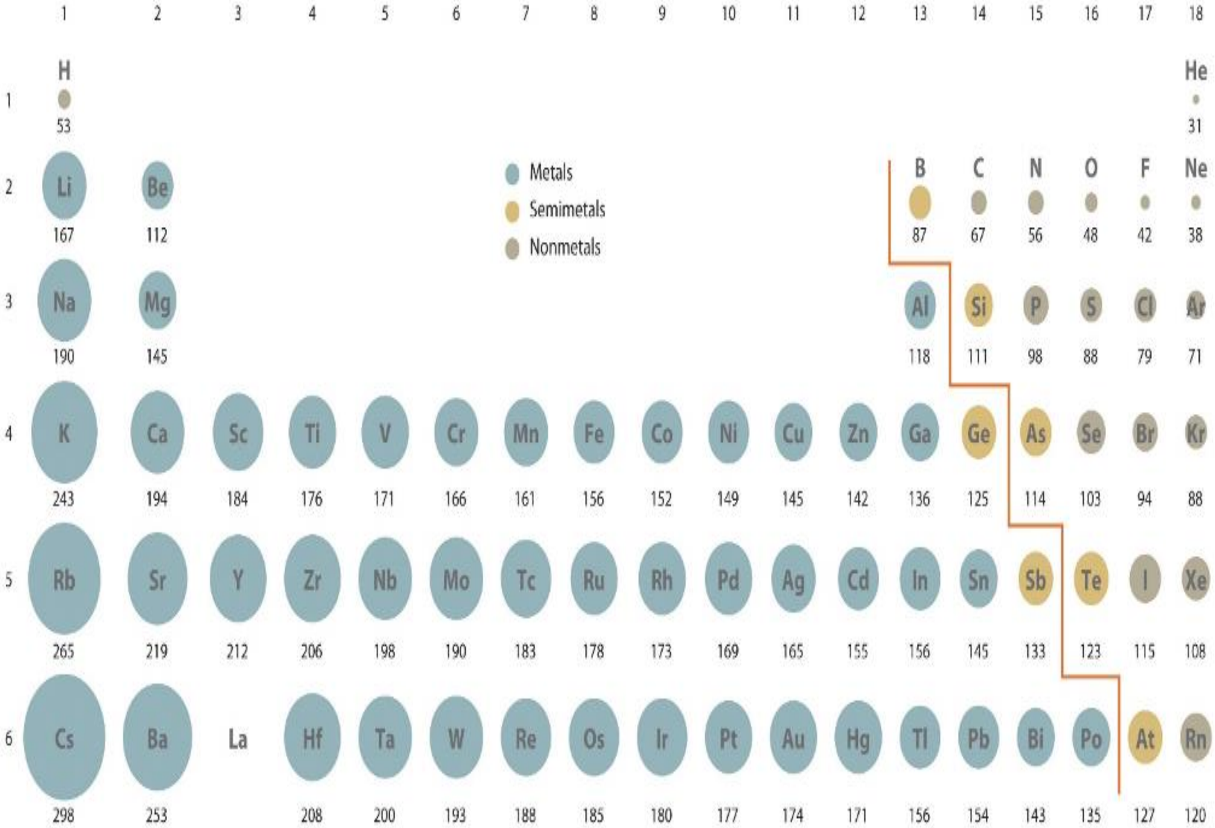
We can explain this effect using the concept of effective nuclear charge. As we go from the left to the right in the periodic table we add electrons to the same shell. A proton is also gets added to the nucleus with each electron added, the electron experiences a greater attractive force from the nucleus. This effect tends to increase the effective nuclear charge.

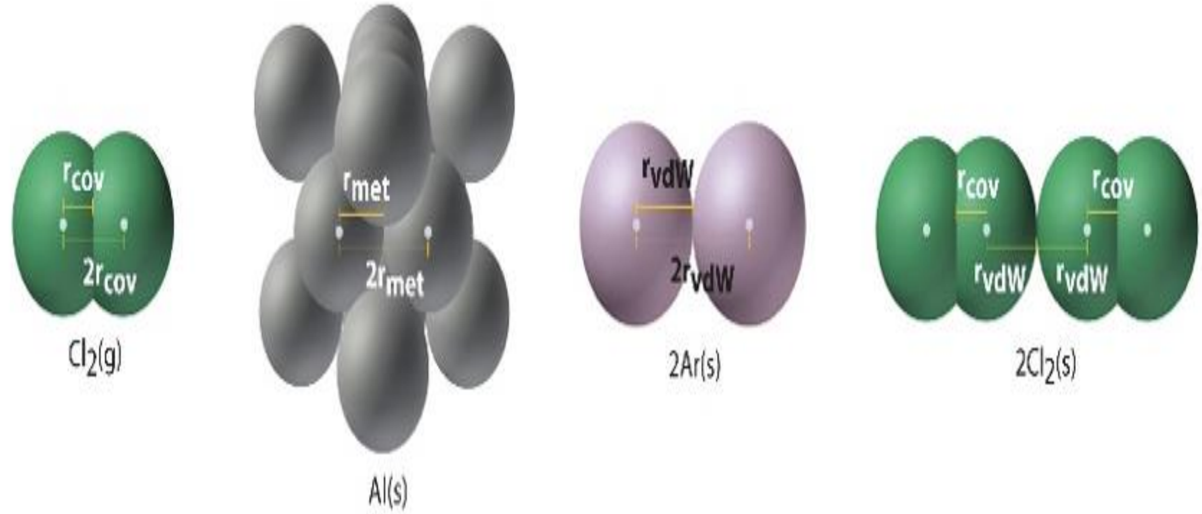
However, there is also an opposite effect. Because of the added electron, there are more electron-electron repulsion and shielding effects, and this tends to decrease the effective nuclear charge. Because the new electron is added to the same shell, the shielding effects do not fully compensate for the additional Coulomb force coming from the additional proton in the nucleus, and thus the effective nuclear charge increases.

This higher effective nuclear charge pulls the electrons closer to the nucleus, and thus the atom size decreases.

For the d-block elements new d electrons get added to a more inner subshell, for example for the d-block elements of the 4th period the d electrons get added to the 3d subshell. Because of that, these 3d electrons can more effectively shield nuclear charge from the outmost two 4s electrons, and thus the decrease of the atomic radius is less pronounced.

- Atomic radius decreases continuously within a period.
- For a new period, the atomic radius jumps dramatically. For example it jumps from 31 pm to 167 pm as we go from the helium to the lithium, and from 38 pm to 190 pm as you go from the neon to the sodium.
- This trend is because the electrons get filled into a new, more outer shell when a new period is begun. This outer shell is located much farther away from the nucleus, and thus the radius of the atom increases. In addition, the electrons in the inner shells can very effectively shield the nuclear charge from the electron added to the new shell which tends to increase atom radius.
- Atomic radii increase as you go down a group. This is because within a group there are the same number and type of valence electrons, but the valence electrons are in a more outer shell associated with a higher quantum number n.
- The effect of jump of atomic radius when a new period is begun is greater than the effect of decline of the radius within a period. As a result, the radius tends to increase as you go down a group.





(a) Covalent radius, r_{cov}
(b) Metallic radius, r_{met}
(c) van der Waals radius, r_{vdW}
(d) Covalent vs. vdW radii

Ionic Radius

- ***Ions are formed when an atom loses or gains electrons.*** When an atom loses an electron it forms a cation and when it gains an electron it becomes an anion. The Ionic radius can be described as the distance between the nucleus of an ion and the outermost shell of the ion.
- The atomic size of a cation will be smaller than that of the parent atom. An anion is relatively larger in size than its parent atom. This is because when an atom gains electrons the total number of electrons increases which tends to create more repulsion between electrons and thus overshadows the net effective nuclear charge.
- For example,

Radius of potassium = 243pm.

Radius of potassium ion = 138pm.

Trends in Ionic Radius in Groups

- In a periodic table while moving down in a group, atoms add extra shell (number of electrons) due to which ionic radius of elements increases down a group.

Ions	Configuration	Ionic radii(nm)	Ions	Configuration	Ionic radii(nm)
Li^+	2	0.076	F^-	2,8	0.133
Na^+	2,8	0.102	Cl^-	2,8,	0.181
K^+	2,8, 8	0.138	Br^-	2,8,18, 8	0.196

Trends in Ionic Radius Across a Period

- In period 3 we find that the atomic radius first decreases and then suddenly increases and then again it slowly decreases. This is because the starting elements in a period tend to form cations, and the elements towards the end of a period tend to form anions.
- Ions are formed as a result of the gain or loss of electrons. The formation of ions plays a vital role in any chemical reaction to form a new substance. By knowing the ionic radii we can study various chemical bonds formed during a reaction.

Period 3	Na^{2+}	Mg^{2+}	Al^{3+}	P^{3-}	S^{2-}	Cl^-
Number of protons	11	12	13	15	16	17
Electronic configuration	2,8	2,8	2,8	2,8,8	2,8,8	2,8,8

- **Ionic radius** 0.102 0.072 0.054 0.212 0.184 0.181

First Ionization Energy

- The first ionization energy is another important periodic property of the elements.
- It is defined as the energy required to remove an electron from a neutral atom in the gas phase because only in the gas phase, atoms do not significantly interact with each other. Therefore, only when looking at an atom in the gas phase we can truly determine the properties of single, isolated atoms.
- All 1st ionization energies are positive. This means that it always requires energy to remove an electron from a neutral atom. All electrons in an atom are bound to the nucleus via a binding energy. If an ionization energy was negative then this would mean that the atom would spontaneously lose an electron, and spontaneously ionize. This would be unreasonable.
- IE increases as we go from the left to the right within a period – The effective nuclear charge increases from left to right within a period. As the effective nuclear charge increases, the pull of the nucleus on the outmost electron increases, and thus the harder it is to remove this electron from the atom.
- The group 3 elements have a lower ionization energy than the group 2 elements, and the group 5 elements have a lower ionization energy than the group 4 elements - Filled and half-filled subshells represent stable electron configurations, and thus the electrons within these subshells have unusually low energy. Hence these electrons are harder to remove from the atoms. The group 2 elements have filled s subshells, and the group 5 elements have half-filled p subshells.
- The increase in ionization energy is less pronounced within the d-block, and even less pronounced with in the f-block. This is because the effective nuclear charge on the outmost electrons does not increase as much because inner d and f orbitals are getting filled. You can also see that the group 13 elements have a lower ionization energy than the group 12 elements. This is because in group 13 a new p subshell is begun and the new electrons get added to the outmost shell where shielding effects are lower.
- As a second trend you can see that whenever a new period is begun, the ionization energy drastically drops. This is because the new electron is added to a new, more outer shell where the effective nuclear charge acting on the new electron is much lower.
- The third trend is that the ionization energy becomes smaller as we go down a group. This is because the effective nuclear charge on the valence electrons decreases because the quantum number n of the valence electrons increases.

- The drop of ionization energy from hydrogen to lithium in the first group is unusually large. This is because hydrogen is the only element for which there are no shielding effects, simply because the hydrogen has only one electron. For that reason the valence 1s electron of the hydrogen is far harder to remove than the valence s electrons of the other group 1 elements.
- $X + IE_1 \rightarrow X^{+} + e^{-}$
- $X^{+} + IE_2 \rightarrow X^{+2} + e^{-}$
- $X^{+2} + IE_3 \rightarrow X^{+3} + e^{-}$
- Increasing in the attraction force applied by nucleus to electrons makes difficult to remove electrons from shells. Second ionization energy is larger than first ionization energy, second ionization energy is larger than third ionization energy. We can say that;
- $IE_1<IE_2<IE_3<....$
- Atoms having electron configuration ns^2np^6 has spherical symmetry property and removing electron is difficult and ionization energy is high. Moreover, atoms having $ns^2np^6ns^1$ has lower ionization energy, because removing one electron from these atoms make them noble gas and more stable. Thus, it is easy to remove electron from them. For example;
- $_{10}Ne$: $1s^22s^22p^6$ and
- $_{11}Na$: $1s^22s^22p^63s^1$
- $IE_{Ne}>IE_{Na}$
- Knowing sequential ionization energies of atom, helps us to find number of valence electrons of atoms. Examine following example;

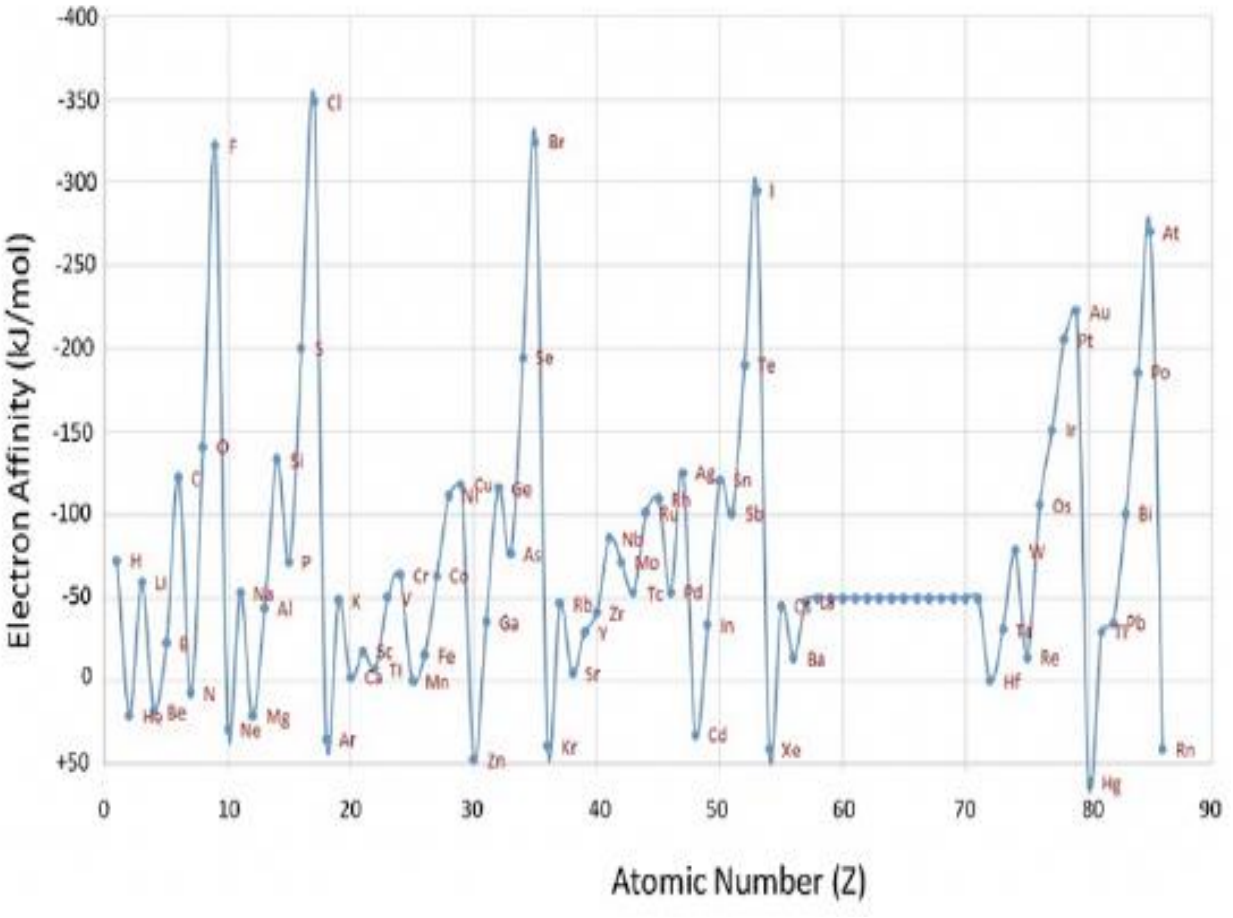
IE_1	**IE_2**	**IE_3**	**IE_4**	**IE_5**
176	**347**	**1850**	**2520**	**3260**

- Increase in second to third ionization energy is greater than others, thus atom has 2 valence electrons.

Electron Affinity

It is defined as the energy required or released when you add an electron to a neutral atom in the gas phase. We look at an atom in the gas phase, because we want to consider an isolated atom that does not make significant interactions with other atoms.

- We can see that most elements have negative electron affinities, meaning that the addition of a free electron to a neutral atom is exothermic, and releases energy, however, this is not always the case. Some elements have negative electron affinities, in particular the noble gases, but also Be, N, Mg, Zn, Cd, and Hg.
- Zn, Cd, and Hg, are group 12 elements with a full d subshell which is particularly stable. An additional electron would need to be added to a p orbital of a higher shell which is energetically quite unfavorable.
- Similarly, Be and Mg have filled s subshells which are also fairly stable. Adding an additional electron would need to start an new subshell, which is energetically not favorable.
- Ca and Sr have electron affinities of about 0, and that of Ba is only slightly negative showing that higher periods make the addition of an electron to a new p shell slightly more favorable. Nitrogen has a half-filled p subshell, which is also a quite stable electron configuration, and therefore adding an electron is not favorable. The addition of an electron is slightly more favorable for the other group 15 elements, however, these also tend to have rather low electron affinities.
- Generally, for the main group elements the electron affinity tends to increase from the group 1 to group 17. However, the trend is broken for group 2 and group 15 elements because these elements have full and half-filled subshells, respectively.
- Group 1 elements have higher electron affinities than group 3 elements. This is because adding an electron to a group 1 element produces a full s subshell which is fairly stable.
- For the d-block elements, the electron affinity tends to increase from group 3 to group 11, but the trend is broken multiple times showing that each element would need to be investigated individually.
- There is a big drop in electron affinity from group 17 to group 18 which is easily explained by the fact that the addition of an electron to a group 17 element produces a filled shell, while a group 18 element already has a full shell, and the addition of an electron would start a new shell.
- Similarly, there is a sharp drop in electron affinity from group 11 to group 12, as an addition of an electron to a group 11 atom produces a full subshell, while the addition of an electron to a group 12 element would require the start of new, more outer subshell. For the p block elements the electron affinity tends to first increase from period 2 to 3, and then decrease. For the s-block there is a steady decrease down a group. For d block elements there is no clear trend for the electron affinity.



Electronegativity

- It is the ability of an atom or a molecule to attract a pair of electrons. The bond formed due to this is mainly determined by the difference between the electronegativity of the atoms.
- Across the period, the electronegativity increases as nuclear charge increases. Moving down the group, the electronegativity decreases as nuclear charge decreases. The reason being the distance between the nucleus of the atom and the valence electrons is long and thus the electrons are easily lost.
- Example
- Along the period – Li< Be < B < C < N < O < F
- Down the group – Li> Na > K > Rb > Cs

Pauling Scale

- Pauling first proposed the concept of electronegativity in 1932 to explain why the covalent bond between two different atoms (A–B) is stronger than the average of the A–A and the B–B bonds. According to valence bond theory, this "additional stabilization" of the heteronuclear bond is due to the contribution of **ionic canonical forms** to the bonding

- The difference in electronegativity between atoms A and B is given by:

$$|\chi_A - \chi_B| = (\mathrm{eV})^{-1/2} \sqrt{E_d(AB) - \frac{E_d(AA) + E_d(BB)}{2}}$$

$$E_d(AB) = \sqrt{E_d(AA)\, E_d(BB)} + 1.3\,(\chi_A - \chi_B)^2\ \mathrm{eV}$$

where the dissociation energies , E_d, of the A–B, A–A and B–B bonds are expressed in electron volts, the factor $(\mathrm{eV})^{-1/2}$ being included to ensure a dimensionless result. Hence, the difference in Pauling electronegativity between hydrogen and bromine is 0.73 (dissociation energies: H–Br, 3.79 eV; H–H, 4.52 eV; Br–Br 2.00 eV)

Mulliken electronegativity

Robert S. Mulliken proposed that the arithmetic mean of the first ionization energy (E_i) and the electron affinity (E_{ea}) should be a measure of the tendency of an atom to attract electrons. As this definition is not dependent on an arbitrary relative scale, it has also been termed **absolute electronegativity**, with the units of kilojoules per mol or electron volts.

$$\chi = \frac{E_i + E_{EA}}{2}$$

- For ionization energies and electron affinities in electron volts,

$$\chi = 0.187\,(E_i + E_{EA}) + 0.17$$

Allred–Rochow electronegativity

A. Louis Allred and Eugene G. Rochow considered that electronegativity should be related to the charge experienced by an electron on the "surface" of an atom. The higher the charge per unit area of atomic surface the greater the tendency of that atom to attract electrons. The effective nuclear charge, Z_{eff}, experienced by valence electrons can be estimated using Slater's rule, while the surface area of an atom in a molecule can be taken to be proportional to the square of the covalent radius, r_{cov}, When r_{cov} is expressed in picometers.

$$X = 3590 \frac{Z_{eff}}{r_{cov}^{2}} + 0.744$$

Oxidation states

- The oxidation state of a pure element is always zero. Ca = 0, Na = 0, Be = 0
- The oxidation state for a pure ion is equivalent to its ionic charge. $Na^{+} = +1$, $Mg^{2+} = +2$
- In general, hydrogen has an oxidation state of +1, while oxygen has an oxidation state of -2.
- The sum of the oxidation states for all atoms of a neutral molecule must add up to zero.
- Eg: $CaCO_3 = 0$, $CaCl_2 = 0$, $NaCl = 0$

Oxidation and Reduction

- Oxidation : Loss of electrons, which causes an increase in oxidation state

  $Ca^{+} \rightarrow Ca^{2+} + e^{-}$ OS = Ca(II)

- Reduction : Gain of electrons, which causes a decrease in oxidation state

  $Ca^{2+} + e^{-} \rightarrow Ca^{+}$ OS = Ca(I)

- **Oxidation involves an increase in oxidation state**
- **Reduction involves a decrease in oxidation state**
- Oxidation state indicates the degree of oxidation for an atom in a chemical compound; it is the hypothetical charge that an atom would have if all bonds to atoms of different elements were completely ionic.
- Oxidation states are typically represented by integers, which can be positive, negative, or zero.
- In some cases, the average oxidation state of an element is a fraction, such as 8/3 for iron in magnetite (Fe_3O_4).
- The highest known oxidation state is +8 in the tetroxides of ruthenium, xenon, osmium, iridium, and some complexes involving plutonium;
- The lowest known oxidation state is −4 for some elements in the carbon group.

- An atom's increase in oxidation state through a chemical reaction is called oxidation, and it involves a loss of electrons; an decrease in an atom's oxidation state is called reduction, and it involves the gain of electrons.

General Rules Regarding Oxidation States

- The oxidation state of a free element (uncombined element) is zero.
- For a simple (monoatomic) ion, the oxidation state is equal to the net charge on the ion. For example, Cl^- has an oxidation state of -1.
- When present in most compounds, hydrogen has an oxidation state of +1 and oxygen an oxidation state of −2. The exceptions to this are that hydrogen has an oxidation state of −1 in hydrides of active metals (such as LiH), and an oxidation state of −1 in peroxides (such as H_2O_2) or -1/2 in superoxides (such as KO).

The algebraic sum of oxidation states for all atoms in a neutral molecule must be zero. In ions, the algebraic sum of the oxidation states of the constituent atoms must be equal to the charge on the ion.

- Transition metals are not included, as they tend to exhibit a variety of oxidation states.
- The above table can be used to conclude that boron (a Group III element) will typically have an oxidation state of +3, and nitrogen (a group V element) an oxidation state of -3.
- The sum of the oxidation states for all atoms in a molecule or polyatomic ion is equal to the charge of the molecule or ion. This helps determine the oxidation state of any one element in a given molecule or ion, assuming that we know the common oxidation states of all of the other elements. For example, in a sulfite ion (SO_3^{2-}), the total charge of the ion is 2-, and each oxygen is assumed to be in its usual oxidation state of -2. Because there are three oxygen atoms in sulfite, oxygen contributes 3 x -2= -6 to the total charge. Therefore, sulfur must have an oxidation state of +4 for the overall charge on sulfite to be

  $X + 3(-2) = -2$

  $X - 6 = -2$

  $X = -2 + 6 = 4$

  $S = +4$

Vanadium forms a number of different ions - for example, V^{2+} and V^{3+}. If you think about how these might be produced from vanadium metal, the 2+ ion will be formed by oxidising the metal by removing two electrons:

$$V \rightarrow V^{2+} + 2e^-$$

The vanadium is now said to be in an oxidation state of +2.

Removal of another electron gives the V^{3+} ion:

$$V^{2+} \rightarrow V^{3+} + e^-$$

The vanadium now has an oxidation state of +3.

Removal of another electron gives a more unusual looking ion, VO^{2+}.

$$V^{3+} + H_2O \rightarrow VO^{2+} + 2H^+ + e^-$$

The vanadium is now in an oxidation state of +4.

$$VO^{2+} + H_2O \rightarrow VO_2^+ + 2H^+ + e^-$$

Exceptions

- *Hydrogen in the metal hydrides : NaH*
- *H = -1*
- *Oxygen in peroxides :* H_2O_2
- O = -1
- *Oxygen in* F_2O
- *O = +2*
- *Chlorine in compounds with fluorine or oxygen*
- *Cl = variable oxidation states*

Valency and Variable Valency

Valency is the combining capacity of an element. The number of electrons donated or accepted by an atom of an element so as to have electronic configuration of nearest noble gas is called its valency.

Variable Valency

The metals donate electrons from their valence shell, so as to form positively charged ions. However, some metals lose electrons from the shell next to the valence shell. In such a situation the element exhibits more than one electropositive valency. Such elements are said to have ***variable valency***.

Variable Electrovalency

- The electrovalency of an element is equal to the number of electrons lost or gained by its atom during the formation of ionic bonds. The s- block elements do not show variable valency. However, p-block elements with higher atomic number transition and inner transition elements show variable valency.
- There are two main reasons for showing variable valency
- Inert pair effect in p-block elements.
- Small energy difference between ns and (n-1)d sub shells in transition elements and ns and (n-2)f sub shells in inner transition elements.

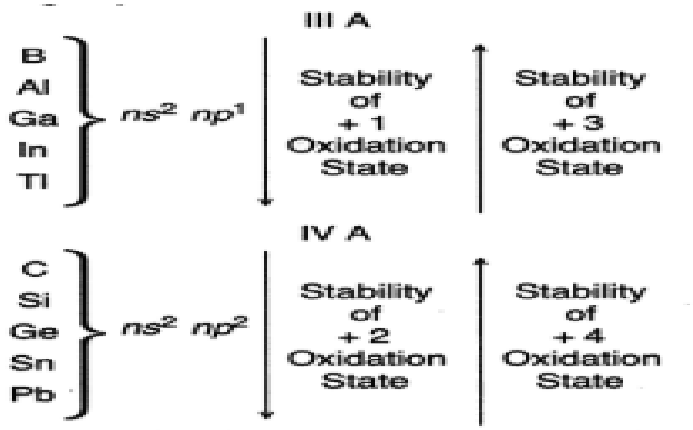
1. Inert pair effect

- The non-participation of the two s electrons in bonding due to the high energy needed for unpairing them.
- The inert pair theory was proposed by Sidgwick. He along with Powell accounted for the shapes of several molecules and correlated the shapes with some of their physical properties.

1. Example of Inert Pair Effect

- The inert pair effect among group 4 and group 5 elements. Sn^{2+} and Pb^{2+} and Sb^{3+} and Bi^{3+} which are the lower oxidation states of the elements are formed because of the inert pair effect. When the s electrons remain paired the oxidation state is lower than the characteristic oxidation state of the group.

The electronic configurations of III A and IV A group elements are as



- The elements of III A group show +3 oxidation state mainly. But as we go down the group the oxidation state +1 becomes more and more pronounced. Similarly the elements of IV A group show +4 oxidation state in general but as we go down the group the +2 state becomes more and more pronounced.
- The two s electrons (ns^2) in the valence shell tend to remain inert and do not participate in formation of bonds. This is called inert pair effect. Thus the inert pair effect is the main cause of variable valency in p block elements.

2. Energy Difference between Orbitals

- In transition elements the variation in oxidation state is due to involvement of incomplete d-orbitals in addition to electrons of ns orbital. So the electrons from both the energy levels can be used for bonding.
- Similarly, inner transition elements show variable valency due to incomplete filling of f-orbitals. So in addition to ns electrons, the electrons from f-orbitals may be used for chemical bond formation.

Variable Valency: Examples

- Certain elements have more than one valency. They exhibit variable valency. For example, copper, tin, iron and mercury exhibit variable valency. Copper combines with oxygen to form cuprous oxide (Cu_2O) and cupric oxide (CuO).
- Valency of oxygen being two, combining capacity of copper in the first case is one and that in the second case is two. The suffix “ous” is used to indicate the lower valency and the suffix “ic” to indicate the higher valency. The following table gives the names of some compounds with variable valencies of elements.

Examples

- Cuprous Oxide (Cu_2O) – Valency = 1, Cu^+
- Cupric oxide (CuO) – Valency = 2, Cu^{2+}
- Ferrous oxide (FeO) – Valency = 2, Fe^{2+}
- Ferric oxide (Fe_2O_3) – Valency = 3, Fe^{3+}
- Mercurous (Hg^+) – Valency = 1
- Mercuric (Hg^{2+}) – Valency = 2
- Stannous (Sn^{2+}) – Valency = 2

- Stannic (Sn^{4+}) – Valency = 4

Isoelectronic Relationship

- Isoelectronicity is an effect observed when two or more molecules have the same structure (positions and connectivities among atoms) and the same electron configuration, but differ by what specific elements are at certain locations in the structure.
- CO, NO^+ and N_2 are isoelectronic, whereas, CH_3COCH_3 and $CH_3N{=}NCH_3$ are not.
- Isoelectronic species can be expected to show useful consistency and predictability in their properties, so identifying a compound as isoelectronic with one already characterised offers clues to possible properties and reactions.

Examples

- The N atom and the O^+ ion are isoelectronic because each has five valence electrons, or more accurately an electronic configuration of [He] $2s^2\ 2p^3$
- Similarly, the cations K^+, Ca^{2+}, Sc^{3+} and anions Cl^-, S^{2-} and P^{3-} are all isoelectronic with the Ar atom.
- CO, CN^-, N_2, NO^+ are isoelectronic because each has two atoms triple bonded together, and due to the charge have analogous electronic configurations (N^- is identical in electronic configuration to O so CO is identical electronically to CN^-).
- CH_3COCH_3 (acetone) and $CH_3N_2CH_3$ (azomethane) are **not** isoelectronic. They do have the same number of electrons but they do not have the same structure.
- Serine, Cysteine, Selenocysteine are isoelectronic.

ATOMIC, MOLECULAR AND EQUIVALENT MASSES

Avagadro's hypothesis

Equal volumes of all gases at the same temperature and pressure contain the same number of molecules.

EQUIVALENT WEIGHT (On the basis of Hydrogen)
The weight of an element that combines with one part by weight of hydrogen.

Examples:

In H_2O, 16 parts by weight of oxygen combine with 2 parts by weight of hydrogen. Therefore 8 parts by weight of oxygen will combine with 1 part by weight of hydrogen.

Therefore equivalent weight of oxygen is 8.

In HCl, 35.5 parts by weight of chlorine combine with 1 part by weight of hydrogen. Therefore the equivalent weight of chlorine is 35.5.

MOLE CONCEPT

This is the unit that consists of 6.023×10^{23} particles.

Avagadro number (N): It is the number of atoms present in exactly 12 grams of ${}_6C^{12}$ isotope. Its value is 6.023×10^{23}

Atomicity:

The number of atoms contained in one molecule of the element. Eg: $CaCO_3$

Atomic weight

The relative atomic mass of an element is the mass of one atom of the element compared with the mass of one atom of hydrogen taken as one unit.

Molecular mass

The relative molecular mass of an element or a compound is the mass of one molecule of the element or compound compared with the mass of one atom of hydrogen taken as one unit.

Equivalent weight of base

It is the number of parts by mass of the base required to neutralize one equivalent mass of an acid.

Equivalent weight of a salt

It is the number of parts by mass of salt which reacts with one equivalent of mass of any other substance.

Equivalent weight of an oxidising agent

It is the number of parts by mass of it, which contains 8 parts by mass of available oxygen utilised for oxidation.

Equivalent weight of an reducing agent

It is the number of parts by mass of it, which can be oxidized by 8 parts by mass of oxygen.

Volume density

It is defined as the ratio of the mass of a certain volume of the gas or vapour to the mass of the same volume of hydrogen at the same temperature and pressure.

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Question Bank

Part A

1. What is periodicity?

2. Name the properties which follow periodic trends.

3. Define a) Ionization energy b) Electronegativity

4. Define periodic law.

5. Compare alkali and alkaline earth metals.

6. Give the name of the elements belonging to group I, group 2, group 17 and group 18

7. What is the periodic trend observed with electron affinity and atomic radii as the periodic properties?

8. Explain the trend observed with ionic radii as a periodic property.

9. Justify “second ionization energy is greater than first ionization energy”

10. Explain the trend observed for electron affinity as a periodic property.

11. What are noble gases? Why they are called so?

12. Name the three electronegativity scales and the corresponding equations.

13. Differentiate oxidation and reduction reaction.

14. Comment on the change in the oxidation states of oxidising and reducing agents.

15. What is the oxidation state of oxygen in hydrogen peroxide?

16. Define variable valency.

17. Determine the oxidation state of Cr in $K_2Cr_2O_7$, Cr^{2+}, CrO_2Cl_2

Part B

1. Explain in detail about ionization energy and its trend in the periodic table.

2. Elaborate on electronegativity and electron affinity and their trend in the periodic table.

3. Discuss variable valency exhibited by elements.

4. Explain oxidation and reduction reactions with example.

5. Explain in detail the periodic trend observed for the periodic properties with examples.

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School of Science and Humanities

Department of Chemistry

SCY1112
GENERAL CHEMISTRY II

UNIT 3

STRUCTURE AND REACTIVITY OF ORGANIC COMPOUNDS

Types of organic reactions - Cleavage of bonds - Homolytic and Heterolytic bond fission - Reactive intermediates - carbocation, carbanion, and free radicals - Structure, shape, stability and reactivity -Carbenes, nitrenes and arynes - Factors affecting stability of the reaction intermediates - Electron displacement effects - Inductive effect, electromeric, mesomeric, resonance, hyperconjugation- Hydrogen bonding - Tautomerism – Keto-enol tautomerism.

3. Introduction:

Organic compound are a class of chemical compounds in which one or more atoms of carbon are covalently linked to atoms of other elements, most commonly hydrogen, oxygen, or nitrogen. The few carbon-containing compounds not classified as organic include carbides, carbonates, and cyanides. In chemistry, reactivity is the impetus for which a chemical substance undergoes a chemical reaction, either by itself or with other materials, with an overall release of energy.

3.1 Types of organic reactions:

- Addition reaction.
- Elimination reaction.
- Substitution reaction.
- Rearrangement reactions.

3.1.1 Addition reaction:

In an addition reaction the number of σ-bonds in the substrate molecule increases, usually at the expense of one or more π-bonds.

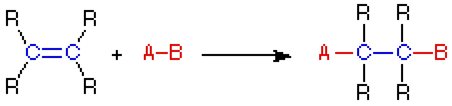


Fig.1. Addition reaction

Example:

The addition of water to a nitrile does not seem to fit any of the above reaction types, but it is simply a slow addition reaction followed by a rapid rearrangement. Rapid rearrangements of this kind are called tautomerizations.

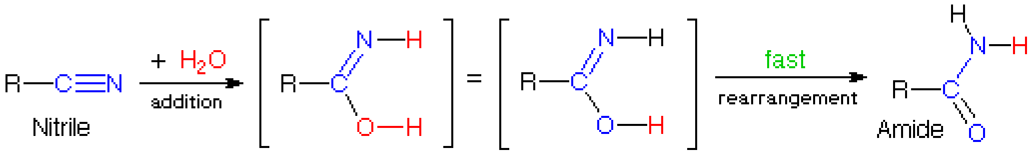


Fig.2. Example of Addition reaction

3.1.2 Elimination Reaction:

The reverse of addition reaction is called elimination reactions, *i.e.* the number of σ-bonds in the substrate decreases, and new π-bonds are often formed. Elimination reaction is a type of reaction is mainly used to transform saturated compounds to unsaturated compounds.

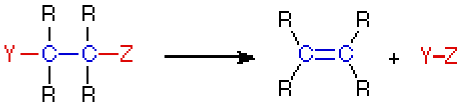


Fig.3. Elimination reaction

An elimination reaction is a type of chemical reaction where several atoms either in pairs or groups are removed from a molecule. The removal usually takes place due to the action of acids and bases or action of metals. It can also happen through the process of heating at high temperatures.

Types of elimination reaction:

i) E$_1$ Reaction:

- In the E$_1$ mechanism which is also known as unimolecular elimination**,** there are usually two steps involved – ionization and deprotonation.
- During ionization, there is a formation of carbocation as an intermediate. In deprotonation, a proton is lost by the carbocation.
- This happens in the presence of a base which further leads to the formation of a pi-bond in the molecule.
- In E$_1$, the reaction rate is also proportional to the concentration of the substance to be transformed.
- It exhibits first-order kinetics**.**
- E 1 mechanism shares the features of the SN$_1$ reaction. The initial step is the formation of a carbocation intermediate through the loss of the leaving group. This slow step becomes the rate-determining step for the whole reaction.

ii) E$_2$ Reaction:

- In an E$_2$ mechanism which refers to bimolecular elimination is basically a one-step mechanism.

- Here, the carbon-hydrogen and carbon-halogen bonds mostly break off to form a new double bond.
- However, in the E_2 mechanism, a base is part of the rate-determining step and it has a huge influence on the mechanism.
- The reaction rate is mostly proportional to the concentrations of both the eliminating agent and the substrate.
- It exhibits second-order kinetics**.**

The E_2 mechanism can generally be represented as below. In the below-mentioned representation, B stands for base and X stands for the halogen.

3.1.3 Substitution Reaction:

Substitution reactions are characterized by replacement of an atom or group (Y) by another atom or group (Z). Aside from these groups, the number of bonds does not change.

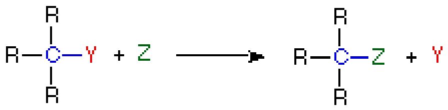


Fig.4. Substituion reaction

The reaction of an ester with ammonia to give an amide, as shown below, appears to be a substitution reaction ($Y = CH_3O$ & $Z = NH_2$); however, it is actually two reactions, an addition followed by an elimination.

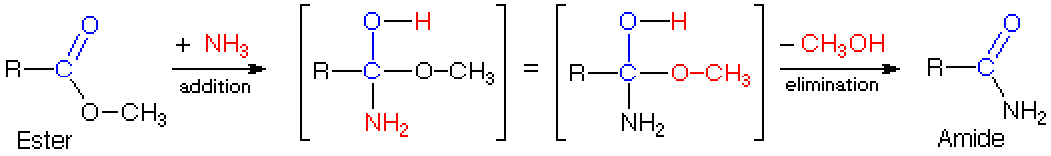


Fig.5. Example for Substitution reaction

3.1.4 Rearrangement Reaction:

A rearrangement reaction generates an isomer, and again the number of bonds normally does not change.

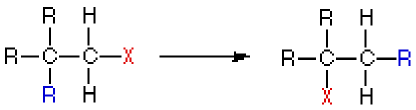


Fig.6. Addition reaction

Example:

Curtius Rearrangement or Curtius Reaction

It involves the heating of an acyl azide which loses nitrogen and then rearranges to an isocyanate.

$RCON_3 \rightarrow R\text{-}N{=}C{=}O + N_2$

If the reaction is performed in an alcoholic or aqueous medium, the isocyanate further reacts to form urethane, amine or substituted urea.

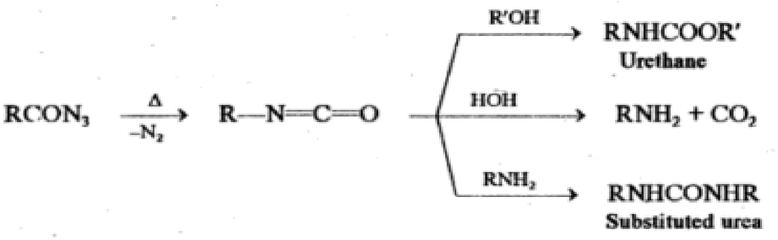


Fig.7. Example of Rearrangement reaction

3.2 Cleavage of bonds

Bond cleavage or bond fission is the splitting of chemical bonds. This is referred to as dissociation when a molecule is cleaved into two or more fragments. In general, there are two classifications for bond cleavage:

i) homolytic cleavage

ii) heterolytic cleavage

i) Homolytic cleavage:

It is the breaking of a covalent bond in such a way that each fragment gets one of the shared electrons. In homolytic cleavage, the two electrons in the bond are divided equally between the products. Homolytic cleavage often produces radicals. In the photolytic bromination of methane, the chain initiation mechanism step is an example of homolytic bond cleavage.

ii) Heterolytic cleavage:

In this cleavage, one atom gets both of the shared electrons. When a covalent bond joining two atoms A and B breaks in such a way that both the electrons of the covalent bond are taken away by one of the bonded atoms, the mode of bond cleavage is called heterolytic Cleavage. In the curved arrow formalism, the movement of single electrons is indicated by half-headed arrows. The movement of electron pairs is indicated by full-headed arrows. The following examples illustrate the outcomes of homolytic and heterolytic bond cleavage.

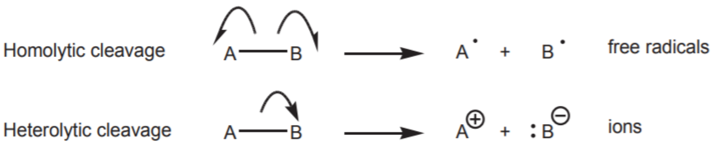


Fig.8. Structural representation of hemolytic and heterolytic cleavage reaction

When the atom in question is a positively charged carbon, the resulting species is called a carbocation. If it is negatively charged, it is called a carbanion. The following represent all three species with carbon as the central atom.

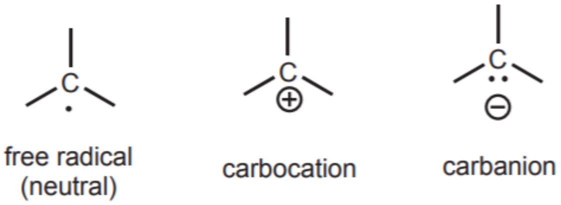


Fig.9. Example for free radical, carbocation and carbanion

3.3 Reactive intermediates

A reactive intermediate is a short-lived, high-energy and reactive molecule. When generated in a chemical reaction, it will quickly convert into a more stable molecule. Only in exceptional cases can these compounds be isolated and stored, e.g. low temperatures, matrix isolation. When their existence is indicated, reactive intermediates can help explain how a chemical reaction takes place. Most chemical reactions take more than one elementary step to complete, and a reactive intermediate is a high-energy, yet stable, product that exists only in one of the intermediate steps. The series of steps together make a reaction mechanism. A reactive intermediate differs from a reactant or product or a simple reaction intermediate only in that it cannot usually be isolated but is sometimes observable only through fast spectroscopic methods. It is stable in the sense that an elementary reaction forms the reactive intermediate and the elementary reaction in the next step is needed to destroy it. When a reactive intermediate is not observable, its existence must be inferred through experimentation. This usually involves changing reaction conditions such as temperature or concentration and applying the techniques of chemical kinetics, chemical thermodynamics, or spectroscopy.

Example: carbocations, radicals, carbanions and carbenes.

3.3.1 Common features

Reactive intermediates have several features in common:

- low concentration with respect to reaction substrate and final reaction product
- often generated on chemical decomposition of a chemical compound
- it is often possible to prove the existence of this species by spectroscopic means
- cage effects have to be taken into account
- often stabilization by conjugation or resonance
- often difficult to distinguish from a transition state
- prove existence by means of chemical trapping

3.3.2 Carbocations (R+)

A carbocation is an ion with a positively-charged carbon atom. Among the simplest examples are methenium CH_3^+, methanium CH_5^+, and ethanium $C_2H_7^+$. All carbocations were called carbonium ions. A carbocation is any positively charged carbon atom, classified in two main categories according to the valence of the charged carbon:

- +3 in carbenium ions (protonated carbenes),
- +5 or +6 in the carbonium ions (protonated alkanes, named by analogy to ammonium). These are much less common.

3.3.2.1 Structure and properties

The charged carbon atom in a carbocation is a "sextet", i.e. it has only six electrons in its outer valence shell instead of the eight valence electrons that ensures maximum stability (octet rule). Therefore, carbocations are often reactive, seeking to fill the octet of valence electrons as well as regain a neutral charge. One could reasonably assume a carbocation to have sp3 hybridization with an empty sp3 orbital giving positive charge. However, the reactivity of a carbocation more closely resembles sp2 hybridization with a trigonal planar molecular geometry. An example is the methyl cation, CH_3^+.

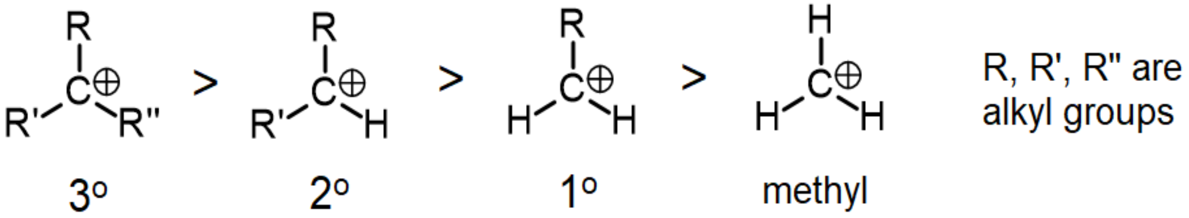


Fig.10. Stability of carbocations

The order of stability of examples of tertiary (3°), secondary (2°), and primary (1°) alkyl carbenium ions, as well as the methyl cation (far right). The methyl group is so unstable because it is only observed in the gas phase.

A carbocation may be stabilized by resonance by a carbon-carbon double bond next to the ionized carbon. Such cations as allyl cation $CH_2=CH–CH_2^+$ and benzyl cation $C_6H_5–CH_2^+$ are more stable than most other carbocations. Molecules that can form allyl or benzyl carbocations are especially reactive. These carbocations where the C+ is adjacent to another carbon atom that has a double or triple bond have extra stability because of the overlap of the empty p orbital of the carbocation with the p orbitals of the π bond. This overlap of the orbitals allows the charge to be shared between multiple atoms – delocalization of the charge and, therefore, stabilizes the carbocation.

3.3.3 Radicals

A radicals is a seven electron intermediate that adopts a flat, sp^2 structure and it has four electron groups. The lone electron resides in a half-filled p-orbital. This sp^2 structure allows radicals to delocalize the single electron through resonance. We will study radical reactions in detail in the second semester.

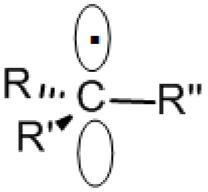


Fig.11. Example of Radical

Being short of the octet, radicals are electrophilic, and therefore they are stabilized by alkyl groups. Thus the order for stability is the same as for carbocations, namely tertiary > secondary > primary > methyl.

3.3.4 Carbanions

A carbanion is an eight electron intermediate with a sp^3 structure with full octet structure. It is very reactive due to the fact that carbon is not very electronegative. Although it is sp^3, it can participate in resonance because it can easily re-hybridize to a sp^2 structure which allows overlap. Carbanions are electron-rich and nucleophilic, so in fact they are destabilized by alkyl groups. This means that the order for stability is the opposite of that for carbocations, namely methyl > primary > secondary > tertiary.

Fig.12. Example of Carbanions

3.3.5 Carbenes

Carbenes are the least obvious of the four common intermediates; in most cases they have a six-electron sp^2 structure that has a lone pair but no charge. Although they are short of a full octet, they also have a reactive lone pair, so carbenes can be either electrophilic or nucleophilic, or sometimes both.

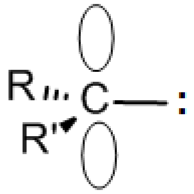


Fig.13. Example of carbene

3.3.6 Reaction of alkenes with carbenes:

Carbenes were once only thought of as short lived intermediates. The reactions of this section only deal with these short lived carbenes which are mostly prepared in situ, at the time of the main reaction. However, there do exist so called persistent carbenes, which are stabilized by a variety of methods often including aromatic rings or transition metals. In general a carbene is neutral and has six valence electrons, two of which are non bonding. These electrons can either occupy the same sp^2 hybridized orbital to form a singlet carbene (with paired electrons), or two different sp^2 orbitals to form a triplet carbene (with unpaired electrons). The reactivity of a singlet carbene is concerted and similar to that of electrophilic or nucleophilic addition. The highly reactive nature of carbenes leads to very fast reactions in which the rate determining step is generally carbene formation.

3.3.6.1 Preparation of methylene (:CH_2)

The preparation of methylene starts with the yellow gas diazomethane, CH_2N_2. Diazomethane can be exposed to light, heat or copper to facilitate the loss of nitrogen gas and the formation of the simplest carbene methylene. The process is driven by the formation of the nitrogen gas which is a very stable molecule.

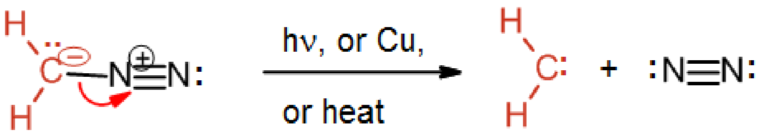


Fig.14. Production of Carbene

3.3.6.2 Carbene reaction with alkenes

A carbene such as methylene will react with an alkene which will break the double bond and result with a cyclopropane. The reaction will usually leave stereochemistry of the double bond unchanged.

As stated before, carbenes are generally formed during the reaction; hence the starting material is diazomethane not methylene.

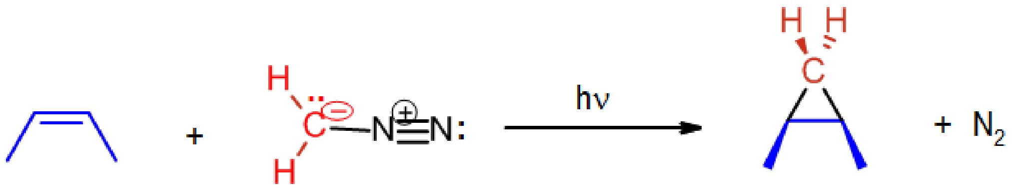


Fig.15. Reaction of carbenes with alkenes

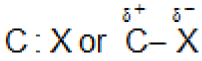
In the above case cis-2-butene is converted to cis-1,2-dimethylcyclopropane. Likewise, below the trans configuration is maintained.

3.4 Electron displacement effects:

3.4.1.1 Inductive Effect:

In a covalent bond between the two dissimilar atoms, the electron pair forming the bond is never shared absolutely equally between the two atoms but is attracted a little more towards the more electronegative atom of the two.

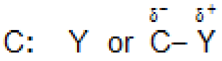
eg. The electron pair forming the C–X bond is somewhat more attracted towards the atom X with the result – it attains a partial negative charge ($-\delta$) while the carbon atoms attain a partial positive charge ($+\delta$).



$$C:X \text{ or } \overset{\delta+}{C}-\overset{\delta-}{X}$$

Fig.16. Example of –I effect

On the other hand, in compounds like C–Y, where Y in an electropositive element or group i.e., C is more electronegative than Y, the electron pair forming the C–Y bond is somewhat displaced towards the carbon atom and thus C and Y attain partial negative and partial positively charges respectively.



$$C: \; Y \text{ or } \overset{\delta-}{C}-\overset{\delta+}{Y}$$

Fig.17. Example of +I effect

According to Ingold sign convention, the former is called as (–I) effect and the later is called as (+I) effect. The inductive effect causes certain degree of polarity in the bond which in term renders the bond much more liable to be attacked by other charged atoms or group. Thus, inductive effect may be defined as the permanent displacement of electron forming a covalent bond towards the more electronegative element or group. The inductive effect is represented by the symbol → , the arrow pointing towards the more electronegative element or group of elements eg. N – butyl chloride . The extent of positive charge keeps on decreasing away from Cl atom and at third and fourth carbon it is almost zero for all practical purposes.

$$\overset{\delta\delta\delta\delta+}{CH_3} \rightarrow \overset{\delta\delta\delta+}{CH_2} \rightarrow \overset{\delta\delta+}{CH_2} \rightarrow \overset{\delta+}{CH_2} \rightarrow \overset{-\delta-}{Cl}$$

Examples of Inductive effect:

i) (–I) effect group (electron attracting)

$$\overset{+}{N}Me_3 > \overset{+}{N}H_3 > NO_2 > CN > COOH > F > Cl > Br > I > OAr > COOR > OR > OH$$
$$> C_6H_5 > CH{=}CH_2 > H$$

ii) (+I) effect – group (electron – repelling)

$$C_6H_5O^- > COO^- > R_3C > CHR_2 > CH_2R > CH_3 > H$$

- **Factors influencing Inductive Effect:**

a) Effect on Bond lengths:

Since the inductive effect leads to ionic character in the bond, the increase in –I effect usually decreases the bond length.

Increasing –I effect

$CH_3 \longrightarrow F$	$CH_3 \longrightarrow Br$	$CH_3 \longrightarrow Cl$	$CH_3 \longrightarrow F$
2.14Å	1.94 Å	1.78Å	1.38 Å

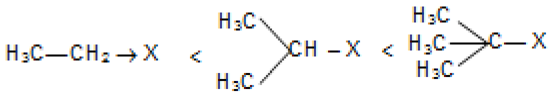
b) Dipole moment:

Since, inductive effect leads to a dipolar character in the molecule, it develops some dipole moment in the molecule, which increases with the increase in the inductive effect.

CH_3 – I, CH_3 — Br, CH_3 — Cl
Increasing dipole moment

c) Reactivity of alkyl halides:

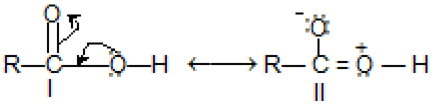
Alkyl halides are more reactive than the corresponding alkanes due to presence of C—X bond which is polar due to I effect, furthermore reactivity increases with increase of branching.



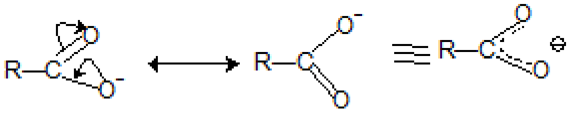
Increasing reactivity due to increasing C — X bond polarity

d) Strength of Carboxylic Acids:

Strength of an acid depends upon the ease with which an acid ionises to give proton. A molecule of carboxylic acid can be represented as a resonance hybrid of the following structures.



In the II structure, the oxygen atom of the hydroxyl group has a positive charge due to which it has a tendency to attract electron pair (inductive effect) of the O—H bond towards itself, which results in the removal of hydrogen atom as proton and hence carboxylic acids behave as acids. Once, the carboxylate anion is formed, it is stabilised more easily by resonance than undissociated acid.



Thus, the acidity of carboxylic acid is due to inductive effect and resonance stabilisation of the carboxylate anion. Thus any group or atom, which is highly electronegative help in removing the hydrogen atom as proton and the group or atom which is less electronegative than C makes the removal of proton difficult. Hence (–I) effect group increases acidic strength and (+I) effect groups decreases the acidic strength of carboxylic acid.

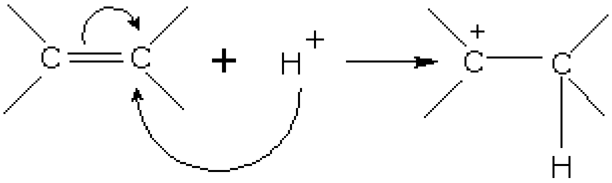
e) Basic strength of Amines:

The basic character of amines is due to presence of unshared electron pair on nitrogen atom which accepts proton; the readiness with which the lone pair of electrons available for protonotion determines the relative strength of amines. Due to +I effect of alkyl group, the nitrogen atom becomes rich in electrons with the result the lone pair of electron on nitrogen atom in amines is more easily available than in ammonia and hence generally, amines are stronger bases than ammonia. On the other (–I) groups or electron groups attached to nitrogen atom makes it difficult for protonation.

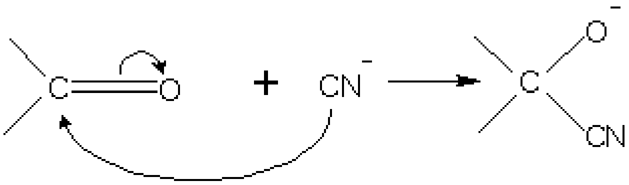
3.4.2 Electromeric Effect:

The electromeric effect is an intramolecular movement of electrons from a pi bond to another atom in the molecule due to attack by a reagent Electromeric effect is a reversible reaction where there is a complete transfer of a pi-electron due to the influence of an electrophile or a nucleophile. The effect disappears upon withdrawal of the attacking reagent. It is also non-specific in terms of its direction which is always that favours the reaction. It is seen only when there is an electron attacking reagent and is also referred as E effect. It is of two types:

i) Positive electromeric effect (+E effect)
In this effect the pi-electrons of the multiple bond are transferred to that atom to which the reagent get attached. For example,

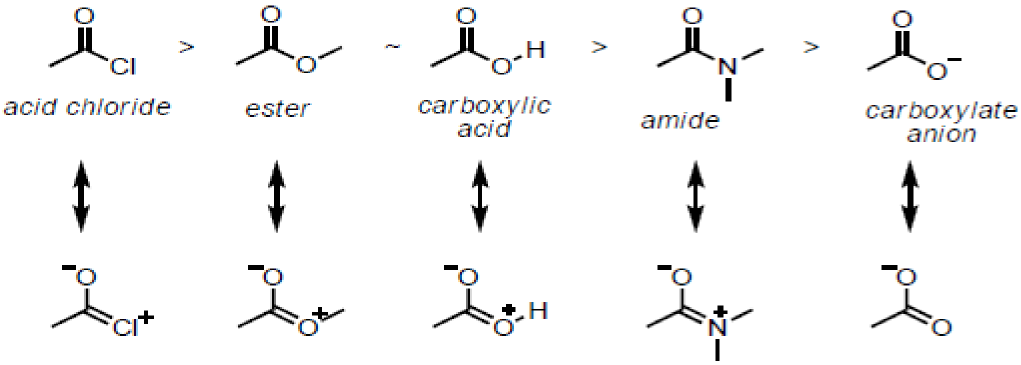


ii) Negative electromeric effect (-E effect)
In this effect the pi-electrons of the multiple bond are transferred to that atom to which the attacking reagents do not get attached. For example,



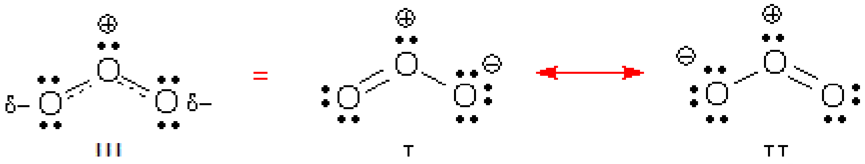
3.4.3 Mesomeric Effect:

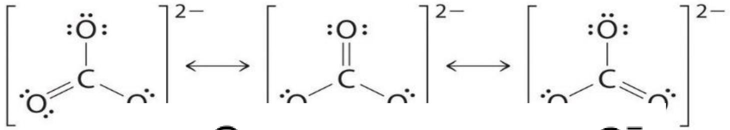
The permanent polarization of a group conjugated with a pi-bond or a set of pi-bonds is transmitted through the pi-elecrons of the system, resulting in a different distribution of electrons in the unsaturated chain. This type of electron distribution in unsaturated compounds conjugated with electron releasing or withdrawing groups or atoms is called mesomeric effect.

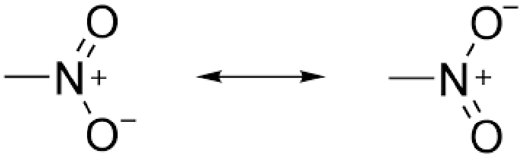


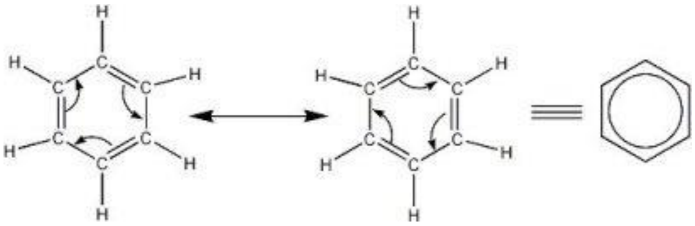
3.4.4 Resonance Effect:

Sometimes, there are several correct Lewis structures for a given molecule. Ozone (O_3) is one example. The compound is a chain of three oxygen atoms, and minimizing the charges while giving each atom an octet of electrons requires that the central oxygen atom form a single bond with one terminal oxygen and a double bond with the other terminal oxygen. When drawing the Lewis structure, the choice of placement for the double bond is arbitrary, and either choice is equally correct. The multiple correct ways of drawing the Lewis structure are called the resonance forms. The following are the examples for resonance structure:





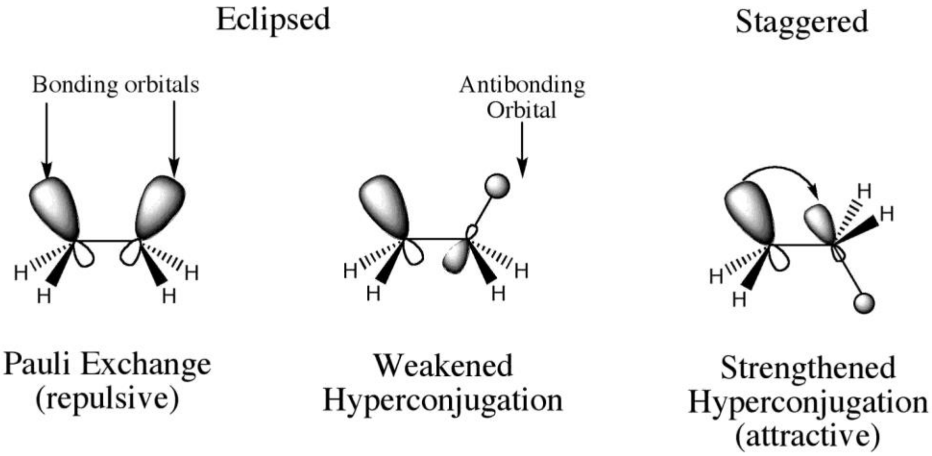




Based on the resonance forms, if ozone has bonds of two different lengths, since single bonds are generally longer than double bonds. However, the ozone molecule is perfectly symmetrical, with bonds that are the same length. None of the resonance forms represent the true structure of the molecule. Rather, the negative charge of the electrons that would form a double bond are delocalized, or distributed evenly across the three oxygen atoms.

3.4.5 Hyperconjugation Effect:

Hyperconjugation helps us to explain the stability of alkyl radicals. It involves the delocalization of sigma-electrons belonging to the C-H bond of the alkyl group attaching to an atom with an unshared p orbital. The more the hyperconjugative hydrogen, the more is the stability.



3.5 Hydrogen Bonding

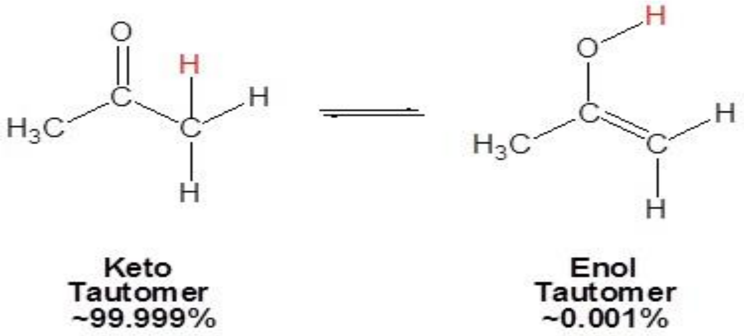
Hydrogen bonding, interaction involving a hydrogen atom located between a pair of other atoms having a high affinity for electrons. This bond is weaker than an ionic bond or covalent bond but stronger than van der Waals forces. Hydrogen bonds can exist between atoms in different molecules or in the same molecule. One atom of the pair (the donor), generally a fluorine, nitrogen, or oxygen atom, is covalently bonded to a hydrogen atom (—FH, —NH, or —OH), whose electrons it shares unequally. Its high electron affinity causes the hydrogen to take on a slight positive charge. The other atom of the pair such as F, N, or O, has an unshared electron pair, which gives it a slight negative charge. Mainly through electrostatic attraction, the donor atom effectively shares its hydrogen with the acceptor atom, forming a bond. Because of its extensive hydrogen bonding, water (H_2O) is liquid over a far greater range of temperatures that would be expected for a molecule of its size. Water is also a good solvent for ionic compounds and many others because it readily forms hydrogen bonds with the solute. Hydrogen bonding between amino acids in a linear protein molecule determines the way it folds up into its functional configuration. Hydrogen bonds between nitrogenous bases in nucleotides on the two strands of DNA (guanine pairs with cytosine, adenine with thymine) give rise to the double-helix structure that is crucial to the transmission of genetic information.

3.6 Tautomerism

Tautomers are isomers of a compound which differ only in the position of the protons and electrons. The carbon skeleton of the compound is unchanged. A reaction which involves simple proton transfer in an intramolecular fashion is called a tautomerism.

3.7 Keto-enoltautomerism

Because of the acidity of α hydrogens carbonyl functional group undergoes keto-enol tautomerism. Tautomers are rapidly interconverted constitutional isomers, usually distinguished by a different bonding location for a labile hydrogen atom and a differently located double bond. The equilibrium between tautomers is not only rapid under normal conditions, but it often strongly favors one of the isomers (acetone, for example, is 99.999% keto tautomer). Even in such one-sided equilibria, evidence for the presence of the minor tautomer comes from the chemical behavior of the compound. Tautomeric equilibria are catalyzed by traces of acids or bases that are generally present in most chemical samples.



Part A:

1. What are the types of organic reactions?
2. Define homolytic cleavage.
3. Define heterolytic cleavage.
4. Explain reactive intermediates.
5. Define carbocation.
6. Define carbanion.
7. What are free radicals?
8. What are carbenes?
9. What are nitrenes?
10. What are tautomers?

Part B:

1. Explain the various electronic displacement effects.
2. Discuss the factors affecting stability of the reaction intermediate.
3. Discuss the formation of carbocation, carbanion and free radicals.
4. Explain the structure, shape and reactivity of carbenes, nitrenes and arynes.
5. Discuss the hemolytic and heterolytic fission reaction with suitable examples.

References:

1. https://chem.libretexts.org/
2. https://byjus.com/chemistry/elimination-reaction/
3.https://chem.libretexts.org/Bookshelves/Organic_Chemistry/Organic_Chemistry_I_(Cortes)/10%3A_Intro_to_Theory_of_Chemical_Reactions/10.06%3A_Covalent_Bond_Cleavage-_Outcomes_and_Reaction_Intermediates

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SCHOOL OF SCIENCE AND HUMANITIES

DEPARTMENT OF CHEMISTRY

UNIT – 4 – ALKANES AND CYCLOALKANES – SCY1112

Structure and Nomenclature

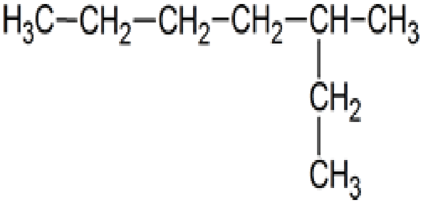
The IUPAC system of nomenclature aims to ensure

Every organic compound has a unique, unambiguous name.

IUPAC name of any compound conveys the structure of that compound to a person familiar with the system.

For example, if you named a compound 3-ethyl-4-methylheptane, you have indicated that the compound contains a total of 10 carbon atoms—seven carbon atoms in the main chain, two carbon atoms in an ethyl group, and one carbon atom in a methyl group. If you were to check the given structure and find 11 carbon atoms, you would know that you had made a mistake. Perhaps the name you should have written was 3-ethyl-4,4-dimethylheptane!

When naming alkanes, a common error of beginning students is a failure to pick out the longest carbon chain. For example, the correct name for the compound shown below is 3-methylheptane, not 2-ethylhexane.



$$H_3C-CH_2-CH_2-CH_2-\underset{\underset{CH_3}{|}}{\underset{CH_2}{\underset{|}{CH}}}-CH_3$$

3-methylheptane, not 2-ethylhexane

Every substituent must have a number, and prefixes like di, tri, tetra, etc should be used. Use commas to separate numbers. Hyphens to separate numbers and substituents. 3-methylhexane is a single word.

Hydrocarbons

The simplest class of organic compounds is the hydrocarbons, which consist entirely of carbon and hydrogen. Petroleum and natural gas are complex, naturally occurring mixtures of many different hydrocarbons that furnish raw materials for the chemical industry.

The four major classes of hydrocarbons are the following: the alkanes, which contain only carbon–hydrogen and carbon–carbon single bonds;

the alkenes, which contain at least one carbon–carbon double bond;

the alkynes, which contain at least one carbon–carbon triple bond; and the aromatic hydrocarbons, which usually contain rings of six carbon atoms that can be drawn with alternating single and double bonds. Alkanes are also called *saturated* hydrocarbons, whereas hydrocarbons that contain multiple bonds (alkenes, alkynes, and aromatics) are *unsaturated*.

Hydrocarbons having no double or triple bond functional groups are classified as alkanes or cycloalkanes, depending on whether the carbon atoms of the molecule are arranged only in chains or also in rings.

The alkanes and cycloalkanes are also members of a larger class of compounds referred to as aliphatic. Simply put, aliphatic compounds are compounds that do not incorporate any aromatic rings in their molecular structure.

The following table lists the IUPAC names assigned to simple continuous-chain alkanes from C-1 to C-10. A common **"ane"** suffix identifies these compounds as alkanes.

Longer chain alkanes are also known. The names methane through decane constitute the root of many IUPAC names. Fortunately, common numerical prefixes are used in naming chains of five or more carbon atoms.

Simple Alkanes

Name	**Molecular Formula**	**Structural Formula**	**Isomers**
Meth**ane**	CH_4	CH_4	1
Eth**ane**	C_2H_6	CH_3CH_3	1
Prop**ane**	C_3H_8	$CH_3CH_2CH_3$	1
But**ane**	C_4H_{10}	$CH_3CH_2CH_2CH_3$	2
Pent**ane**	C_5H_{12}	$CH_3(CH_2)_3CH_3$	3
Hex**ane**	C_6H_{14}	$CH_3(CH_2)_4CH_3$	5
Hept**ane**	C_7H_{16}	$CH_3(CH_2)_5CH_3$	9
Oct**ane**	C_8H_{18}	$CH_3(CH_2)_6CH_3$	18
Non**ane**	C_9H_{20}	$CH_3(CH_2)_7CH_3$	35
Dec**ane**	$C_{10}H_{22}$	$CH_3(CH_2)_8CH_3$	75

SOME IMPORTANT BEHAVIOR TRENDS AND TERMINOLOGIES

The formulas and structures of these alkanes increase uniformly by a CH_2 increment.

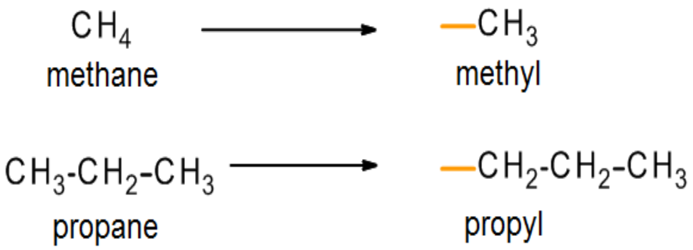
A uniform variation of this kind in a series of compounds is called **homologous**.

These formulas all fit the $\mathbf{C_nH_{2n+2}}$ rule (for acyclic and non-cyclic) alkanes. This is also the highest possible H/C ratio for a stable hydrocarbon.

Since the H/C ratio in these compounds is at a maximum, we call them **saturated** (with hydrogen).

Alkyl groups

Acyclic alkanes can be described by the general formula C_nH_{2n+2}. An alkyl group is formed by removing one hydrogen from the alkane chain and is described by the formula C_nH_{2n+1}. The removal of this hydrogen results in a stem change from **-ane** to **-yl**.



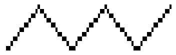
The orange "bond" shows the point of attachment

Alkyl Groups Names

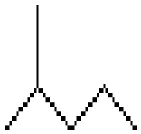
Group	**Name**
CH_3–	Methyl
C_2H_5–	Ethyl
$CH_3CH_2CH_2$–	Propyl
$(CH_3)_2CH$–	Isopropyl
$CH_3CH_2CH_2CH_2$–	Butyl
$(CH_3)_2CHCH_2$–	Isobutyl
$CH_3CH_2CH(CH_3)$–	sec-Butyl
$(CH_3)_3C$–	tert-Butyl

- R– Alkyl

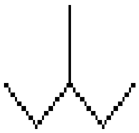
Beginning with butane (C_4H_{10}), and becoming more numerous with larger alkanes, we note the existence of alkane isomers. For example, there are five C_6H_{14} isomers, shown below as abbreviated line formulas (**A** through E):



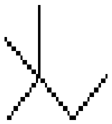
A



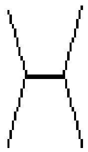
B



C



D



E

Although these distinct compounds all have the same molecular formula, only one (**A**) can be called hexane.

The **IUPAC** system requires first that we have names for simple unbranched chains, as noted above, and second that we have names for simple alkyl groups that may be attached to the chains. Examples of some common **alkyl groups** are given in the following table. Note that the "ane" suffix is replaced by "**yl**" in naming groups. The symbol **R** is used to designate a generic (unspecified) alkyl group.

IUPAC Rules for Alkane Nomenclature

- Find and name the longest continuous carbon chain.
- Identify and name groups attached to this chain.
- Number the chain consecutively, starting at the end nearest a substituent group.
- Designate the location of each substituent group by an appropriate number and name.
- Assemble the name, listing groups in alphabetical order.
- The prefixes di, tri, tetra etc., used to designate several groups of the same kind, are not considered when alphabetizing.
- For the above isomers of hexane the IUPAC names are:
- B 2-methylpentane
- C 3-methylpentane
- D 2,2-dimethylbutane
- E 2,3-dimethylbutane.

General Methods of Synthesis of Alkanes

Decarboxylation

Decarboxylation refers to the process of removal of CO_2 from the molecules having -COOH group. Saturated monocarboxylic acid salt of sodium potassium on dry distillation with soda lime gives alkane.

$$RCOONa \xrightarrow[-CO_2]{Soda Lime} R - H$$

$$RCOONa + NaOH \overset{CaO}{\rightarrow} R - H + Na_2CO_3$$

The alkane formed by decarboxylation process always contains one carbon atom less than the original acid.The yield is good in case of lower members but poor for higher members.

Soda lime is prepared by soaking quick lime CaO in caustic soda solution and then drying the products. It is generally written as NaOH + CaO. Its reaction is milder than caustic soda. Otherwise the reaction will occur violently. Also CaO used alongwith NaOH keeps it dry (NaOH is hygroscopic) to aid fusion.

The decarboxylation of sodium formate yields H_2.

$HCOONa + NaOH \rightarrow H_2 + Na_2CO_3$

$CH_3COONa + NaOH \rightarrow CH_4 + Na_2CO_3$

Wurtz Reaction

In Wurtz reaction a solution of alkyl halide in ether on heating with sodium gives alkane.

$$R - X + 2Na + X - R \overset{DryEther}{\rightarrow} R - R' + 2NaX$$

An alkyl halide on Wurtz reaction leads to the formation of symmetrical alkane having an even number of carbon atoms. Two different alkyl halides, on Wurtz reaction give all possible alkanes.

$$CH_3X + Na + C_2H_5X \rightarrow CH_3CH_2CH_3 + CH_3CH_3 + CH_3CH_2CH_2CH_3$$

The different involved are steps are:

$CH_3X + 2Na + C_2H_5X \rightarrow CH_3CH_2CH_3 + 2NaX$

$CH_3X + 2Na + C_2H_5X \rightarrow CH_3CH_3 + 2NaX$

$C_2H_5X + 2Na + C_2H_5X \rightarrow C_2H_5C_2H_5 + 2NaX$

The separation of mixture into individual members is not easy because their boiling points are near to each other and thus Wurtz reaction is not suitable for the synthesis of alkanes containing odd number of carbon atoms.

When Zn is used in Wurtz reaction in place of Na, the reaction is named as Frankland method.

Limitations of Wurtz reaction :

a.Methane can not be obtained by this method

b.The reaction fails in case of tertiary halides

Mechanism of Wurtz reaction :

The mechanism of Wurtz reaction is although not clear however two mechanisms are proposed for this reaction.

The first proposed mechanism of Wurtz reaction involved formation of an Intermediate organometallic compound:

$RX + 2Na \rightarrow [RNa] + NaX$

Intermediate

$RX + [RNa] \rightarrow R\text{-}R + NaX$

Another proposed mechanizm of Wurtz reaction involved formation of Intermediate free radicals:

$RX + Na \rightarrow R^{\cdot} + Nax$

Free radicals

$R^{\cdot} + R^{\cdot} \rightarrow R\text{-}R$

By the Reduction of Alkyl Halides

Alkyl halides on reduction with nascent hydrogen form alkanes. $R\text{-}X + 2[H] \rightarrow R\text{-}H + HX$. The nascent hydrogen may be obtained by any one of the following

Zn + HCI

Zn + CH_3COOH

Zn-Cu couple in ethanol

Red P + HI

Al-Hg + ethanol

Alkyl halides can also be reduced catalytically to alkane by H_2/Pd or $LiAIH_4$ or by H_2/Ni. The yields are generally high and the hydrocarbons formed are pure.

Zn-Cu couple is prepared by adding Zn granules in aqueous $CuSO_4$ solution where copper is deposited on the Zn pieces.

By Hydrogenation of Alkenes((>C=C<) : Sabatier and Senderen's Method

Alkenes and alkynes on catatlytic hydrogenation give alkanes

$$CH_2 = CH_2 + H_2 \xrightarrow{Ni, 200^0 C} CH_3\text{-}CH_3$$

$$CH{\equiv}CH + 2H_2 \xrightarrow{Ni, 200^0 C} CH_3\text{-}CH_3$$

Catalyst Ni is used in finely divided form. If Pt or Pd are used as catalyst, reaction occurs at normal temperature. Also some times Raney nickel is used as catalyst. It is obtained by boiling Ni-AI alloy with NaOH, when AI dissolves leaving Ni in finely divided state. The filtered, washed and died Ni is known as Raney Nickel. Raney Ni is effective at room temperature and atmospheric pressure.

Kolbe's Electrolysis Method

Alkanes are formed, on electrolysis of concentrated aqueous solution of sodium or potassium salt of saturated mono carboxylic acids

$$RCOONa_{aq} \xrightarrow{electrolysis} \overbrace{R\text{-}R + 2CO_2}^{\text{Anode}} + \overbrace{2NaOH + H_2}^{\text{Cathode}}$$

Electrolysis of an acid salt gives symmetrical alkane. However, in case of mixture of carboxylic acid salts, all probable alkanes are formed.

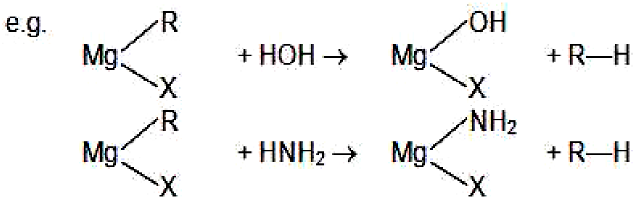
$$R^1COOK + R^2COOK \xrightarrow{electrolysis} R^1\text{-}R^2 + 2CO_2 + H_2 + 2NaOH$$

(R^1-R^1 and R^2-R^2 are also formed).

By Grignard Reagents

Organic compounds in which a metal atom is directly linked to carbon atom are known as organometallic compound. e.g. HC≡CNa, $(C_2H_5)_4$ Pb, $(C_2H_5)_2$ Zn

Alkyl or aryl magnesium halide (R-MgX) are also called Grignard reagents or organometallic compounds.Grignard reagent on double decomposition with water or with other compounds having active H(the hydrogen attached on O, N, F or triple bonded carbon atom are known as active hydrogen) give alkane.



By Reduction of Alcohols, Aldehydes, Ketones or Fatty Acids and their Derivatives

The reduction of either of the above in presence of red P & HI gives corresponding alkane.

$$R—OH \xrightarrow[200^\circ C]{Red\ P+2HI} R—H + H_2O + I_2$$

$$R—CHO \xrightarrow[200^\circ C]{Red\ P+4HI} R—CH_3 + H_2O + 2I_2$$

$$R—COR \xrightarrow[200^\circ C]{Red\ P+4HI} RCH_2R + H_2O + 2I_2$$

$$R—COOH \xrightarrow[200^\circ C]{Red\ P+6HI} RCH_3 + 2H_2O + 3I_2$$

$$R—COOR' \xrightarrow{As\ above} RCH_3 + R'H$$

$$(R—CO)_2O \xrightarrow{As\ above} 2RCH_3$$

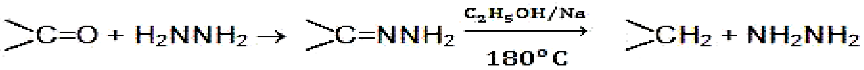
$$RCOCl \xrightarrow{As\ above} RCH_3$$

$$RCONH_2 \xrightarrow{As\ above} RCH_3$$

By Reduction of Carbonyl Compounds

The reduction of carbonyl compounds by amalgamated zinc and conc. HCl also yields alkanes. This is **Clemmensen reduction.**

1. $CH_3CHO + 2H_2 \xrightarrow{Zn+Hg/HCl} CH_3CH_3 + H_2O$
2. $CH_3COOH + 2H_2 \xrightarrow{Zn+Hg/HCl} CH_3CH_2CH_3 + H_2O$
3. Carbonyl compounds may also be reduced to alkanes by Wolf Kishner reaction



$$>C=O + H_2NNH_2 \rightarrow >C=NNH_2 \xrightarrow[180^\circ C]{C_2H_5OH/Na} >CH_2 + NH_2NH_2$$

By the Hydrolysis of AI or Be Carbides

Only CH_4 can be obtained by the hydrolysis of Be or Al carbides.

$$Al_4C_3 + 12H_2O \xrightarrow{\Delta} 4Al(OH)_3 + 3CH_4$$

$$Be_2C + 4H_2O \xrightarrow{\Delta} 2Be(OH)_2 + CH_4$$

Note :

1. Calcium carbide reacts with water to give acetylene.

2. Magnesium carbide, Mg2C_2 reacts with water to give propyne.
3. CH_4 can be obtained by passing a mixture of H_2S and CS_2 through red and Cu tube

$$CS_2 + 2H_2S \xrightarrow{Cu} CH_4 + 4Cu_2S$$

By Hydroboration of Alkenes

Alkenes on hydroboration give trialkyl borane as a result of addition of diborane on olefinic bond. This trialkyl borane on treatment with acetic acid or propanoic acid yields alkane.

$$2R-CH=CH_2 \xrightarrow{B_2H_6} 2(RCH_2CH_2)3B \xrightarrow{CH_3COOH} 2RCH_2CH_3$$

By Corey- House Synthesis

Alkyl chloride say chloroethane reacts with lithium in presence of ether to give lithium alkyl then reacts with CuI to give lithium dialkyl cuprate. This lithium dialkyl cuprate now again reacts with alkyl chloride to given alkane.

$$CH_3CH_2Cl + 2Li \xrightarrow{Ether} CH_3CH_2Li + LiCl$$

$$2CH_3CH_2Li + CuI \ ? \ Li(CH_3CH_2)_2\,Cu + LiL$$

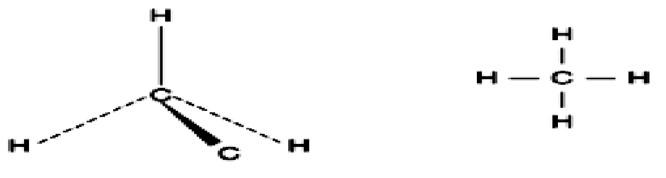
$$Li(CH_3CH_2)_2Cu + CH_3CH_2Cl \ ? \ CH_3CH_2CH_2CH_3 + CH_3CH_2Cu + LiCl$$

Physical Properties of Alkanes

1. Structures of Alkanes

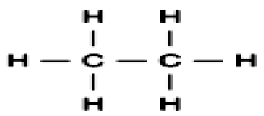
All the carbon atoms present in an alkane are sp3 hybridized that is, every carbon atom forms four sigma bonds with carbon or hydrogen atoms. General configuration of alkane is CnH2n+2. They exhibit tetrahedral geometry with a bond angle of 109.47° between them.

The methane molecule has a symmetrical tetrahedral structure.



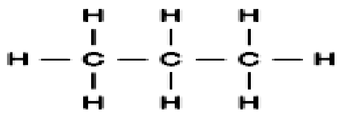
3-D representation 2-D representation

Spatial and graphical formula of methane



Ethane

$CH_3 — CH_3$



Propane

$CH_3 — CH_2 — CH_3$

2. Solubility of Alkanes

Due to very little difference of electroneativity between carbon and hydrogen and covalent nature of C-C bond or C-H bond, alkanes are generally non-polar molecules.

As we generally observe, polar molecules are soluble in polar solvents whereas non-polar molecules are soluble in non-polar solvents. Hence, alkanes are hydrophobic in nature that is, alkanes are insoluble in water.

However, they are soluble in organic solvents as the energy required to overcome the existing Van Der Waals forces and generate new Van Der Waals forces is quite comparable.

3. Boiling Point of Alkanes

As the intermolecular Van Der Waals forces increase with the increase of the molecular size or the surface area of the molecule we observe

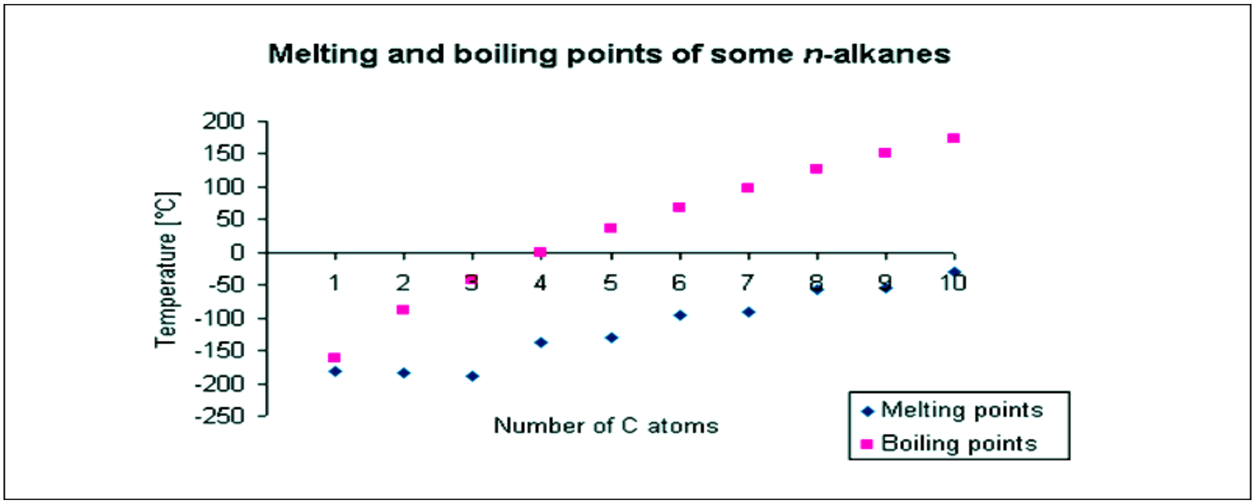
The boiling point of alkanes increases with increasing molecular weight.

The straight-chain alkanes are observed to have a higher boiling point in comparison to their structural isomers.

4. Melting Point of Alkanes

The melting point of alkanes follows the same trend as their boiling point that is, it increases with an increase in molecular weight.

This is attributed to the fact that higher alkanes are solids and it's difficult to overcome intermolecular forces of attraction between them. It is generally observed that even-numbered alkanes have higher trend in melting point in comparison to odd-numbered alkanes as the even-numbered alkanes pack well in the solid phase, forming a well-organized structure which is difficult to break.



Chemical Properties of Alkanes

Alkanes are the least reactive type of organic compound. Alkanes are not absolutely unreactive. Two important reactions that they undergo are combustion, which is the reaction with oxygen and halogenation, which is the reaction with halogens.

1. Combustion

A combustion reaction is a chemical reaction between a substance and oxygen that proceeds with the evolution of heat and light. Alkanes readily undergo combustion reactions when ignited. When sufficient oxygen is present to support total combustion then carbon dioxide and water are the products. The exothermic nature of alkane combustion reactions explains the extensive use of alkanes as fuels. Natural gas, used in home heating is predominantly methane.

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O + \text{energy}$$

$$2C_6H_{14} + 19O_2 \longrightarrow 12CO_2 + 14H_2O + \text{energy}$$

2. Halogenation

Halogenation of an alkane produces a hydrocarbon derivative in which one or more halogen atoms have been substituted for hydrogen atoms. An example of an alkane halogenation reaction is

$$CH_3\text{-}CH_3 + Br_2 \longrightarrow CH_3\text{-}CH_2\text{-}Br + HBr$$

Alkane halogenation is an example of a substitution reaction a type of reaction that often occurs in organic chemistry.

A general equation for the substitution of a single halogen atom for one of the hydrogen atoms of an alkane is

$$\mathbf{R\text{-}H + X_2 \rightarrow R\text{-}X + H\text{-}X}$$

Chemical Reactivity of Alkanes

Alkanes are stable compounds and are generally unreactive.

The most important application of alkanes is in oxidation reactions; they are used in internal combustion engines as fuel.

Applying heat and a catalyst can crack larger, more complex alkanes and produce smaller, more useful alkanes and alkenes.

Oxidation Reactions

The most important reaction that alkanes undergo is combustion. Smaller, linear alkanes generally oxidize more readily than larger, more branched molecules. Alkanes can be burned in the presence of oxygen to produce carbon dioxide, water, and energy; in situations with limited oxygen, the products are carbon monoxide, water, and energy. For this reason, alkanes are frequently used as fuel sources. The combustion of methane is shown:

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O + \text{energy}$$

$$CH_4 + 3O_2 \xrightarrow{\text{Incomplete Combustion}} 2CO + 4H_2O$$

Carbon black, which is used in the manufacture of ink, paints, polishes etc., is prepared by incomplete combustion.

Controlled Oxidation of Alkanes

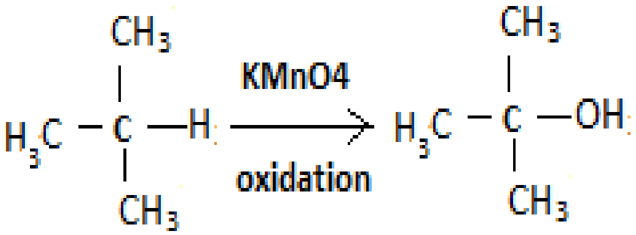
Alkanes on heating with a regulated supply of air or O_2 in the presence of suitable catalyst give different products under different conditions.

$$2CH_4 + O_2 \xrightarrow[523\ K/100\ atm]{Cu} 2CH_3OH$$

$$CH_4 + O_2 \xrightarrow[\Delta]{Mo_2O_5} HCHO + H_2O$$

$$2CH_3CH_3 + 3O_2 \xrightarrow[\Delta]{(CH_3COO)_2Mn} 2CH_3COOH + 2H_2O$$

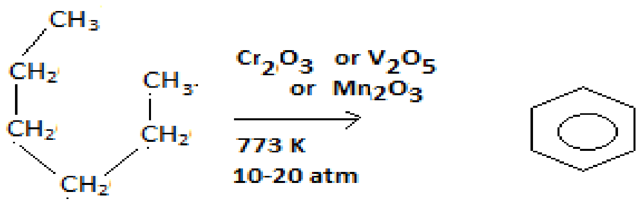
Alkanes usually resist oxidation with oxidising agents such as $KMnO_4$, $K_2Cr_2O_7$ etc. However, alkanes containing tertiary hydrogen can be oxidised to corresponding alcohols.



$$H_3C-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-H \xrightarrow[\text{oxidation}]{KMnO4} H_3C-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-OH$$

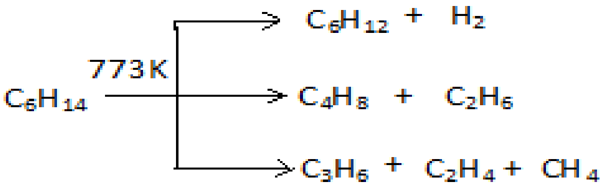
Aromatization of Alkanes

Straight chain alkanes containing six or more carbon atoms on heating to 773K at 10-20 atmospheric pressure in the presence of oxides of a catalyst consisting of oxides of chromium, vanadium and molybdenum supported over alumina get dehydrogenated and converted into benzene and its homologues.



Pyrolysis of Alkanes

Higher alkanes on heating to higher temperature decompose into lower hydrocarbons (alkanes, alkenes etc.). Such a decomposition is known as **pyrolysis** or **cracking**.



Halogenation

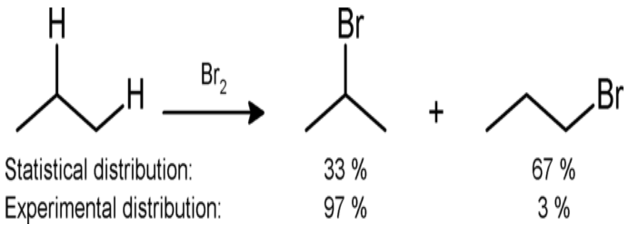
With the addition of a halogen gas and energy, alkanes can be halogenated with the reactivity of the halogens proceeding in the following order: $Cl_2 > Br_2 > I_2$.

In this reaction, UV light or heat initiates a chain reaction, cleaving the covalent bond between the two atoms of a diatomic halogen. The halogen radicals can then abstract protons from the alkanes, which can then combine or react to form more radicals. Alkanes can be halogenated at a number of sites, and this reaction typically yields a mixture of halogenated products.

When the mixture of hydrocarbon and halogen is heated at 520-670 K in dark or is subjected to ultraviolet light at room temperature, the free radical substitution reaction takes place.

The reactivity of hydrogen towards free radical substitution is 3° > 2° > 1°. For example, when butane is used in free radical substitution reaction, the products we get are 1-Chlorobutane and 2-Chlorobutane. 2-Chlorobutane being the major product.

The rate of reaction of alkanes with halogens follows the order : $F_2 > Cl_2 > Br_2 > I_2$. Fluorination of alkanes is too vigorous to be controlled under normal conditions while iodination is very slow and a reversible reaction.

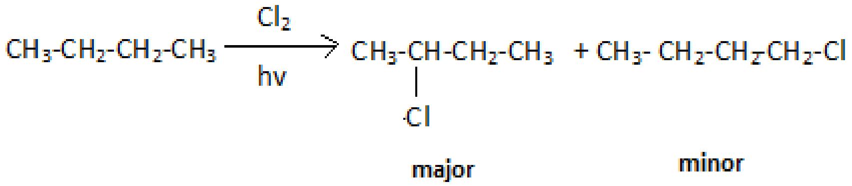


$$CH_4(g) + Cl_2(g) \longrightarrow CH_3Cl(g) + HCl(g)$$

Reaction with bromine gives an **alkyl bromide.**

$$CH_4(g) + Br_2(l) \xrightarrow{\text{light}} CH_3Br(g) + HBr(g)$$

$$CH_3\text{-}CH_3 \quad + \quad Cl_2 \xrightarrow[hv]{520\text{-}670\ K} CH_3\text{-}CH_2\text{-}Cl$$



$$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_3 \xrightarrow[hv]{Cl_2} CH_3\text{-}\underset{\displaystyle Cl}{\underset{|}{CH}}\text{-}CH_2\text{-}CH_3 \; + CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}Cl$$

Mechanism of free radical substitution reaction

Free radical substitution reaction is a chain reaction. Let's take the example of CH_4 and Cl_2 to understand the mechanism. The free radical substitution reaction consists of the following steps :

Initiation step

When a mixture of CH_4 and Cl_2 is heated at 520-670 K or is subjected to ultraviolet light at room temperature, Cl_2 absorbs energy and undergoes homolytic fission.

$$Cl_2 \xrightarrow[hv]{520\text{-}670\ K} 2Cl^{\bullet}$$

Propagation step

Propagation step consists of two substeps

1. The free radical of chlorine (formed in initiation step) attacks the CH_4 molecule and removes a hydrogen atom from CH_4 forming $\cdot CH_3$ and HCl.

$$CH_4 \; + Cl^{\bullet} \longrightarrow CH_3^{\bullet} \; + \; HCl$$

2. $\cdot CH_3$ thus produced, reacts with a molecule of Cl_2 which results in the formation of methyl chloride.

$$CH_3^{\bullet} + Cl_2 \longrightarrow CH_3\text{-}Cl + Cl^{\bullet}$$

3. This reaction continues until all the hydrogen atoms of methane are replaced by halogen atoms.

$$CH_4 \xrightarrow[hv]{Cl_2} CH_3\text{-}Cl \xrightarrow[hv]{Cl_2} CH_2Cl_2 \xrightarrow[hv]{Cl_2} CH\text{-}Cl_3 \xrightarrow[hv]{Cl_2} CCl_4$$

Termination step

The chain reaction may terminate if two of the same or different free radicals combine among themselves without producing new free radicals.

$$Cl^{\bullet} + Cl^{\bullet} \longrightarrow Cl_2$$

$$CH_3^{\bullet} + CH_3^{\bullet} \longrightarrow CH_3\text{-}CH_3$$

$$CH_3^{\bullet} + Cl^{\bullet} \longrightarrow CH_3\text{-}Cl$$

MECHANISM OF NITRATION OF ALKANE

1. Replacement of H atom of alkane by $-NO_2$ group is known as nitration.

2. Nitration of alkane is made by heating vapours of alkanes and HNO_3 at about 400°C to give nitroalkanes. This is also known as vapour phase nitration.

$$CH_4(g) + HNO_3(g) \rightarrow CH_3NO_2 + H_2O$$

3. During nitration, C-C bonds of alkanes are also decomposed due to strong oxidant nature of HNO_3 to produce all possible nitroalkanes.

MECHANISM OF SULPHONATION OF ALKANES

(i) Replacement of H atom of alkane by $-SO_3H$ is known as sulphonation.

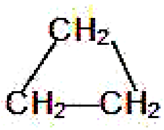
(ii) Lower normal alkanes are not sulphonated, but higher normal alkanes show sulphonation (hexane onwards) when heated with oleum (i.e., conc. H_2SO_4) at 400°C.

$$C_6H_{14} + H_2SO_4 \rightarrow C_6H_{13}SO_3H + H_2O$$

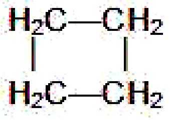
(iii) Lower members are sulphonated in vapour phase sulphonation.

Cycloalkanes or Cyclic hydrocarbons

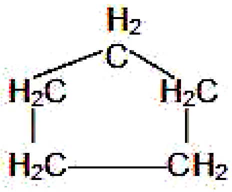
This class of hydrocarbons are carbocyclic hydrocarbons in which carbon atoms are joined by single covalent bonds to form a closed ring of carbon atoms. They are alicyclic in nature and have the general formula C_nH_{2n}. Following are some homologous members of this category.



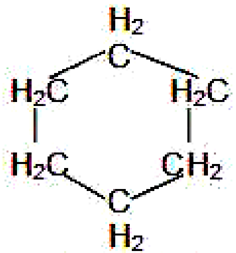
cyclopropone



cyclobutane



cyclopentane



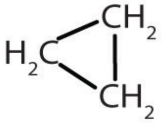
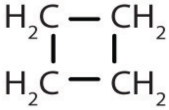
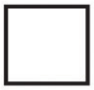
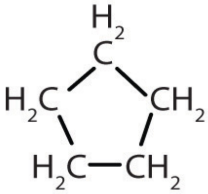
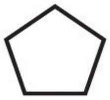
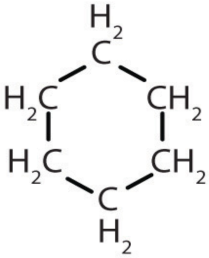
cyclohexane

In a cyclic hydrocarbon, the ends of a hydrocarbon chain are connected to form a ring of covalently bonded carbon atoms.

Cyclic hydrocarbons are named by attaching the prefix *cyclo*– to the name of the alkane, the alkene, or the alkyne.

The simplest cyclic alkanes are *cyclopropane* (C_3H_6) a flammable gas that is also a powerful anesthetic, and *cyclobutane* (C_4H_8).

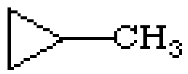
The most common way to draw the structures of cyclic alkanes is to sketch a polygon with the same number of vertices as there are carbon atoms in the ring; each vertex represents a CH_2 unit. The structures of the cycloalkanes that contain three to six carbon atoms are shown schematically in the figure below:

Name	Molecular Formula	Structural Formula
cyclopropane	C_3H_6	 or 
cyclobutane	C_4H_8	 or 
cyclopentane	C_5H_{10}	 or 
cyclohexane	C_6H_{12}	 or 

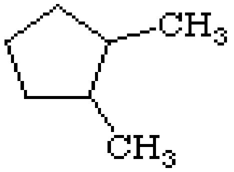
Lower members of cyclo alkanes are usually reported by simple geometrical drawing as etc. i.e. a triangle for cyclopropane, a square for cyclobutane, a pentagon for cyclopentane and a hexagon for cyclohexane.

The removal of one H atom from cycloalkanes give rise to cycloalkyl radicals.

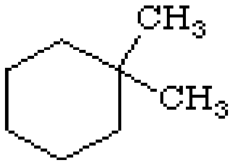
Substituted Cycloalkanes



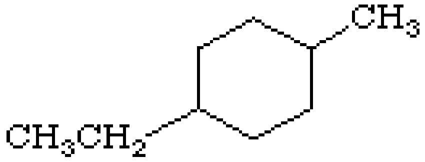
methylcyclopropane
(no number is needed)



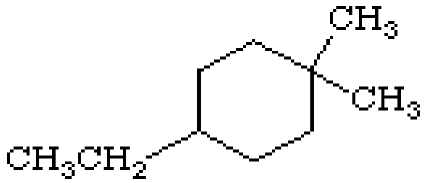
1,2-dimethylcyclopentane



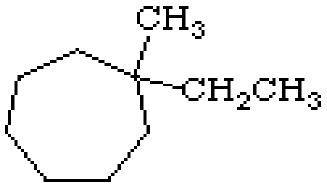
1,1-dimethylcyclohexane



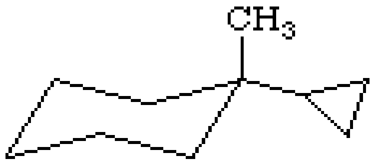
1-ethyl-4-methylcyclohexane
(assign numbers alphabetically)



4-ethyl-1,1-dimethylcyclohexane
(assign numbers to give lowest number at
first point of difference; arrange alphabetically)



1-ethyl-1methylcycloheptane



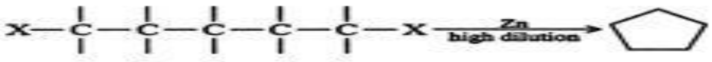
1-cyclopropyl-1-methylcyclohexane

Preparation methods

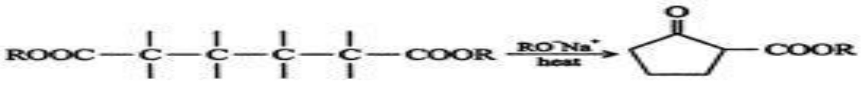
Carbene insertion

Simmons-Smith reaction

Modified Wurtz reaction

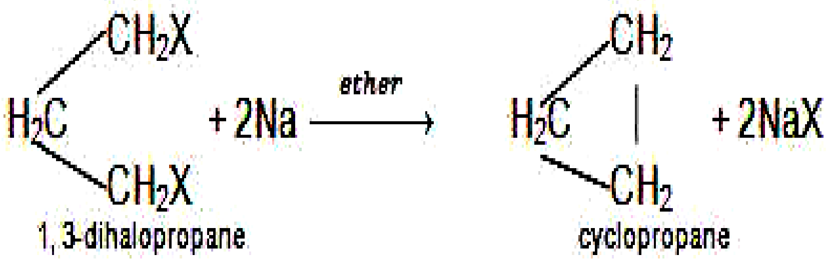


Dieckmann condensation

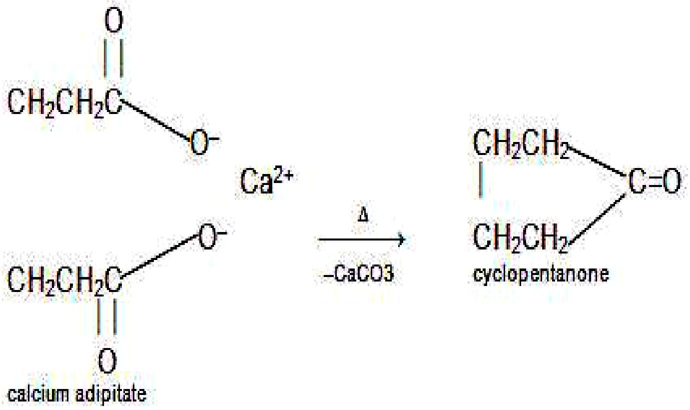


Following methods are commonly used for the preparation of cycloalkanes.

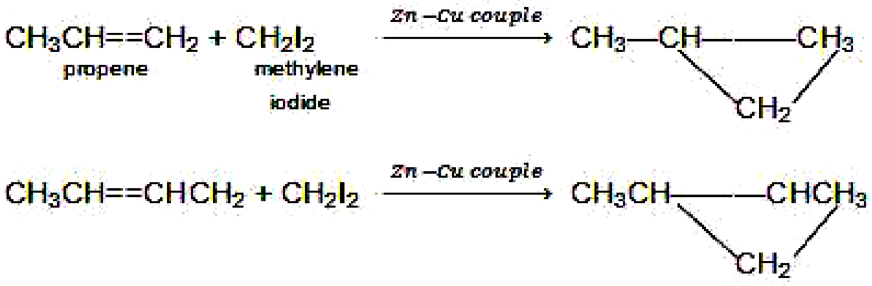
(a) From dihalogen compounds : α-ω elimination from dihalides having halogen atoms on two ends of carbon chain (α-ω dihalides) with Na or Zn dust gives rise to the formation of cycloalkanes. The method can be regarded as intramolecular Wurtz reaction and is called Freund reaction. This can be used to prepare cycloalkanes from three to six carbon atoms.



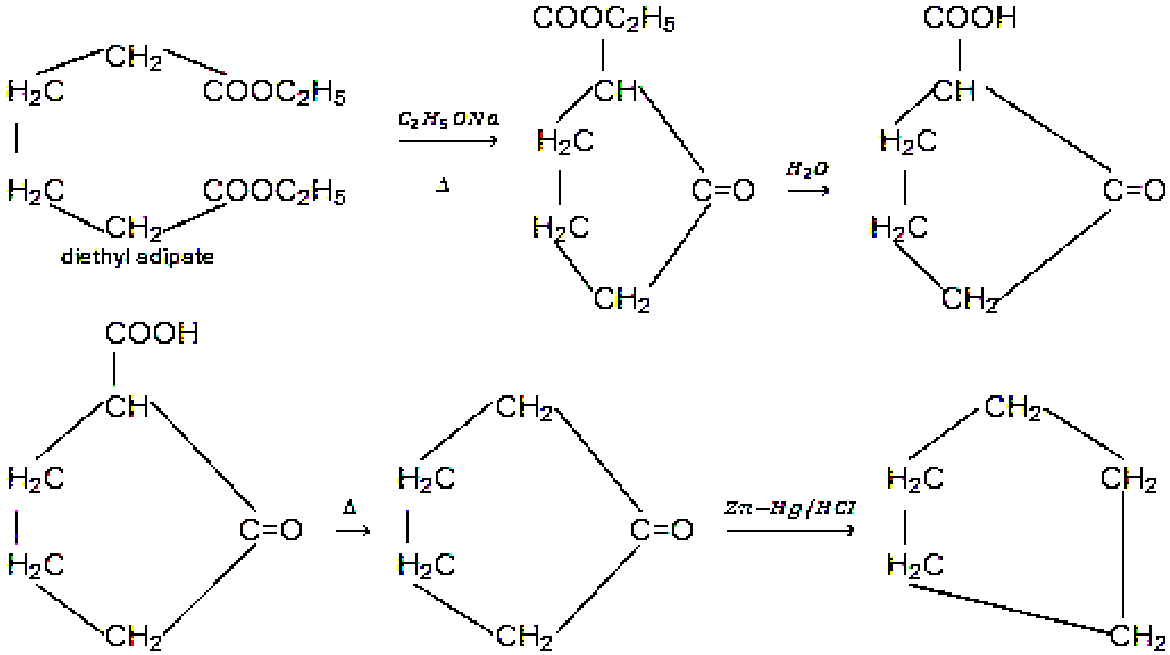
(b) By Clemmensen reduction : The reduction of cyclic ketones by Zn-Hg/HCI gives cycloalkanes.



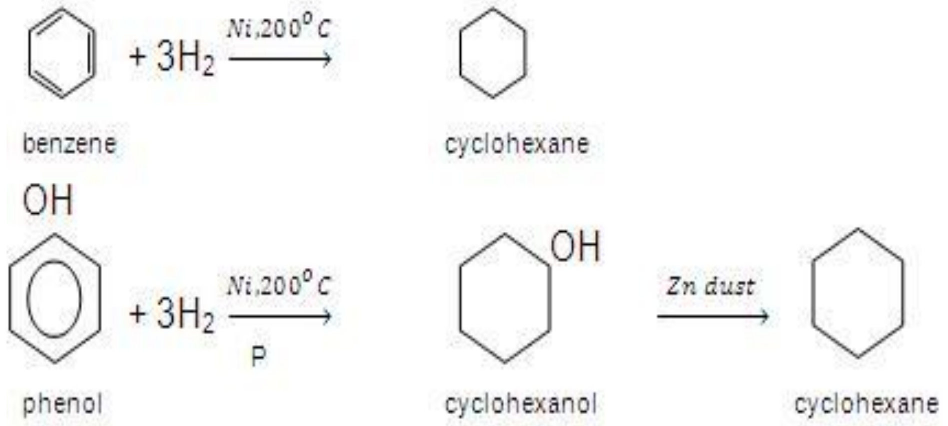
(c) From alkenes : Alkenes on treating with CH_2I_2 in presence of Zn-Cu couple or by diazomethane (CH_2N_2) in presence of UV light gives derivatives of cycloalkanes.



(d) By Dieckmann cylisation : Esters of dicarboxylic acids on heating in presence of sodium ethoxide undergo intramolecular Claisen condensation to gives cyclic β-keto esters. These β-keto esters on hydrolysis and subsequent heating gives cyclic ketones which are reduced by Zn-Hg/HCI to give cycloalkanes.



(e) From aromatic compounds: Six membered cyclo compounds can be easily obtained by the catalytic reduction of benzene and its derivatives.



Physical Properties of Cycloalkanes

Cyclopropane and cyclo butane are gases, next three members are liquid and higher members are solid.

These are insoluble in water but soluble in alcohol or acetone.

Their density increases with increase in molecular weight. Lower members are lighter than water and floats over it. It is therefore cyclohexane floats over water.

The boiling points increase with increase in molecular weight. The boiling point are also higher than their corresponding alkenes and alkanes.

Chemical Properties of Cycloalkanes

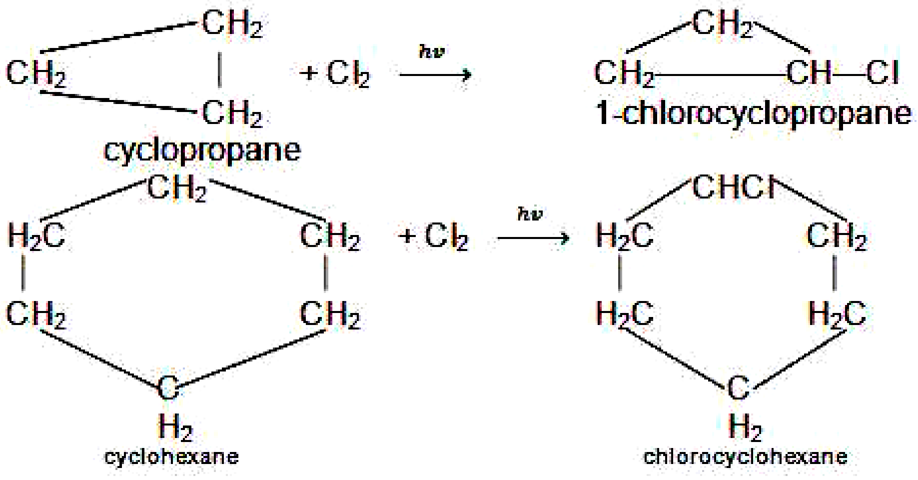
Cyclopropane and cyclobutane are comparatively less stable due to more strain in ring (Follow Baeyer's strain theory) and thus tend to breakup and open the ring to act like a double bond species to give addition reactions.

The cycloalkanes from cyclopentane and onwards show remarkable similaries with alkanes due to their stability.

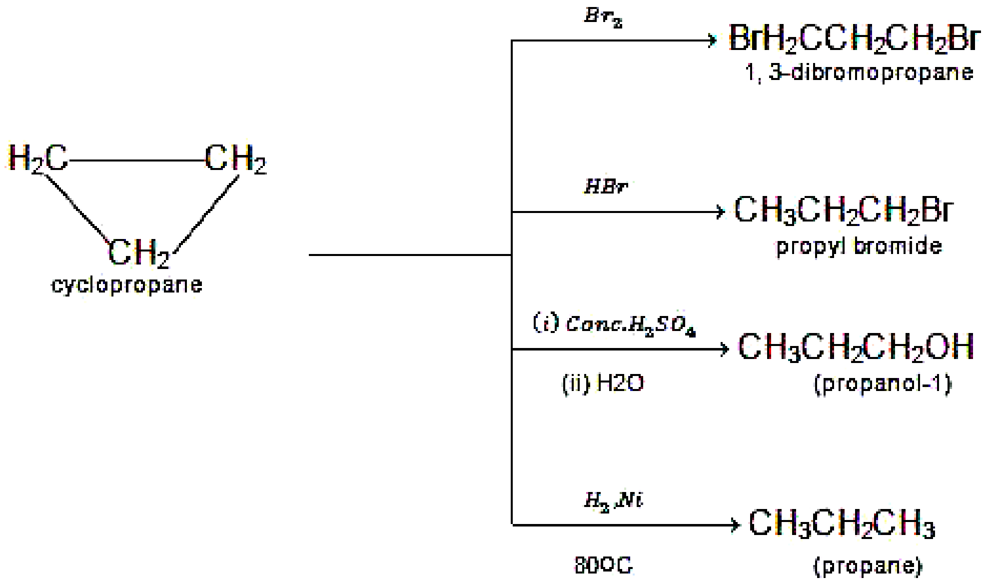
The stability of higher cycloalkanes is due to less strained ring as well as each carbon atom being sp^3 hybridized like alkanes.

It is therefore higher cycloalkanes are not attacked by acids, alkalies and common oxidizing under normal conditions.

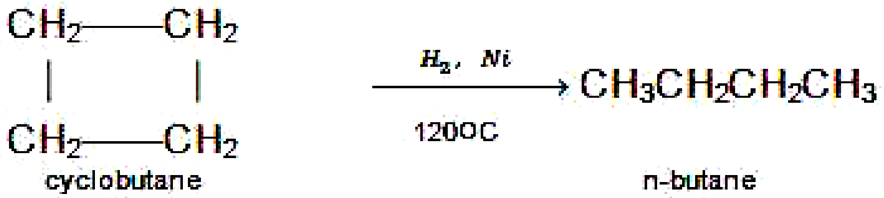
Following are some important reaction of cycloalkanes. **(a) Free radical substitution :** Cycloalkanes are halogenated in presence of sun light or UV light like alkane.



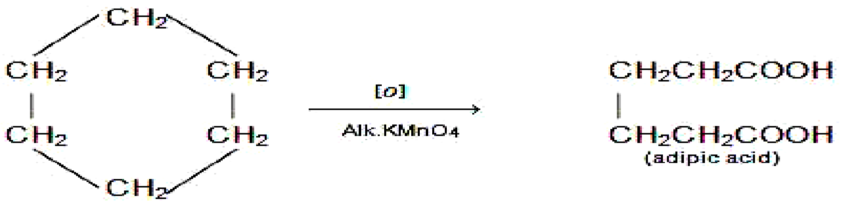
(b) Addition reactions : Cyclopropane being the most strained ring and more reactive undergoes addition reactions like alkenes.



Cyclobutane is relatively less reactive as it does not undergo addition reactions under normal conditions. However it undergoes these reactions under special conditions.



(c) Oxidation : Cycloalkanes are oxidized by alkaline potassium permanganate to dicarboxylic acids involving ring fusion.



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Question Bank

Part A

1. What are hydrocarbons? Name the simplest hydrocarbon.

2. Differentiate saturated and unsaturated hydrocarbons.

3. Define alkanes and cycloalkanes.

4. What are aliphatic alkanes and cycloalkanes? Give examples.

5. Write briefly on the IUPAC nomenclature of alkanes.

6. Name the first four cycloalkanes and draw their structures.

7. Draw the structure of 2,2-dimethylbutane.

8. Show the preparation of alkanes by decarboxylation reaction with equations.

9. Explain the preparation of alkanes by Wurtz reaction.

10. What is Clemmenson reduction?

11. What is Grignard reagent? Explain its use in the synthesis of alkanes.

12. Explain hydroboration.

13. Differentiate complete and controlled oxidation of alkanes.

14. Define cracking.

15. Explain Dieckmann condensation reaction.

Part B

1. Discuss the classification of hydrocarbons based on their structures.

2. Write short note on cyclic hydrocarbons with examples and their structures.

3. What are the different isomers of hexane. Give their IUPAC names.

4. Explain any four methods of synthesis of alkanes.

5. Explain Wurtz reaction with the mechanism.

6. Elaborate on Kolbe's electrolysis method with mechanism.

7. Explain the role of Grignard reagent in the synthesis of alkanes.

8. Discuss Corey-House methos of synthesis of alkanes.

9. Explain the important physical and Chemical properties of alkanes.

10. Enumerate the process of aromatization of alkanes.

11. Elaborate on the steps involved in the free radical mechanism of synthesis of alkanes.

12. Discuss any two methods of synthesis of cycloalkanes.

13. Predict the product of Dieckmann cyclization of diethyl adipate with the equations.

14. Explain in detail the physical and chemical properties of cycloalkanes.

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School of Science and Humanities

Department of Chemistry

SCY1112

GENERAL CHEMISTRY II

Unit 5

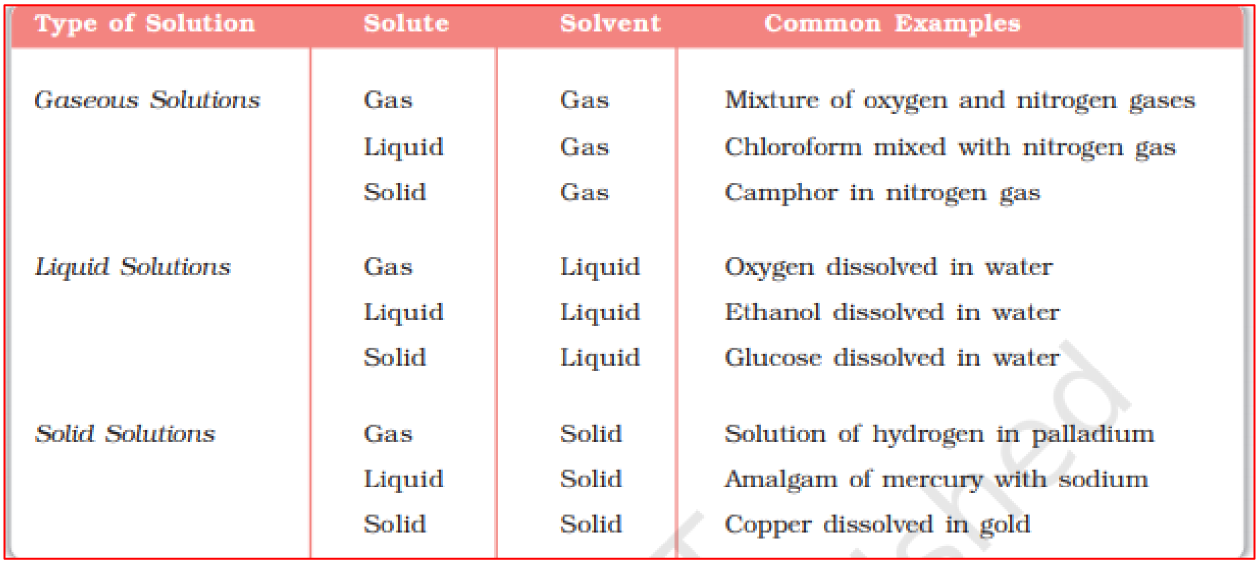
Solutions and Colloids

Solutions - Solutions of gases in liquids - Henrys law - solution of liquids in liquids. Raoult's law. Binary liquid mixtures - ideal solutions - deviations from ideal behaviour - vapour pressure - composition and vapour pressure - temperature curves - azeotropic distillation, Partially miscible binary systems (CST-UCST, LCST, and both UCST and LCST). Colloids - lyophilic and lyophobic colloids. Optical and Kinetic properties, electrophoresis and electro osmosis, peptisation, and coagulation (Definition only)

5. Introduction

Solutions are homogeneous mixtures of two or more than two components. By homogenous mixture we mean that its composition and properties are uniform throughout the mixture. Generally, the component that is present in the largest quantity is known as solvent. Solvent determines the physical state in which solution exists. One or more components present in the solution other than solvent are called solutes

5.1 Types of solutions



Type of Solution	Solute	Solvent	Common Examples
Gaseous Solutions	Gas	Gas	Mixture of oxygen and nitrogen gases
	Liquid	Gas	Chloroform mixed with nitrogen gas
	Solid	Gas	Camphor in nitrogen gas
Liquid Solutions	Gas	Liquid	Oxygen dissolved in water
	Liquid	Liquid	Ethanol dissolved in water
	Solid	Liquid	Glucose dissolved in water
Solid Solutions	Gas	Solid	Solution of hydrogen in palladium
	Liquid	Solid	Amalgam of mercury with sodium
	Solid	Solid	Copper dissolved in gold

There are several ways by which we can describe the concentration of the solution quantitatively,

(i) Mass percentage (w/w):
(ii) Volume percentage (V/V)
(iii) Mass by volume percentage (w/V):
(iv) Parts per million:
(v) Mole fraction:

5.2 Solution of gases in liquids:

Many gases dissolve in water. Oxygen dissolves only to a small extent in water. It is this dissolved oxygen which sustains all aquatic life. On the other hand, hydrogen chloride gas (HCl) is highly soluble in water. Solubility of gases in liquids is greatly affected by pressure and temperature. The solubility of gases increase with increase of pressure. For solution of gases in a solvent, consider a system in which the lower part is solution and the upper part is gaseous system at pressure p and temperature T. Assume this system to be in a state of dynamic equilibrium, i.e., under these conditions rate of gaseous particles entering and leaving the solution phase is the same. Now increase the pressure over the solution phase by compressing the gas to a smaller volume. This will increase the number of gaseous particles per unit volume over the solution and also the rate at which the gaseous particles are striking the surface of solution to enter it. The solubility of the gas will increase until a new equilibrium is reached resulting in an increase in the pressure of a gas above the solution and thus its solubility increases.

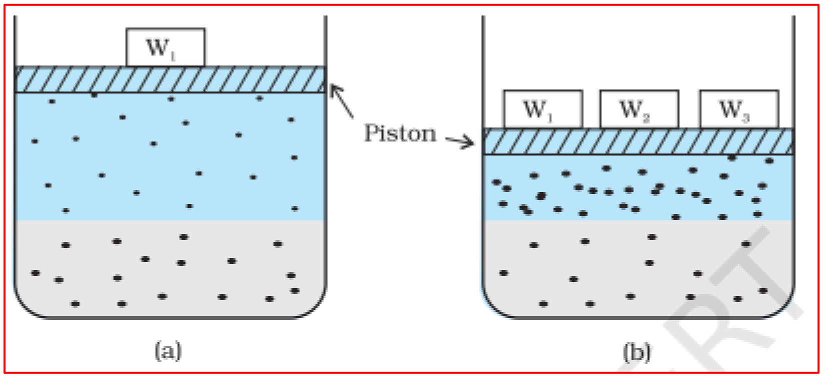


Fig.1. Effect of pressure on the solubility of a gas

5.2.1 Henry’s law:

Henry was the first to give a quantitative relation between pressure and solubility of a gas in a solvent which is known as Henry’s law. The law states that at a constant temperature, the solubility of a gas in a liquid is directly proportional to the partial pressure of the gas present above the surface of liquid or solution. Dalton, a contemporary of Henry, also concluded independently that the solubility of a gas in a liquid solution is a function of partial pressure of the gas. If we use the mole fraction of a gas in the solution as a measure of its solubility, then it can be said that the mole fraction of gas in the solution is proportional to the partial pressure of the gas over the solution. The most commonly used form of Henry’s law states that “the partial pressure of the gas in vapour phase (p) is proportional to the mole fraction of the gas (x) in the solution” and is expressed as:

$$p = K_H\, x$$

where, K_H is the Henry’s law constant.

If we draw a graph between partial pressure of the gas versus mole fraction of the gas in solution, then we should get a plot of the type as shown in Fig. 2

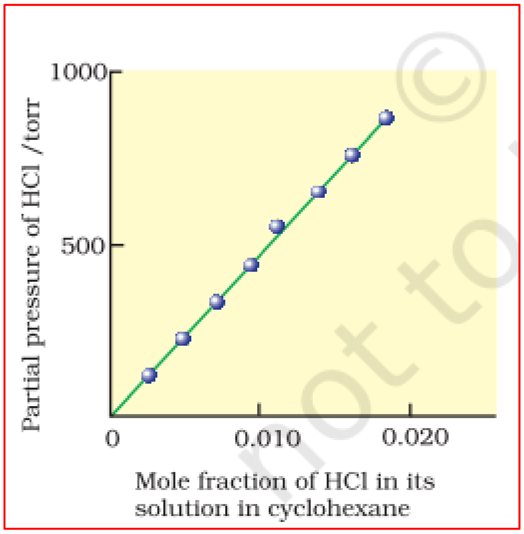
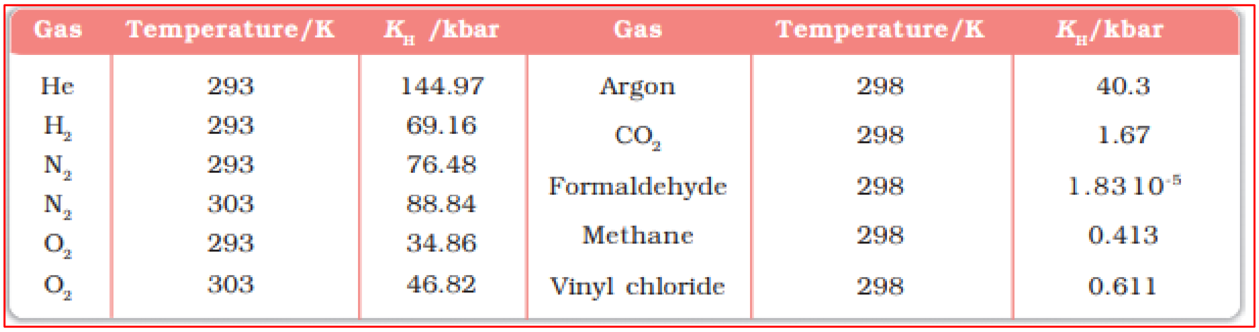


Fig.2.Experimental results for the solubility of HCl gas in cyclohexaneat 293K

Different gases have different K_H values at the same temperature. This suggests that K_H is a function of the nature of the gas. It is obvious that higher the value of K_H at a given pressure, the lower is the solubility of the gas in the liquid.

Table 1: Values of Henry's Law constant for gases in water



Gas	Temperature/K	K_H /kbar	Gas	Temperature/K	K_H/kbar
He	293	144.97	Argon	298	40.3
H_2	293	69.16	CO_2	298	1.67
N_2	293	76.48	Formaldehyde	298	$1.83 10^{-5}$
N_2	303	88.84	Methane	298	0.413
O_2	293	34.86	Vinyl chloride	298	0.611
O_2	303	46.82			

Applications:

- To increase the solubility of CO_2 in soft drinks and soda water, the bottle is sealed under high pressure.
- At high altitudes the partial pressure of oxygen is less than that at the ground level. This leads to low concentrations of oxygen in the blood and tissues of people living at high altitudes or climbers. Low blood oxygen causes climbers to become weak and unable to think clearly, symptoms of a condition known as anoxia.

5.3 Solutions of liquids in liquids:

Let us consider a binary solution of two volatile liquids and denote the two components as 1 and 2. When taken in a closed vessel, both the components would evaporate and eventually an equilibrium would be established between vapour phase and the liquid phase. Let the total vapour pressure at this stage be p_{total} and p_1 and p_2 be the partial vapour pressures of the two components 1 and 2 respectively. These partial pressures are related to the mole fractions x_1 and x_2 of the two components 1 and 2 respectively.

The French chemist, Francois Marte Raoult (1886) gave the quantitative relationship between them. The relationship is known as the Raoult's law which states that for a solution of volatile liquids, the partial vapour pressure of each component of the solution is directly proportional to its mole fraction present in solution. Thus, for component 1

$$p_1 \propto x_1$$

$$\text{and } p_1 = p_1^0 \, x1$$

where $p^0{}_1$ is the vapour pressure of pure component 1 at the same temperature.

Similarly, for component 2

$$p_2 = p_2^0 \, x2$$

where $p^0{}_2$ represents the vapour pressure of the pure component 2.

According to Dalton's law of partial pressures, the total pressure (p_{total}) over the solution phase in the container will be the sum of the partial pressures of the components of the solution and is given as:

$$p_{total} = p_1 + p_2$$

Substituting the values of p_1 and p_2, we get,

$$p_{total} = x_1 \, p_1^0 + x_2 \, p_2^0$$

$$= (1 - x_2) \, p_1^0 + x_2 \, p_2^0$$

$$= p^0{}_1 + (p_2^0 - p_1^0) \, x_2$$

Following conclusions can be drawn from th above equation,

(i) Total vapour pressure over the solution can be related to the mole fraction of any one component.

(ii) Total vapour pressure over the solution varies linearly with the mole fraction of component 2.

(iii) Depending on the vapour pressures of the pure components 1 and 2, total vapour pressure over the solution decreases or increases with the increase of the mole fraction of component 1.

A plot of p_1 or p_2 versus the mole fractions x_1 and x_2 for a solution gives a linear plot as shown in Fig.3. These lines (I and II) pass through the points for which x1 and x2 are equal to unity. Similarly the plot (line III) of ptotal versus x_2 is also linear. The minimum value of p_{total} is p_1^0 and the maximum value is p_2^0, assuming that component 1 is less volatile than component 2, i.e., $p_1^0 < p_2^0$.

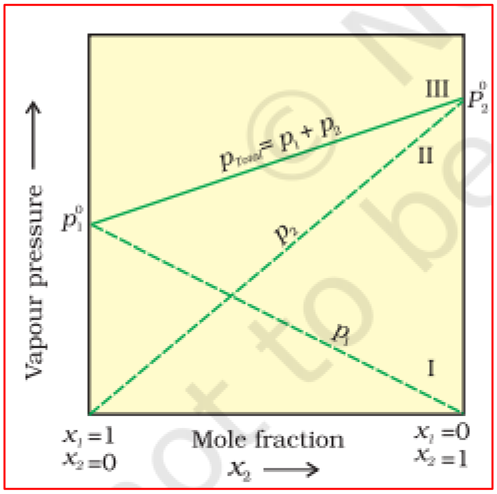


Fig.3. The plot of vapour pressure and mole fraction of an ideal solution at constant temperature. The dashed lines I and II represent the partial pressure of the components.

5.4 Binary Liquid Mixtures:

Raoult's law in its general form can be stated as, for any solution the partial vapour pressure of each volatile component in the solution is directly proportional to its mole fraction.

In a binary solution, let us denote the solvent by 1 and solute by 2. When the solute is non-volatile, only the solvent molecules are present in vapour phase and contribute to vapour pressure. Let p1 be the vapour pressure of the solvent, x1 be its mole fraction, pi 0 be its vapour pressure in the pure state. Then according to Raoult's law ,

$$p_1 \propto x_1$$

$$\text{and } p_1 = x_1 \, p^0{}_1$$

The proportionality constant is equal to the vapour pressure of pure solvent, $p^0{}_1$. A plot between the vapour pressure and the mole fraction of the solvent is linear.

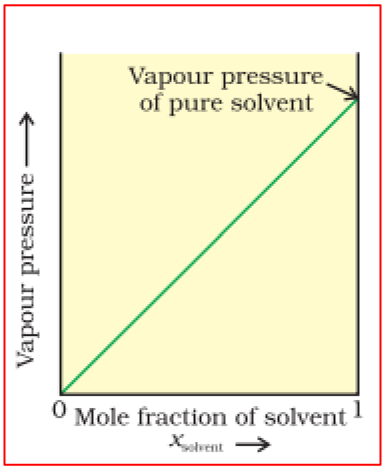


Fig.4. If a solution obeys Raoult's law for all concentrations, its vapour pressure would vary linearly from zero to the vapour pressure of the pure solvent

5.4.1 Ideal Solutions:

The solutions which obey Raoult’s law over the entire range of concentration are known as ideal solutions. The ideal solutions have two other important properties. The enthalpy of mixing of the pure components to form the solution is zero and the volume of mixing is also zero, i.e.,

$$\Delta_{mix}H = 0, \Delta_{mix}V = 0$$

It means that no heat is absorbed or evolved when the components are mixed. Also, the volume of solution would be equal to the sum of volumes of the two components. At molecular level, ideal behaviour of the solutions can be explained by considering two components A and B. In pure components, the intermolecular attractive interactions will be of types A-A and B-B, whereas in the binary solutions in addition to these two interactions, A-B type of interactions will also be present. If the intermolecular attractive forces between the A-A and B-B are nearly equal to those between A-B, this leads to the formation of ideal solution. A perfectly ideal solution is rare but some solutions are nearly ideal in behaviour. Solution of n-hexane and n-heptane, bromoethane and chloroethane, benzene and toluene, etc. fall into this category.

5.4.2 Deviation from ideal behavior:

When a solution does not obey Raoult’s law over the entire range of concentration, then it is called non-ideal solution. The vapour pressure of such a solution is either higher or lower than that predicted by Raoult’s law. If it is higher, the solution exhibits positive deviation and if it is lower, it exhibits negative deviation from Raoult’s law. The plots of vapour pressure as a function of mole fractions for such solutions are shown in Fig. 5.

The cause for these deviations lie in the nature of interactions at the molecular level. In case of positive deviation from Raoult’s law, A-B interactions are weaker than those between A-A or B-B, i.e., in this case the intermolecular attractive forces between the solute-solvent molecules are weaker than those between the solute-solute and solvent-solvent molecules. This means that in such solutions, molecules of A (or B) will find it easier to escape than in pure state. This will increase the vapour pressure and result in positive deviation. Mixtures of ethanol and acetone behave in this manner. In pure ethanol, molecules are hydrogen bonded. On adding acetone, its molecules get in between the host molecules and break some of the hydrogen bonds between them. Due to weakening of interactions, the solution shows positive deviation from Raoult's law [Fig. 5(a)]. In a solution formed by adding carbon disulphide to acetone, the dipolar interactions between solute-solvent molecules are weaker than the respective interactions among the solute-solute and solvent-solvent molecules. This solution also shows positive deviation. In case of negative deviations from Raoult's law, the intermolecular attractive forces between A-A and B-B are weaker than those between A-B and leads to decrease in vapour pressure resulting in negative deviations. An example of this type is a mixture of phenol and aniline. In this case the intermolecular hydrogen bonding between phenolic proton and lone pair on nitrogen atom of aniline is stronger than the respective intermolecular hydrogen bonding between similar molecules. Similarly, a mixture of chloroform and acetone forms a solution with negative deviation from Raoult's law. This is because chloroform molecule is able to form hydrogen bond with acetone molecule. This decreases the escaping tendency of molecules for each component and consequently the vapour pressure decreases resulting in negative deviation from Raoult's law is shown in fig.5b.

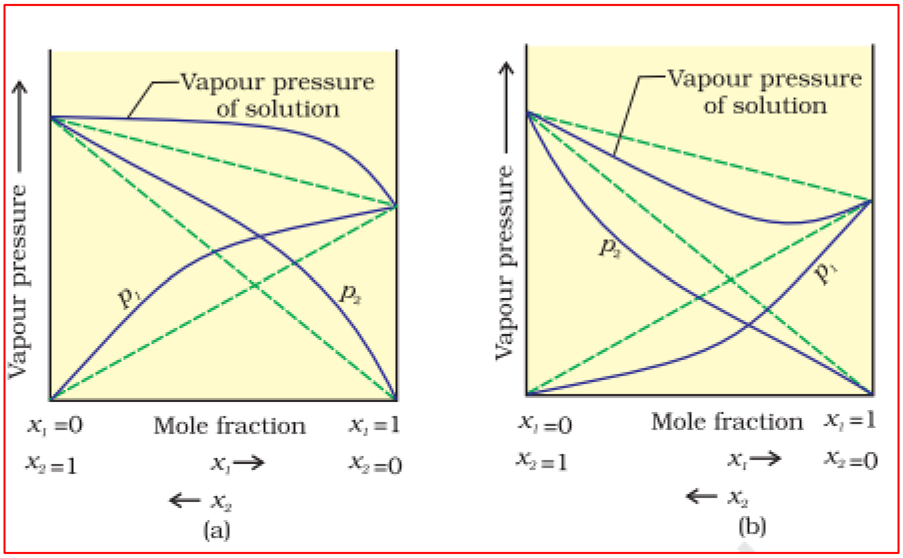


Fig.5. The vapour pressures of two component systems as a function of composition (a) a solution that shows positive deviation from Raoult's law and (b) a solution that shows negative deviation from Raoult's law.

5.5 Azeoptropic Distillation:

Some liquids on mixing, form azeotropes which are binary mixtures having the same composition in liquid and vapour phase and boil at a constant temperature. In such cases, it is not possible to separate the components by fractional distillation. There are two types of azeotropes called minimum boiling azeotrope and maximum boiling azeotrope. The solutions which show a large positive deviation from Raoult’s law form minimum boiling azeotrope at a specific composition. For example, ethanol-water mixture (obtained by fermentation of sugars) on fractional distillation gives a solution containing approximately 95% by volume of ethanol. Once this composition, known as azeotrope composition, has been achieved, the liquid and vapour have the same composition, and no further separation occurs. The solutions that show large negative deviation from Raoult’s law form maximum boiling azeotrope at a specific composition. Nitric acid and water is an example of this class of azeotrope. This azeotrope has the approximate composition, 68% nitric acid and 32% water by mass, with a boiling point of 393.5 K.

5.5.1 Process for Azeotropic Distillation:

Azeotropic Distillation can be defined as the process of separating the components of an azeotropic mixture by distillation. An azeotropic mixture is a mixture containing two or more liquids that cannot be separated by simple distillation because the vapours formed from the boiling of azeotropic mixtures contain almost the same proportions of liquids as the liquid itself. Therefore, azeotropic distillation is a specialized type of distillation which involves the use of specific techniques to break the azeotropes.

The most common method of breaking an azeotrope involves the addition of a material separation agent that has the ability to change the molecular interactions between the components of the azeotrope. The addition of such a material separation agent tends to alter the activity of the activity coefficient of the components of the azeotropic mixture, thereby changing the relative volatility of the azeotropic mixture as a whole.

Water and ethanol are known to form an azeotropic mixture. This mixture can be separated via the process of azeotropic distillation. In order to achieve this, material separation agents such as benzene, hexane, cyclohexane, pentane, diethyl ether, and acetone are commonly used. Historically, benzene was the most commonly used entrainer for this purpose. However, the discovery of the carcinogenic nature of benzene is believed to have caused a decline in the use of benzene in the azeotropic distillation of mixtures of water and ethanol. In modern practices, the ethanol-water azeotrope is usually broken with the help of toluene. Other suitable options for the dehydration of a mixture of water and ethanol include cyclohexane, isooctane, and even heptane.

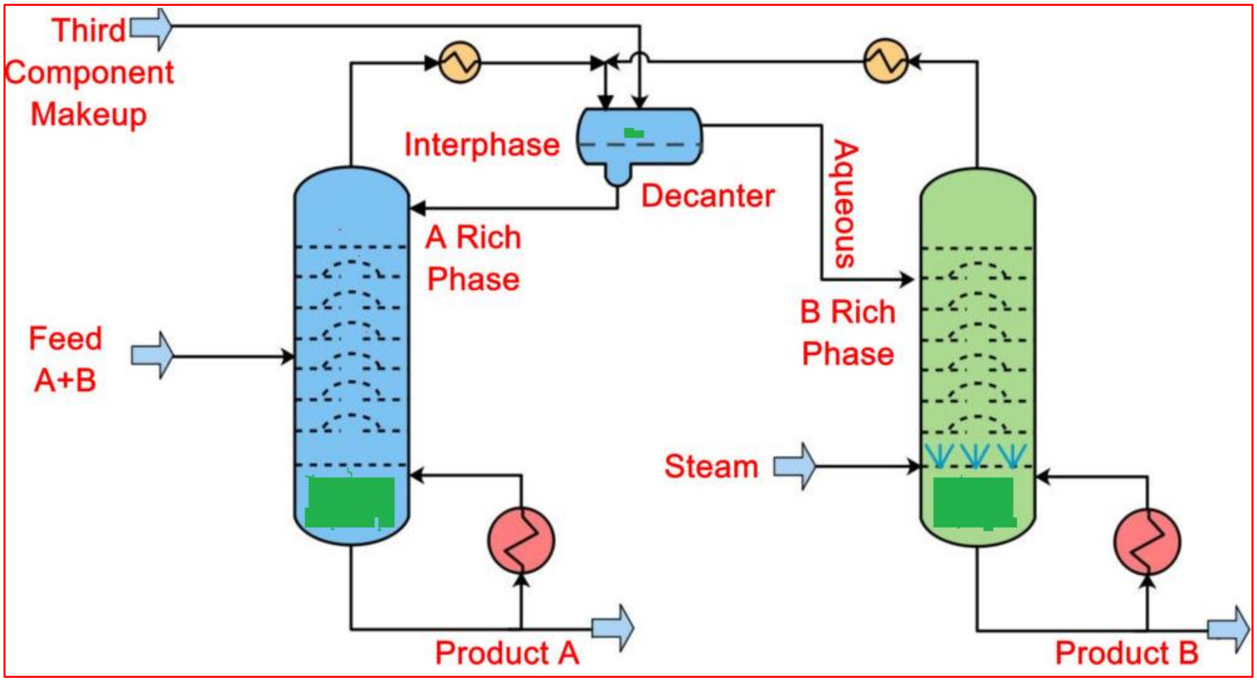


Fig.6. Process of Azeotropic Distillation

Partially Miscible Binary System

Solubility of liquids in liquids

There are mixture of liquids of the following categories:

Liquids showing complete miscibility eg: water and ethanol

Liquids showing complete immiscibility eg: water and mercury

Liquids showing partial miscibility eg: water and phenol

Components of an ideal solution are miscible in all proportions. Such complete miscibility is observed with some real binary systems like ethanol – water mixture.

When the attraction between molecules of the same component is greater than between the mlecules of the different components, there is a positive deviation from Raoult's law and the miscibility of the components decreases. That is greater the self association, greater is immiscibility and greater will be the degree of positive deviation according to Raoult's law.

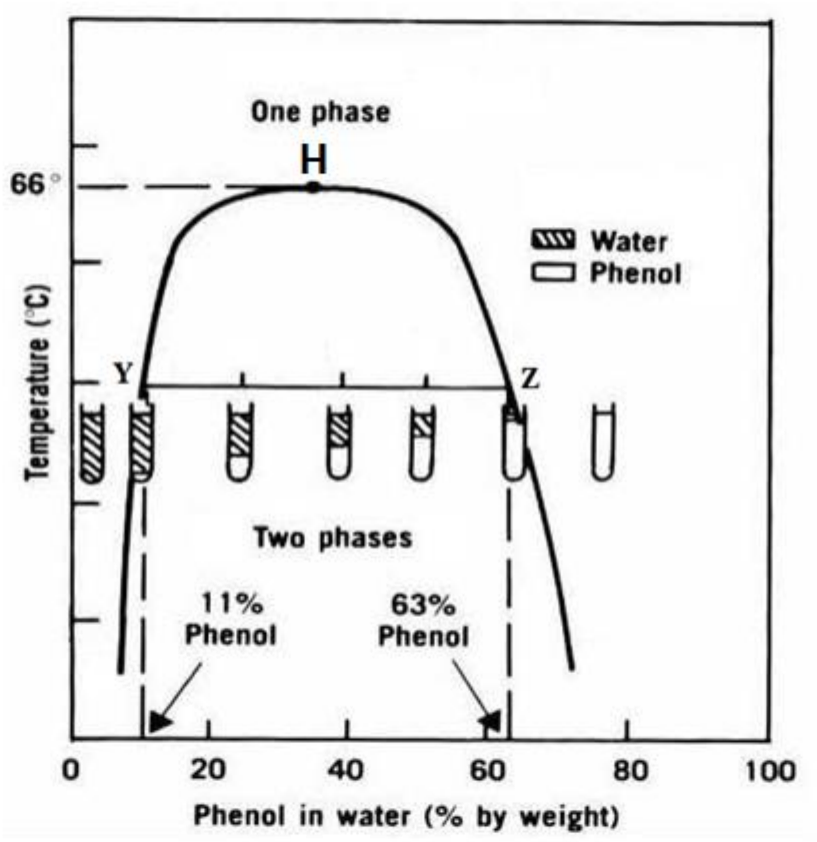
Partially Miscible Liquids

In case of partial miscibility, degree of miscibility depend on the temperature.

1. Solubility increases with the increase in temperature eg: water-phenol mixture

In this system, there is a positive deviation from Raoult's law due to greater attraction betweeen like molecules than between unlike molecules. Here, an increase in temperature reduces the positive deviation and thereby increases miscibility. Each phase in this system consists of a saturated solution of one component in the other liquid. The saturated solutions are called conjugate solutions.

In phenol- water system, addition of phenol to water produces a single phase initially at a fixed temperature of 50 degree celcius. When the concentration of phenol in water is increased, a second phase starts to appear viz, phase A which is a water rich phase containing 11% phenol. Phase B or the phenol rich phase consists of 63% phenol. At higher percentages of phenol, above 63%, again a single phenol-rich liquid phase is formed. Thus at 50°C, aqueous phase saturated with phenol contains 11% phenol and phenolic phase saturated with water contains 63% phenol.

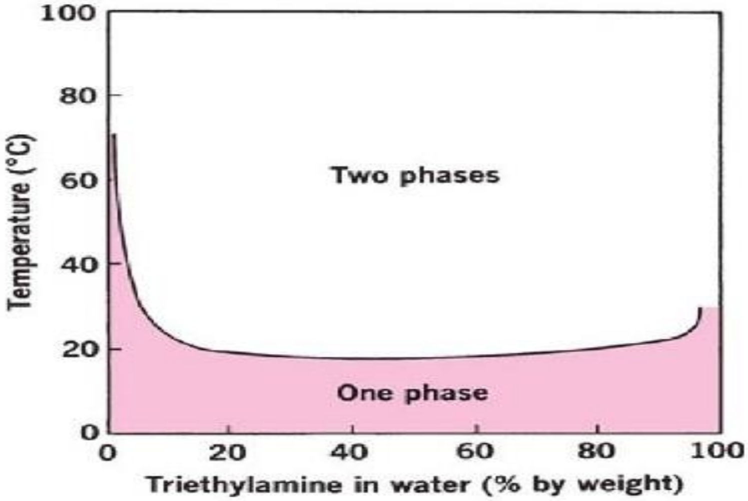


The line YZ is called "tie line" which is parallel to the base line. All systems along the tie line will separate into phases of constant composition of Y and Z. These phases are termed as conjugate phases.

The critical solution temperature (Upper consolute temperature) : It is the maximum temperature at which the two phase region exists. In the case of phenol-water system, it is 66.8°C (Point H). All combinations of phenol and water above this temperature are completely miscible and yield one-phase liquid systems.

2. Solubility decreases with the increase in temperature eg: water – triethylamine mixture

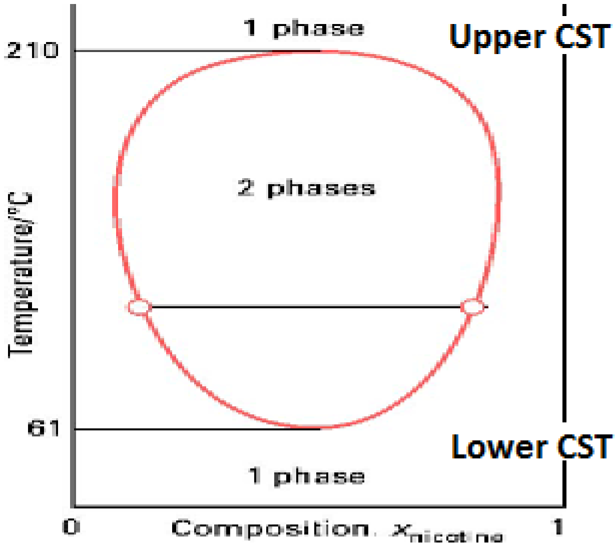
The solubility of liquid pairs decreases with the increase in temperature. The system exhibits a lower consolute temperature. Below the line the two liquids are miscible in all proportions. Above the line there is separation of the two layers.



3. Solubility increases with decrease and increase in temperature eg: water-nicotine

Systems showing upper and lower consolute temperature : Nicotine-water mixture

This mixture shows both upper and lower consolute temperature. In the intermediate temperature region, the two liquids are partially miscible.



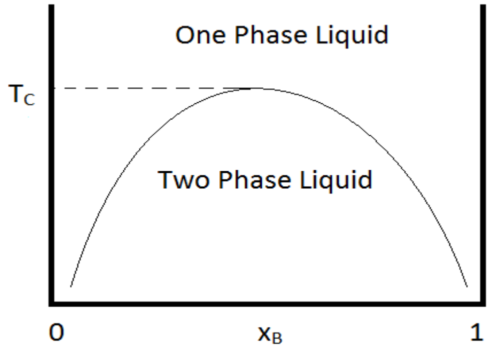
4. Solubility is not affected by temperature.

The pair, diethyl ether and water, has neither an upper nor a lower consolute temperature and shows partial miscibility over the entire temperature range at which the mixture exists.

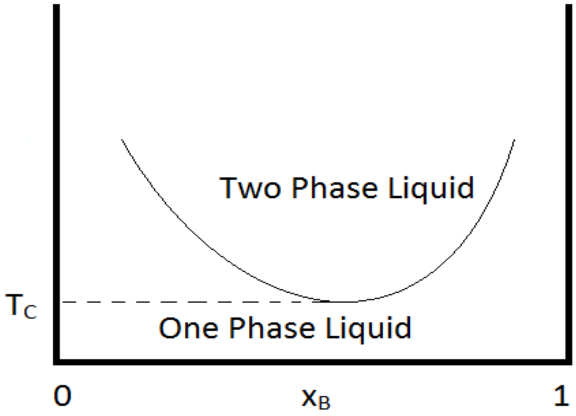
Effect of temperature on the degree of miscibility in these systems can be described by phase diagrams.

Phase diagram is a plot of temperature versus composition curves at constant pressure.

A pair of liquids is considered partially miscible if there is a set of compositions over which the liquids will form a two-phase liquid system. This is a common situation and is the general case for a pair of liquids where one is polar and the other non-polar (such as water and vegetable oil.) Another case that is commonly used in the organic chemistry laboratory is the combination of diethyl ether and water. In this case, the differential solubility in the immiscible solvents allows the two-phase liquid system to be used to separate solutes using a separatory funnel method.



As is the case for most solutes, their solubility is dependent on temperature. For many binary mixtures of immiscible liquids, miscibility increases with increasing temperature. And then at some temperature (known as the upper critical temperature), the liquids become miscible in all compositions. An example of a phase diagram that demonstrates this behavior is shown in Figure. An example of a binary combination that shows this kind of behavior is that of methyl acetate and carbon disufide, for which the critical temperature is approximately 230 K at one atmosphere. Similar behavior is seen for hexane/nitrobenzene mixtures, for which the critical temperature is 293 K.



Another condition that can occur is for the two immiscible liquids to become completely miscible below a certain temperature, or to have a lower critical temperature. An example of a pair of compounds that show this behavior is water and trimethylamine. A typical phase diagram for such a mixture is shown in Figure. Some combinations of substances show both an upper and lower critical temperature, forming two-phase liquid systems at temperatures between these two temperatures. An example of a combination of substances that demonstrate the behavior is nicotine and water.

Effect of added substances on Critical solution temperature

CST is very sensitive to impurities or added substances.

1. If an added substance is soluble in only one of the two liquids or if the solubility in the two liquids vary markedly, the solubilityof the liquid pair is decreased due to salting-out.

If the original binary mixture has an upper CST, the temperature increases. If the binary mixture has a lower CST, the temperature decreases by the addition of the third component.

Example: If 0.1M naphthalene is added to a mixture of phenol and water, which dissolves only in phenol and increases the CST about 20^{o}C.

If 0.1M KCl is added to a phenol-water mixture, it dissolves only in water and increases the CST by 8^{o}C.

2. If the added compound is soluble in both the liquids to the same extent, the solubility of the liquid pair increases. The increase in solubility of the two partially miscible solvents by an additive is referred to as **blending**. Here, UCST is lowered and LCST is raised.

Example : Addition of succinic acid or Na oleate to a phenol-water system.

Colloids

A mixture in which one substance is divided into minute particles (called colloidal particles) and dispersed throughout a second substance. The substances are present as larger particles than those found in solution, but are too small to be seen with a microscope. There are no strict boundaries on the size of colloidal particles, but they tend to vary between 10^{-9} m to 10^{-6} m in size.

The mixture is also called a colloidal solution, colloidal system, or colloidal dispersion. The three forms in which all matter exists are solid, liquid or gas. Colloidal systems can be any combination of these states.

A colloidal system is not a true solution but it is not a suspension either because it does not settle out like a suspension will over time.

Colloids are larger than most inorganic molecules and remain suspended indefinitely. They are large molecules, such as proteins, or groups of molecules. They have many properties, depending on their large specific surface.

Colloid formation can be classified in two systems, namely reversible and irreversible. In an irreversible system, the products are so stable or removed so well that the original reactants cannot be reproduced. A reversible system is one in which the products can be made to react to reproduce the original reactants.

A colloid is primarily a heterogeneous mixture in which the minute particles of one substance are dispersed in another substance, called the dispersion medium.

The minute particles here are 1 to 1000 nanometers in diameter but they still remain suspended and do not settle at the bottom of the mixture. They are visible under an optical or an electron (smaller particles) microscope.

Dispersed Phase and Dispersion Medium

A colloid is a mixture in which one substance which has fine particles (dispersed phase) mixed into another substance (dispersion medium). The particles of the colloids have a range from 1 to 1000 nm in diameter. The solution is called **colloidal dispersion** because the particles of solutions do not mix or settle down. They are dispersed in the solution.

The substances which are dispersed in the solution are called the dispersed phase, and the solution in which it is dispersed is called dispersion medium.

Types of Colloids

Colloids can be classified according to different properties of the dispersed phase and medium.

Firstly, based on the types of particles of the dispersed phase, colloids can be classified as:

- **Multimolecular colloids**
- **Macromolecular colloids**
- **Associated colloids**

1. Multimolecular Colloids

When the dissolution of smaller molecules of substance or many atoms takes place, they combine to form a species whose size is in the range of colloidal size. The species formed is known as the multimolecular colloids.
For example, the Sulphur solution contains particles which have thousands of S_8.

2. Macromolecular Colloids

In this type of colloids, the macromolecules form a solution with a suitable solvent. The size of the particles of this macromolecular solution lies in the range of colloidal particles size. Thus, this solution is also known as the macromolecular colloids. The colloids formed here are similar to that of the actual solution in many respects and are very stable.
Example: Starch, proteins, enzymes, and cellulose are the naturally occurring macromolecular colloids whereas polyethene, synthetic rubber, etc. are the synthetic macromolecules.

3. Associated Colloids

Some substances act as a strong electrolyte when they are in low concentrations, but they react as colloidal sols when they are in high concentration. In higher concentration, particles aggregate showing colloidal behaviour. These aggregated particles are known as the **micelles**. They are also known as the associated colloids. The formation of the micelles occurs above a particular temperature called the **Kraft temperature** (T_k) and also above a specific concentration called the critical micelle concentration. These colloids can be reverted by diluting it. Examples of some associated colloids are soaps and synthetic detergents.

Examples of Colloids

Based on the physical state of the dispersion medium and of the dispersed phase, colloids can be classified into:

- **Foam**
- **Solid Foam**
- **Aerosol**
- **Emulsion**
- **Gel**

- **Solid Aerosol**
- **Sols**
- **Solid sols**

Based on the nature of the interaction between the dispersion medium and the dispersed phase, colloids can be classified into lyophilic and lyophobic.

- Lyophilic

If the dispersed phase has an affinity for the dispersion medium, the colloid is called a lyophilic colloid. The words ***lyo*** and ***philic*** means '**liquid**' and '**loving**' respectively. Thus, even if the dispersed phase is separated from the dispersion medium, they can readily be reconstituted by simply mixing them. Moreover, they are difficult to coagulate due to their stable nature. They are also known as **intrinsic colloids**. Examples are starch, rubber, protein, etc.

- Lyophobic

If the dispersed phase has little or no affinity for the dispersion medium, the colloid is called a lyophobic colloid. The words ***lyo*** and ***phobic*** means '**liquid**' and '**fearing**' respectively. Hence, they are liquid-hating. They are difficult to prepare because the dispersed phase does not readily form a colloid with the dispersion medium, they require some special methods. They are unstable and require stabilizing agents for their preservation. They are also known as **extrinsic colloids**. Examples are sols of metals like silver and gold, sols of metallic hydroxides, etc.

Physical properties of colloids

1. The nature of the colloidal solution is heterogeneous i.e. unlike. These solutions dwell with two different phases:
    - **Dispersed medium**
    - **Dispersed phase**

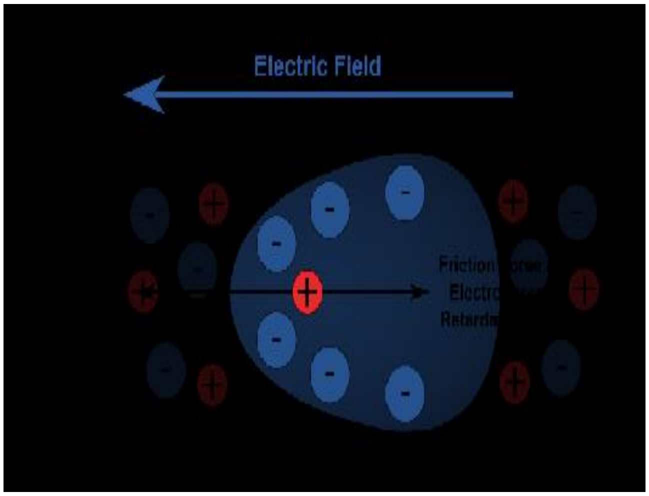
Despite the fact that colloidal dispersions are unlike in description (nature), yet the dispersed fragments are not detectable by the human eye. This is due to the microscopic size of the particles in the solution.
The colour of the colloidal dispersion is determined by particles in the solution based on their size. The wavelengths of light that is absorbed will be longer if the size of the particle is large.
As a result of its size, the colloidal fragments can easily be passed through a traditional filter paper. However, these particles can be filtered by using membranes such as animal, cellophane, and ultrafilters.

Electrical properties of colloids

1. **Electrical double layer theory**: In this theory, charge is imparted to the particles by placing ions which are adsorbed preferentially at immovable points which for the first layer. The second layer consists of diffused mobile ions. The charge present on both the layers is equal. This two-layer arrangement leads to a development of potential called **zeta**

or Electrokinetic potential. As a result of this potential developed across the particles, under the influence of electric field these particles move.

2. **Electrophoresis**: It is a process in which an electric field is been applied to a colloidal solution which is responsible for the movement of colloidal particles. Depending upon the accumulation near the electrodes the charge of the particles can be predicted. The charge of the particles is positive if the particles get collected near a negative electrode and vice versa.



3. Electro-osmosis: It is a process in which the dispersing medium of the colloidal solution is brought under the influence of electric field and the particles are arrested.

Optical properties of colloids

Tyndall's effect is defined as the phenomenon in which light is scattered by the colloidal particles. The light is been absorbed by the particles present in the solution. Once the light is been absorbed a part of the light gets scattered in all the directions. The result of scattering exhibits this effect.

Kinetic properties of colloids

During the observation of the colloidal dispersion under an ultra-microscope, it is clearly seen that the particles are in a continuous movement in the solution. This random zigzag movement of the particles in the colloidal solution is called Brownian effect. This movement is mainly due to the unique bombardment of the molecules present in the dispersed medium on the colloidal particles.

References

Question Bank

Part A

1. Diffrentiate UCST and LCST

2. How are binary liquids classified based on solubility of liquid in liquid.

3. Explain a Tie line in the phase diagram of a binary liquid.

4. What are colloids?

5. Define electrophorosis.

6. Explain Tyndall effect and Brownian movement.

7. Name the three different types of colloids.

8. Define solution.

9. State Henry's law.

10. State Raoult's law.

11. What are azeotropes?

12. Explain the principle of azeotropic distillation.

Part B

1. Explain the optical properties of colloidal solution.

2. Write short note on the physical properties of colloids.

3. Differentite dispersed and dispersion medium.

4. Explain the phase diagram of phenol-water system and describe the formation of UCST.

5. Explain the effect added impurity on the critical solution temperature.

6. Explain the process of azeotropic distillation with a neat diagram.

7. Discuss the solution behavior which deviates from ideal solution.

8. Explain the various temperature and composition curves of solution for ideal behaviour.

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