FOUNDATION FOR CHEMISTRY

M.Sc. CHEMISTRY

SEMESTER-I, PAPER-III

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M.Sc. CHEMISTRY: FOUNDATION FOR CHEMISTRY

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FOREWORD

Since its establishment in 1976, Acharya Nagarjuna University has been forging ahead in the path of progress and dynamism, offering a variety of courses and research contributions. I am extremely happy that by gaining 'A+' grade from the NAAC in the year 2024, Acharya Nagarjuna University is offering educational opportunities at the UG, PG levels apart from research degrees to students from over 221 affiliated colleges spread over the two districts of Guntur and Prakasam.

The University has also started the Centre for Distance Education in 2003-04 with the aim of taking higher education to the door step of all the sectors of the society. The centre will be a great help to those who cannot join in colleges, those who cannot afford the exorbitant fees as regular students, and even to housewives desirous of pursuing higher studies. Acharya Nagarjuna University has started offering B.Sc., B.A., B.B.A., and B.Com courses at the Degree level and M.A., M.Com., M.Sc., M.B.A., and L.L.M., courses at the PG level from the academic year 2003-2004 onwards.

To facilitate easier understanding by students studying through the distance mode, these self-instruction materials have been prepared by eminent and experienced teachers. The lessons have been drafted with great care and expertise in the stipulated time by these teachers. Constructive ideas and scholarly suggestions are welcome from students and teachers involved respectively. Such ideas will be incorporated for the greater efficacy of this distance mode of education. For clarification of doubts and feedback, weekly classes and contact classes will be arranged at the UG and PG levels respectively.

It is my aim that students getting higher education through the Centre for Distance Education should improve their qualification, have better employment opportunities and in turn be part of country's progress. It is my fond desire that in the years to come, the Centre for Distance Education will go from strength to strength in the form of new courses and by catering to larger number of people. My congratulations to all the Directors, Academic Coordinators, Editors and Lesson-writers of the Centre who have helped in these endeavors.

Prof. K. Gangadhara Rao
M.Tech., Ph.D.,
Vice-Chancellor I/c
Acharya Nagarjuna University.

M.Sc. CHEMISTRY

SEMESTER-I, PAPER-III

103CH24 - FOUNDATION FOR CHEMISTRY

SYLLABUS

Learning Objectives:

- ✓ To know the fundamentals in analytical & inorganic estimations.
- ✓ To know the possible intermediates formed during course of chemical reactions.
- ✓ To know the type of bonding in organic molecules.
- ✓ To know about molecular symmetry, molecular representations and their applicational aspects.
- ✓ To know the types & characterisation of environmental segments.

UNIT-I

Titrimetric Analysis: Acid-base titrations, redox titrations, complexometric titrations, precipation titrations-principle, example and corresponding indicators, Pri., Sec.-standards.

UNIT-II

Treatment of Analytical Data: Errors, classification, accuracy, precision, SD, MD, Student-T test F-test, Gassian distributation

UNIT-III

Reactive Intermediates: Generation, Structure, Stability and reactivity of Carbocations, Carbanions, free radicals, Carbenes, nitrenes and Benzyne; Electrophiles, Nucleophiles, Catalysts-definition and examples.

Nature of Bonding in Organic Molecules: Localised and Delocalized covalent bonds, Delocalised chemical bonding conjugation, cross conjugation, hyper conjugation, tautomerism.

UNIT-IV

Symmetry and Group theory in Chemistry: Symmetry elements, symmetry operation, definition of group, suib group, relation between order of a finite group and its sub group. Point symmetry group. Schonfiles symbols, representation of groups by Matrices (representation for the Cn, Cnv, Cnh, Dn etc. groups to be worked out, explicitely). Character of a representation. The great orthogonality theorem (without proof) and its importance. Character tables and their use. Application of group theory in IR and Raman spectroscopy.

UNIT-V

Environmental Chemistry: Classification of environmental segments, types of pollutions, acid rains, Global warming.

Chemistry of Biomolecules: Definition, functional uses and examples for Carbohydrates, lipids (fats and oils), enzymes. Chemistry of purines and pyrimidines, Nucleic acids - Structure and functions of DNA & RNA.

Reference Books:

1) Advanced Organic Chemistry - Reaction, Mechanism and Structure, Jerry March, John Wiley.
2) Advanced Organic Chemistry, F.A.Carey and R.J. Sundberg, Plenum.
3) A Guide Book to Mechanism in Organic Chemistry, Peter Sykes, Longman.
4) Organic Chemistry, I.L. Finar, Vol. I & II, Fifth ed. ELBS, 1975.
5) Organic Chemistry, Hendrickson, Cram and Hammond (Mc Graw-Hill).

Learning Outcomes:

- The student will understand the required tools in analytical and inorganic estimations.
- Understanding of various types of reaction intermediates and the bonding present in various organic compounds.
- Students are able to understand the basics on various environmental concerns.
- Students know about types of various biomolecules and their functions with reference to structure.
- Student understand the types of pollutions.

ACHARYA NAGARJUNA UNIVERSITY: CENTRE FOR DISTANCE EDUCATION

M.Sc. – Chemistry - Program code: 04

Program Structure

Program code	Program	Internal assessment	External exams	Max. Marks	credits
SEMISTER 1					
101CH24	Inorganic Chemistry-I	30	70	100	4
102CH24	Organic Chemistry-I	30	70	100	4
103CH24	Foundation for Chemistry	30	70	100	4
104CH24	Physical Chemistry-I	30	70	100	4
105CH24	Inorganic & Physical Chemistry **Practical-I**	30	70	100	4
106CH 24	Organic Chemistry **Practical-II**	30	70	100	4
SEMISTER 2					
201CH24	Physical Chemistry-II	30	70	100	4
202CH24	Organic Chemistry-II	30	70	100	4
203CH24	Essential Lab Techniques for Industry	30	70	100	4
204CH24	Inorganic Chemistry-II	30	70	100	4
205CH24	Inorganic & Physical Chemistry **Practical-I**	30	70	100	4
206CH24	Organic Chemistry **Practical-II**	30	70	100	4
SEMISTER 3					
301CH24	Applied Inorganic Analysis	30	70	100	4
302CH24	Analysis of Applied Industrial Products	30	70	100	4
303CH24	Optical Thermal & Radiochemical Methods of Analysis	30	70	100	4
304CH24	Principles and Techniques in Classical Analysis	30	70	100	4
305CH24	Classical Methods of Analysis **Practical-I**	30	70	100	4
306CH24	Instrumental Methods of Analysis **Practical-II**	30	70	100	4
SEMISTER 4					
401CH24	Advanced Methods of Analysis	30	70	100	4
402CH24	Analysis of Drugs, Foods, Diary Products & Biochemical Analysis	30	70	100	4
403CH24	Separation Techniques & Electro Analytical Techniques	30	70	100	4
404CH24	Environmental Chemistry & Analysis	30	70	100	4
405CH24	Classical & Instrumental Methods of Analysis **Practical-I**	30	70	100	4
406CH24	Spectral Problems **Practical-II**	30	70	100	4

(103CH24)

M.Sc. DEGREE EXAMINATION, MODEL QUESTION PAPER
M.Sc. CHEMISTRY - FIRST SEMESTER
PAPER-III: FOUNDATION FOR CHEMISTRY

Time: Three Hours **Maximum: 70 Marks**

UNIT-I

1 a) Define primary and secondary standards with suitable examples **[4]**

or

b) Explain the principle of complexometric titrations with an example.

2 a) Discuss the principle, procedure, and applications of redox titrations. Explain with examples and describe appropriate indicators used. **[10]**

or

b) Elaborate on acid-base titrations, their principles, types, and indicators used. Include the concept of equivalence point and how indicators are selected.

UNIT-II

3 a) Differentiate between accuracy and precision with suitable examples. **[4]**

or

b) Explain the significance of Student's t-test in analytical chemistry.

4 a) Discuss the classification of errors in analytical measurements. Explain systematic and random errors with examples and methods to minimize them. **[10]**

or

b) Explain Gaussian distribution and its importance in analytical chemistry. Describe standard deviation, mean deviation, and their calculation methods with examples.

UNIT-III

5 a) Compare the stability and reactivity of carbocations and carbanions. **[4]**

or

b) Explain hyperconjugation with suitable examples.

6 a) Discuss the generation, structure, stability, and reactivity of carbenes and nitrenes. Include their role in organic reactions with examples. **[10]**

or

b) Explain the concept of delocalized chemical bonding. Elaborate on conjugation, cross-conjugation, and tautomerism with appropriate examples.

UNIT-IV

7 a) Define point symmetry group and explain Schönflies symbols. **[4]**

or

b) What is the significance of the Great Orthogonality Theorem in group theory?

8 a) Explain the representation of groups by matrices. Work out the matrix representations for Cn, Cnv, and Dn point groups with examples. **[10]**

or

b) Discuss the applications of group theory in IR and Raman spectroscopy. Explain how symmetry elements help in predicting IR and Raman active modes.

UNIT-V

9 (a) Explain the mechanism and effects of acid rain on the environment. **[4]**

or

(b) Describe the structure and function of DNA.

10 a) Discuss global warming, its causes, effects, and mitigation strategies from a chemical perspective. **[10]**

or

b) Explain the chemistry, classification, and functions of carbohydrates and lipids. Include their structural characteristics and biological importance.

CONTENTS

LESSON - 1

TITRIMETRIC ANALYSIS

1.1 TITRIMETRIC ANALYSIS:

The term "titrimetric analysis" refers to quantitative chemical analysis carried out by determining the volume of a solution of accurately known concentration which is required to react quantitatively with a measured volume of a solution of the substance to be determined. The solution of accurately known strength is called the standard solution, the weight of the substance to be determined is calculated from the volume of the standard solution used and the chemical equation and relative molecular masses of the reacting compounds.

1.1.1) Classification of Reactions in Titrimetric Analysis:

The reactions employed in titrimetric analysis fall into four main classes. The first three of these involve no change in oxidation state as they are dependent upon the combination of ions. But the fourth class, oxidation-reduction reactions, involves a change of oxidation state or, expressed another way, a transfer of electrons.

a) Neutralization reactions, or acidimetry and alkalimetry:

These include the titration of free bases, or those formed from salts of weak acids by hydrolysis, with a standard acid (acidimetry), and the titration of free acids, or those formed by the hydrolysis of salts of weak bases, with a standard basis (alkalimetry). The reactions involve the combination of hydrogen and hydroxide ions to form water.

b) Complex formation reactions:

These depend upon the combination of ions, other than hydrogen or hydroxide ions, to form soluble, slightly dissociated ion or compound, as in the titration of a solution of a cyanide with silver nitrate.

$$2CN^- + Ag^+ \rightleftharpoons [Ag(CN)_2]^-$$

or of chloride ion with mercury(II) nitrate solution

$$2Cl^- + Hg^{++} \rightleftharpoons HgCl_2$$

Ethylenediamine tetra-acetic acid (EDTA), largely as the disodium salt of EDTA, is very important reagent for complex formation titrations and has become one of the most important reagents used in titrimetric analysis. Equivalence point detection by the use of metal-ion indicators has greatly enhanced its value in titrimetric.

c) Precipitation Reactions:

These reactions depend upon the combination of ions to form a simple precipitate as in the titration of silver ion with a solution of a chloride. No change in oxidation state occurs.

d) Redox Reactions (Oxidation-reduction reactions):

Reactions which are involving change of oxidation number or transfer of electrons among the reacting substances are known as Oxidation-Reduction reactions. The standard solutions that are used in the reactions are either oxidizing or reducing agents. The principal oxidizing agents are potassium permanganate, potassium dichromate, cerium(IV) sulphate, iodine, potassium iodate, and potassium bromate. Frequently used reducing agents are iron(II), tin(II) compounds, sodium thiosulphate, arsenic(III) oxide, mercury(I) nitrate, Vanadium(II) chloride or sulphate, chromium(II) chloride or sulphate, and titanium(III) chloride or sulphate.

1.1.2) Acid-Base Titrations or Neutralization Titrations:

The mechanism of neutralization process can be understood by studying the changes in the hydrogen ion concentration during the course of the appropriate titration. The change in pH in the neighborhood of the equivalence point is of the greatest importance, as it enables an indicator to be selected which will give the smallest titration error. The curve obtained by plotting pH as the ordinate against the percentage of the acid neutralized (or the number of mL of the alkali added) as abscissa is known as the neutralization (or, more generally, the titration) curve. This may be evaluated experimentally by determination of the pH at various stages during the titration by a potentiometric method or it may be calculated from theoretical principles.

1.1.2.1) Neutralization of a Strong Acid with a Strong Base:

For this calculation it is assumed that both the acid and the base are completely dissociated and the activity coefficients of the ions are unity in order to obtain the pH values

during the course of the neutralisation of the strong acid and the strong base, or vice versa, at the laboratory temperature. For simplicity of calculation consider the titration of 100 mL of 1M hydrochloric acid with 1M sodium hydroxide solution. The pH of 1M hydrochloric acid is 0. When 50 mL of the 1M base have been added, 50 mL of unneutralized 1M acid will be present in a total volume of 150 mL.

$[H^+]$ will therefore be 50 x 1/150 = 3.33 x 10^{-1}, or pH = 0.48

For 75 mL of base, $[H^+]$ = 25 x 1/175 = 1.43 x 10^{-1}, pH = 0.84

For 90 mL of base, $[H^+]$ = 10 x 1/190 = 5.26 x 10^{-2}, pH = 1.3

For 98 mL of base, $[H^+]$ = 2 x 1/198= 1.01 x 10^{-2}, pH = 2.0

For 99 mL of base, $[H^+]$ = 1 x 1/199 = 5.03 x 10^{-3}, pH = 2.3

For 99.9 mL of base, $[H^+]$ =0.1 x 1/199.9 = 5.00 x 10^{-4}, pH = 3.3

Upon the addition of 100 mL of base, the pH will change sharply to 7, i.e. the theoretical equivalence point. The resulting solution is simply one of sodium chloride. Any sodium hydroxide added beyond this will be in excess of that needed for neutralization.

With 100.1 mL of base, $[OH^-]$= 0.1/200.1 = 5.00 x 10^{-4}, pOH = 3.3 and pH = 10.7

With 101 mL of base, $[OH^-]$ = 1 /201 = 5.00 x 10^{-3}, pOH = 2.3, and pH = 11.7

These results show that as the titration proceeds, initially the pH rises slowly, but between the addition of 99.9 and 100.1 mL of alkali, the pH of the solution rises from 3.3 to 10.7, i.e. in the vicinity of the equivalence point the rate of change of pH of the solution is very rapid.

The complete results, up to the addition of 200 mL of alkali, are collected in **Table 1.1**; this also includes the figures for 0.1 M and 0.01 M solutions of acid and base respectively. The additions of alkali have been extended in all three cases to 200 mL; it is evident that the range from 200 to 100 mL and beyond represents the reverse titration of 100 mL of alkali with the acid in the presence of the non-hydrolysed sodium chloride solution. The data in the table are presented graphically in **Fig. 1.1**.

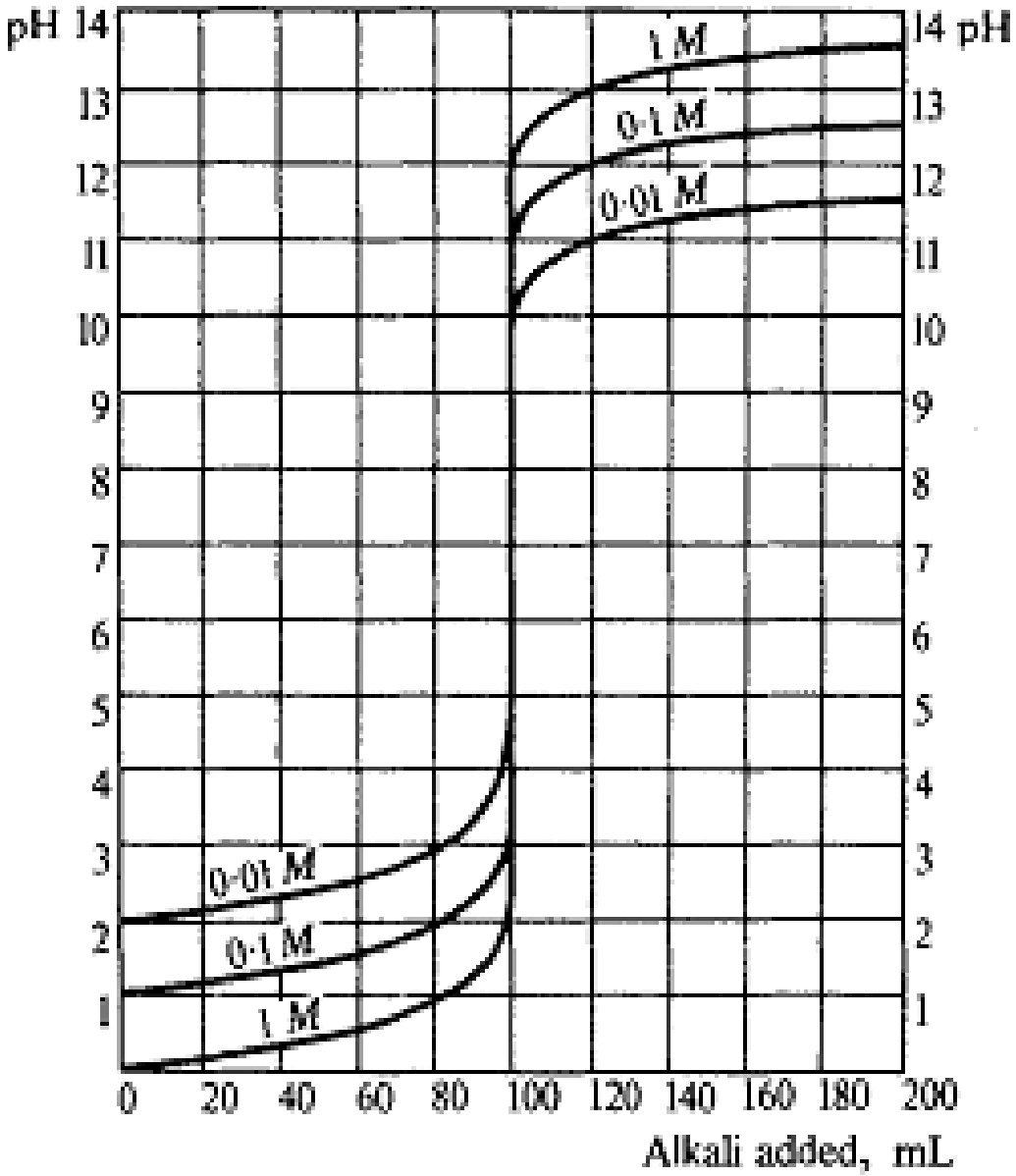

Figure 1.1: Neutralisation curves of 100 mL of HCl with NaOH of same concentration.

Table 1.1: pH during titration of 100 mL of HCl with NaOH of Equal Concentration

NaOH added (mL)	IM solution (pH)	0.1 A/ solution (pH)	0.01A/ solution (pH)
0	0.0	1.0	2.0
50	0.5	1.5	2.5
75	0.8	1.8	2.8
90	1.3	2.3	3.3
98	2.0	3.0	4.0
99	2.3	3.3	4.3
99.5	2.6	3.6	4.6
99.8	3.0	4.0	5.0
99.9	3.3	4.3	5.3
100.0	7.0	7.0	7.0
100.1	10.7	9.7	8.7
100.2	11.0	10.0	9.0
100.5	11.4	10.4	9.4
101	11.7	10.7	9.7
102	12.0	11.0	10.0
110	12.7	11.7	10.7
125	13.0	12.0	11.0
150	13.3	12.3	11.3
200	13.5	12.5	11.5

In quantitative analysis it is the changes of pH near the equivalence point which are of special interest. This part of **Fig. 1.1** is accordingly shown on a larger scale in **Fig. 1.2**, on which are also indicated the colour-change intervals of some of the common indicators.

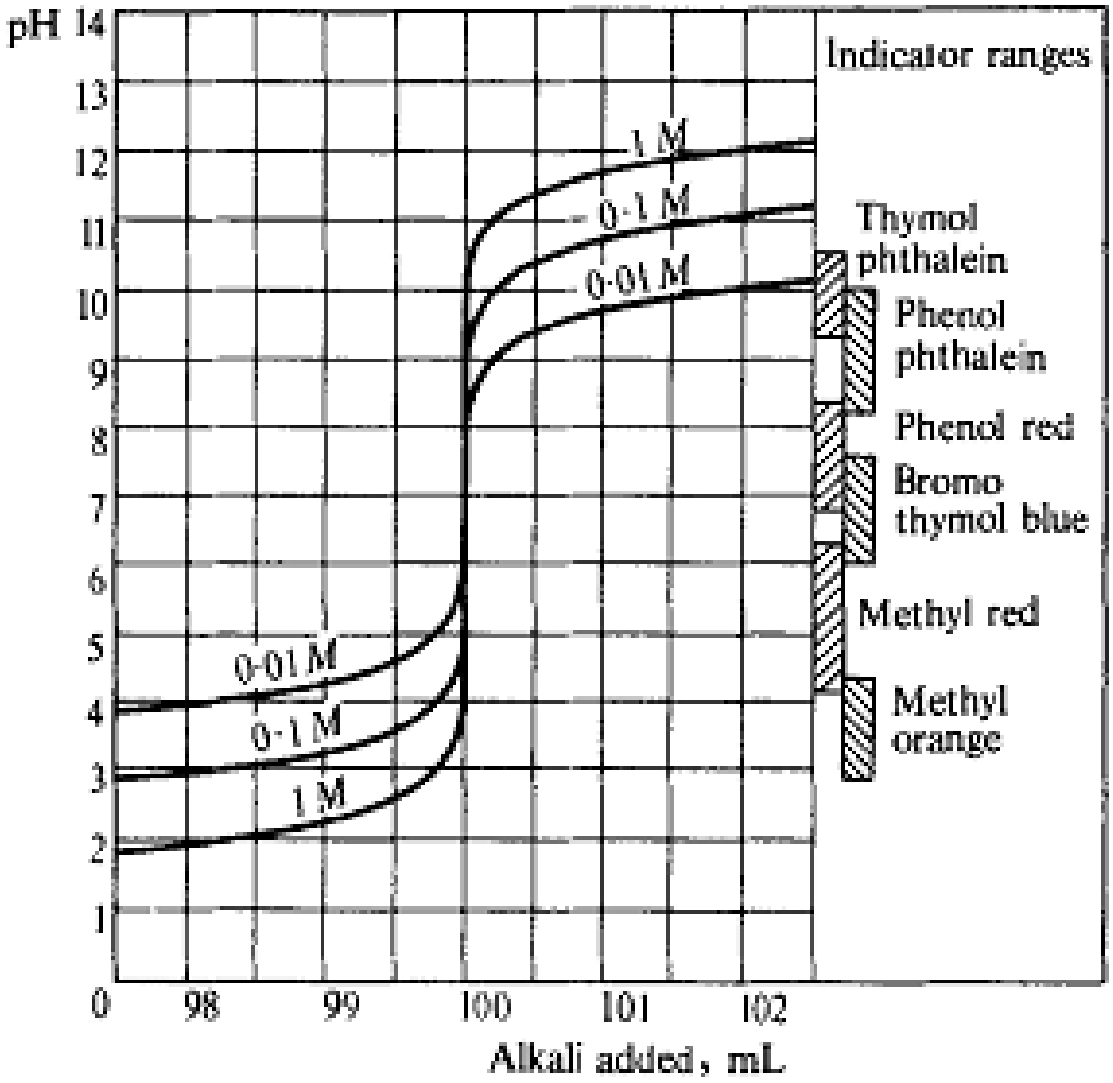

Figure 1.2: Neutralization curves of 100 mL of HCl with NaOH of same concentration in vicinity of equivalence point (calculated)

With 1M solutions, it is evident that any indicator with an effective range between pH 3 and 10.5 may be used. The colour change will be sharp and the titration error negligible.

With 0.1 M solutions, the ideal pH range for an indicator is limited to 4.5-9.5. Methyl orange will exist chiefly in the alkaline form when 99.8 mL of alkali have been added, and the titration error will be 0.2 per cent, which is negligibly small for most practical purposes; it is therefore advisable to add sodium hydroxide solution until the indicator is present completely in the alkaline form. The titration error is also negligibly small with phenolphthalein.

With 0.01*M* solutions, the ideal pH range is still further limited to 5.5—8.5; such indicators as methyl red, bromothymol blue, or phenol red will be suitable. The titration error for methyl orange will be 1-2 per cent.

The above considerations apply to solutions which do not contain carbon dioxide. In practice, carbon dioxide is usually presentarising from the small quantity of carbonate in the sodium hydroxide and/or from the atmosphere. The gas is in equilibrium with carbonic acid, of which both stages of ionisation are weak. This will introduce a small error when indicators of high pH range (above pH 5) are used, e.g. phenolphthalein or thymolphthalein. More acid indicators, such as methyl orange and methyl yellow, are unaffected by carbonic acid. The difference between the amounts of sodium hydroxide solution used with methyl orange and phenolphthalein is not greater than 0.15-0.2 mL of 0.1 M sodium hydroxide when 100 mL of 0.1 M hydrochloric acid are titrated. A method of eliminating this error, other than that of selecting an indicator with a pH range below pH 5, is to boil the solution while still acid to expel carbon dioxide and then to continue the titration with the cold solution. Boiling the solution is particularly efficacious when titrating dilute (e.g. 0.01 M) solutions.

1.1.2.2) Neutralization of a Weak Acid with a Strong Base:

The neutralization of 100 mL of 0.1 M acetic acid (ethanoic acid) with 0.1 M sodium hydroxide solution will be considered here; other concentrations can be treated similarly. The pH of the solution at the equivalence point is given by

$$pH = 1/2pK_w + 1/2pK_a - 1/2pc = 7 + 2.37 - 1/2(1.3) = 8.72$$

For other concentrations, we may employ the approximate Mass Action expression:

$$[H^+] \times [CH_3COO^-]/[CH_3COOH] = Ka \qquad (6)$$

$$\text{or } [H^+] = [CH_3COOH] \times K_a/[CH_3COO^-]$$

$$\text{or } pH = \log [Salt]/[Acid] + pKa \qquad (7)$$

The concentration of the salt (and of the acid) at any point is calculated from the volume of alkali added, due allowance being made for the total volume of the solution.

The initial pH of 0.1M acetic acid is computed from equation (6); the dissociation of the acid is relatively so small that it may be neglected in expressing the concentration of acetic acid. Hence from equation (6):

$[H^+] \times [CH_3COO^-]/[CH_3COOH] = 1.82 \times 10^{-5}$

or $[H^+]^2/0.1 = 1.82 \times 10^{-5}$

or $[H^+] = \sqrt{1.82 \times 10^{-6}} = 1.35 \times 10^{-3}$

or pH = 2.87

When 50 mL of 0.1 *M* alkali have been added,

$[Salt] = 50 \times 0.1/150 = 3.33 \times 10^{-2}$

and $[Acid] = 50 \times 0.1/150 = 3.33 \times 10^{-2}$

$pH = \log(3.33 \times 10^{-2}/3.33 \times 10^{-2}) + 4.74 = 4.74$

The pH values at other points on the titration curve are similarly calculated. After the equivalence point has been passed, the solution contains excess of OH^- ions which will repress the hydrolysis of the salt; the pH may be assumed, with sufficient accuracy for our purpose, to be that due to the excess of base present, so that in this region the titration curve will almost coincide with that for 0.1 M hydrochloric acid (**Fig. 1.1**and **Table 1.1**). All the results are collected in **Table 1.2**, and are depicted graphically in Fig. 2.3. The results for the titration of 100mL of 0.1M solution of a weaker acid ($K_a = 1 \times 10^{-7}$) with 0.1 M sodium hydroxide at the laboratory temperature are also included.

Table 1.2: Neutralization of 100 mL of 0.1M acetic acid (A* =1.82 x 10^{-5}) and of 100 mL of 0.1MHA (K_a = 1 x 10^{7}) with 0,1 M sodium hydroxide.

Vol. of 0.1*M*NaOH used (mL)	0.1 *M* acetic acid (pH)	0.1*M*HA ($K_a = 1 \times 10^{-7}$) (pH)
0	2.9	4.0
10	3.8	6.0
25	4.3	6.5
50	4.7	7.0
90	5.7	8.0
99.0	6.7	9.0

99.5	7.0	9.3
99.8	7.4	9.7
99.9	7.7	9.8
100.0	8.7	9.9
100.2	10.0	10.0
100.5	10.4	10.4
101	10.7	10.7
110	11.7	11.7
125	12.0	12.0
150	12.3	12.3
200	12.5	12.5

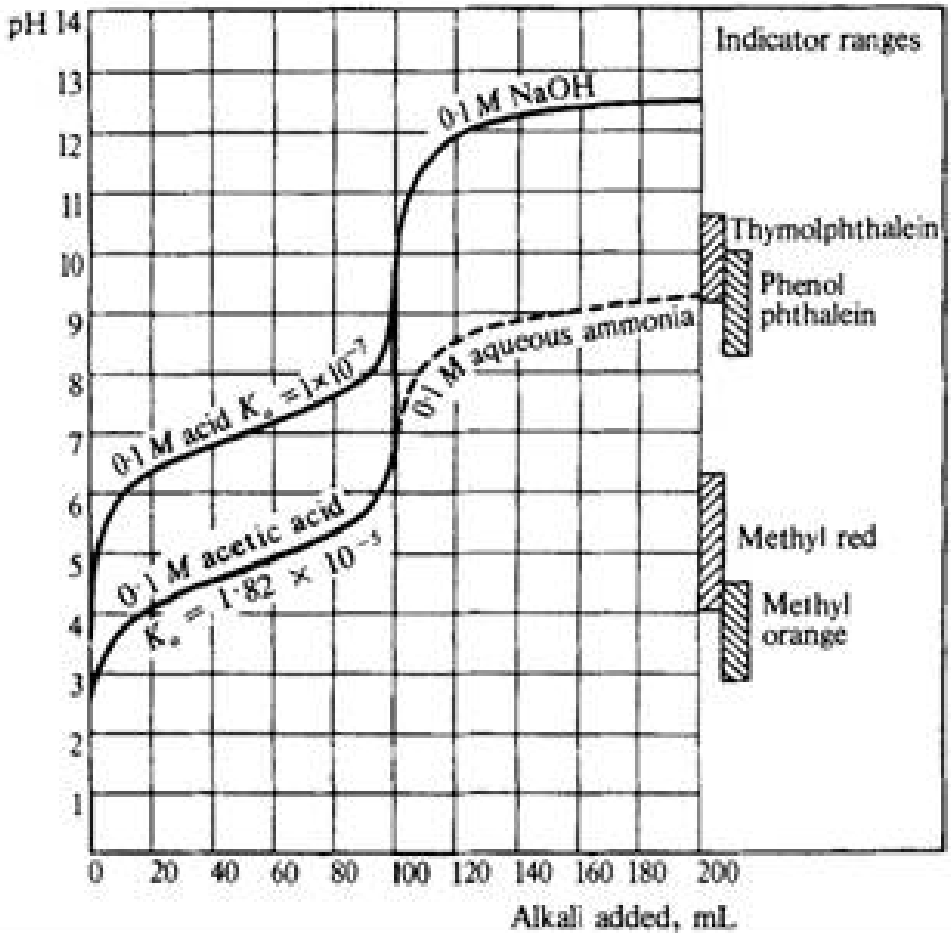

Figure 1.3: Neutralization curves of 100 mL of 0.1 M acetic acid and of 0.1 M acid with 0.1 M sodium hydroxide

For 0.1*M* acetic acid and 0.1*M* sodium hydroxide (**Fig. 1.3**), it is evident from the titration curve that neither methyl orange nor methyl red can be used as indicators. The equivalence point is at pH 8.7, and it is necessary to use an indicator with a pH range on the slightly alkaline side, such as phenolphthalein, thymolphthalein, or thymol blue (pH range, as base, 8.0-9.6). For the acid with $K_a = 10^{-7}$, the equivalence point is at pH = 10, but here the rate of change of pH in the neighborhood of the stoichiometric point is very much less pronounced, owing to considerable hydrolysis. Phenolphthalein will commence to change colour after about 92 mL of alkali have been added, and this change will occur to the equivalence point; thus the end point will not be sharp and the titration error will be appreciable. With thymolphthalein, however, the colour change covers the pH range 9.3-10.5; this indicator may be used, the end point will be sharper than for phenolphthalein, but nevertheless somewhat gradual, and the titration error will be about 0.2 per cent. Acids that have dissociation constants less than 10^{-7} cannot be satisfactorily titrated in 0.1M solution with a simple indicator.

In general, it may be stated that weak acids ($K_a > 5 \times 10^{-6}$) should be titrated with phenolphthalein, thymolphthalein, or thymol blue as indicators.

1.1.2.3) Neutralization of a Weak Base with a Strong Acid:

This may be illustrated by the titration of 100 mL of 0.1*M* aqueous ammonia ($K_b = 1.85 \times 10^{-5}$) with 0.1*M* hydrochloric acid at the ordinary laboratory temperature. The pH of the solution at the equivalence point is given by the equation:

$$pH = 1/2pK_w - 1/2pK_b + 1/2pc = 7 - 2.37 + 1/2(1.3) = 5.28$$

For other concentrations, the pH may be calculated with sufficient accuracy as follows (compare previous section):

$$[NH_4^+] \times [OH^-]/[NH_3] = K_b \qquad 8$$

$$\text{or } [OH^-] = [NH_3] \times K_b/[NH_4^+] \qquad 9$$

$$\text{or } pOH = \log[\text{Salt}]/[\text{Base}] + pK_b \qquad 10$$

$$\text{or } pH = pK_w - pK_b - \log[\text{Salt}]/[\text{Base}] \qquad 11$$

After the equivalence point has been reached, the solution contains excess of H^+ ions, hydrolysis of the salt is suppressed, and the subsequent pH changes may be assumed, with sufficient accuracy, to be those due to the excess of acid present.

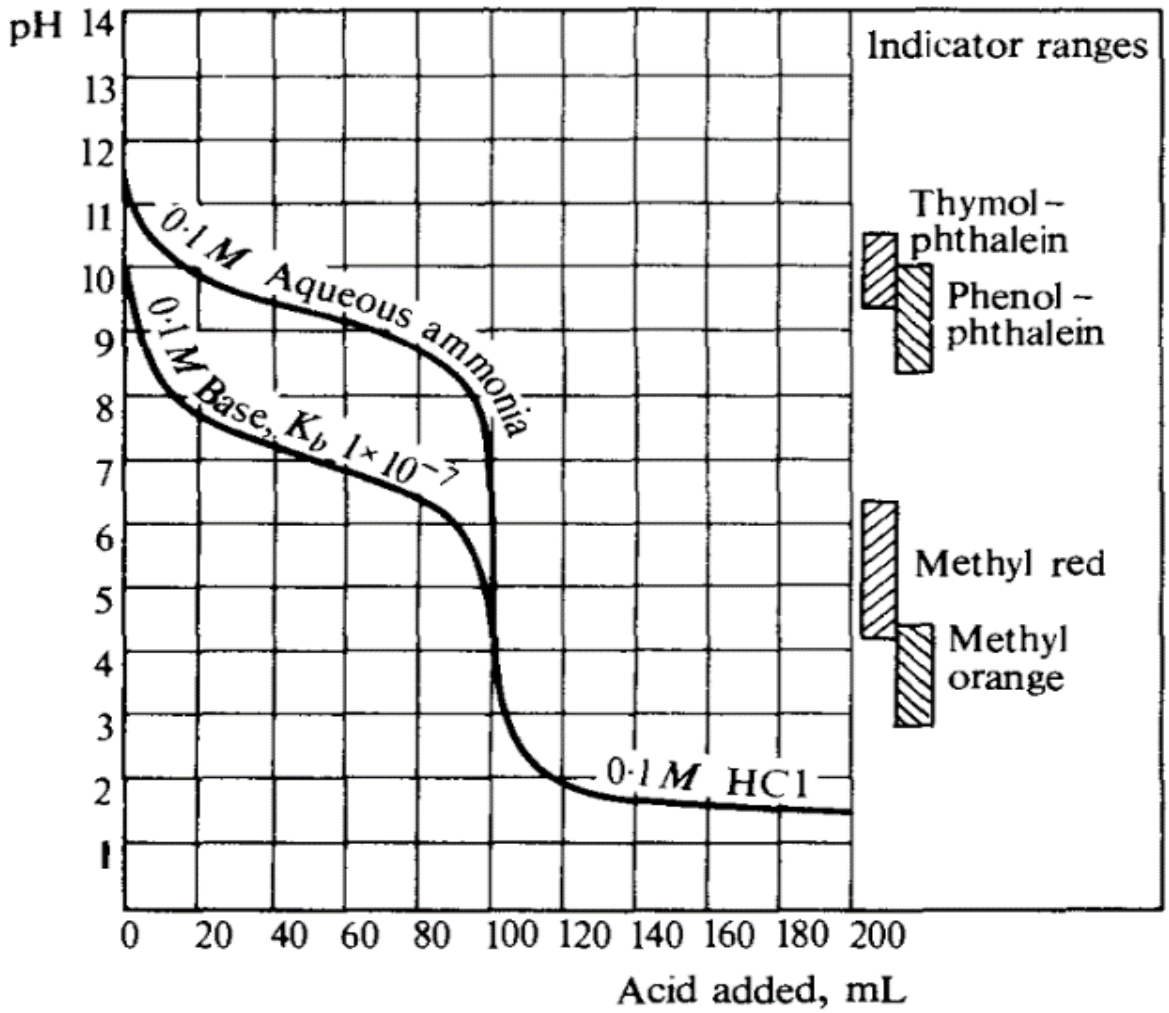

Figure 1.4: Neutralisation curves of 100 mL 0.1 A/ aqueous ammonia (= 1.8 x 10 ^{5}) and of 0.1 A/ base (K_a = 1 x 10$^{\sim 1}$) with 0.1 M hydrochloric acid.

The results computed in the above manner are represented graphically in **Fig. 1.4**; the results for the titration of 100 mL of a 0.1*M* solution of a weaker base (K_b = 1 x 10^{-7}) are also included.

Neither thymolphthalein nor phenolphthalein can be employed in the titration of 0.1*M* aqueous ammonia. The equivalence point is at pH 5.3, and it is necessary to use an indicator with a pH range on the slightly acid side (3-6.5), such as methyl orange, methyl red, bromophenol blue, or bromocresol green. The last-named indicators may be utilized for the titration of all weak bases (K_b> 5 x 10^{-6}) with strong acids

For the weak base (K_b= 1 x 10^{-7}), bromophenol blue or methyl orange may be used; no sharp colour change will be obtained with bromocresol green or with methyl red, and the titration error will be considerable.

1.1.2.4) Neutralization of a Weak Acid with a Weak Base:

This case is exemplified by the titration of 100 mL of 0.1 M acetic acid (K_a = 1.82 x 10^{-5}) with 0.1 M aqueous ammonia (K_b =1.8 x 10^{-5}). The pH at the equivalence point is given by

$$pH = 1/2pK_w + 1/2pK_a – 1/2pK_b = 7.0 + 2.38 - 2.37 = 7.1$$

The neutralizationcurve up to the equivalence point is almost identical with that using 0.1 *M* sodium hydroxide as the base; beyond this point the titration is virtually the addition of 0.1*M* aqueous ammonia solution to 0.1*M* ammonium acetate solution and equation (11) is applicable to the calculation of the pH. The titration curve for the neutralization of 100 mL of 0.1*M* acetic acid with 0.1 *M* aqueous ammonia at the laboratory temperature is shown by the broken line in **Fig. 1.5**. The chief feature of the curve is that the change of pH near the equivalence point and, indeed, during the whole of the neutralization curve is very gradual. There is no sudden change in pH, and hence no sharp end point can be found with any simple indicator. A mixed indicator, which exhibits a sharp colour change over a very limited pH range, may sometimes be found which is suitable. Thus, for acetic acid-ammonia solution titrations, neutral red-methylene blue mixed indicator may be used, but on the whole, it is best to avoid the use of indicators in titrations involving both a weak acid and a weak base.

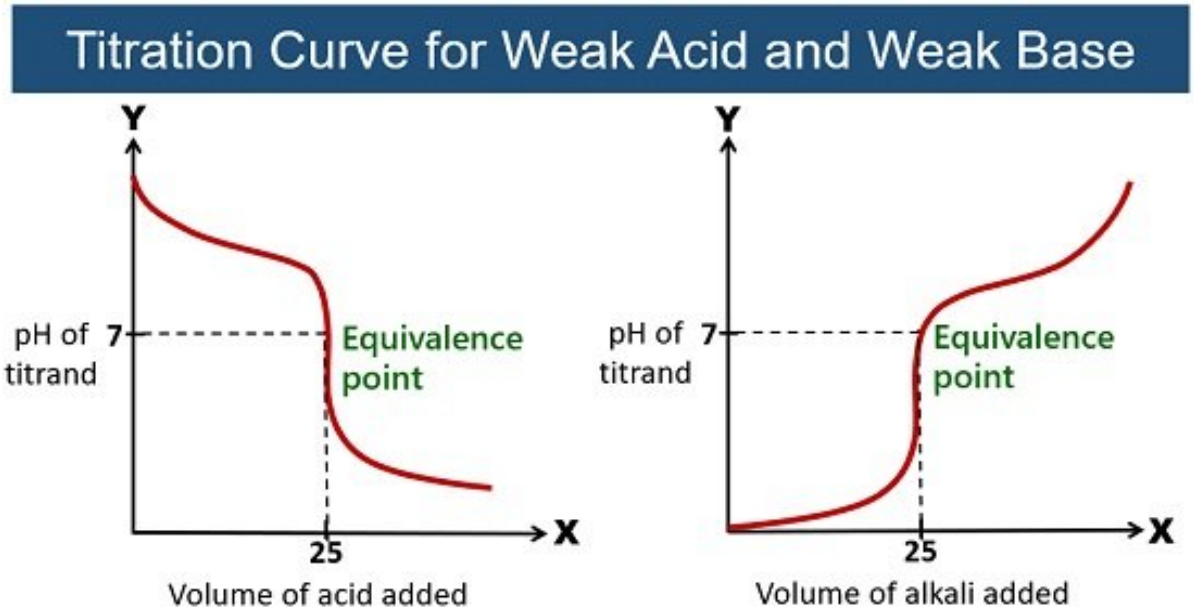

Figure 1.5: Neutralization curves for 100 mL of 0.1 M acetic acid (K_a = 1.82 x 10^{-5}) with 0.1 M aqueous ammonia (K_b =1.8 x 10^{-5})

1.1.2.5) Neutralization of a Polyprotic Acid with aStrong Base:

The shape of the titration curve will depend upon the relative magnitudes of the various dissociation constants. It is assumed that titrations take place at the ordinary laboratory temperature in solutions of concentration of 0.1 *M* or stronger. For a diprotic acid, if the difference between the primary and secondary dissociation constants is very large (K_1/K_2> 10000), the solution behaves like a mixture of two acids with constants K_1, and $K2$ respectively; the considerations given previously may be applied. Thus, for sulphurous acid, K_1, = 1.7 x $10^{-2}$and K_2 = 1.0 x 10^{-7}, it is evident that there will be a sharp change of pH near the first equivalence point, but for the second stage the change will be less pronounced, yet just sufficient for the use of, say, thymolphthalein as indicator (**see Fig. 1.3**). For carbonic acid, however, for which K_1, =4.3 x 10^{-7} and K_2 = 5.6 x 10^{-11}, only the first stage will bejust discernible in the neutralization curve (**see Fig. 1.3**); the second stage is far too weak to exhibit any point of inflexion and there is no suitable indicator available for direct titration. As indicator for the primary stage, thymol blue may be used, although a mixed indicator of thymol blue (3 parts) and cresol red (1 part) is more satisfactory; with phenolphthalein the color change will be somewhat gradual and the titration error may be several per cent.

It can be shown that the pH at the first equivalence point for a diprotic acid is given by

$$[H^+] = \sqrt{\frac{K_1 K_2 c}{K_1 + c}}$$

Provided that the first stage of the acid is weak and that K_1, can be neglected by comparison with *c*, the concentration of salt present, this expression reduces to

$$[H^+] = \sqrt{K_1 K_2}, \text{ or } pH = \tfrac{1}{2}pK_1 + \tfrac{1}{2}pK_2.$$

With a knowledge of the pH at the stoichiometric point and also of the course of the neutralization curve, it should be an easy matter to select the appropriate indicator for the titration of any diprotic acid for which K_1/K_2 is at least 10^4. For many diprotic acids, however, the two dissociation constants are too close together and it is not possible to differentiate between the two stages. If K_2 is not less than about 10^{-7}, all the replaceable hydrogen may be titrated, e.g. sulphuric acid (primary stage-a strong acid), oxalic acid, malonic, succinic, and tartaric acids.

Similar remarks apply to triprotic acids. These may be illustrated by reference to phosphoric(V) acid (orthophosphoric acid), for which K_1, =7.5 x 10^{-3}, K_2 = 6.2 x 10^{-8}, and K_3 = 5 x 10^{-13}. Here K_1,/K_2= 1.2 x 10^5 and K_2/K_3 = 1.2 x 10^5, so that the acid will behave as a mixture of three monoprotic acids with the dissociation constants given above. Neutralization proceeds almost completely to the end of the primary stage before the secondary stage is appreciably affected, and the secondary stage proceeds almost to completion before the tertiary stage is apparent. The pH at the first equivalence point is given approximately by (1/2pK_1, + 1/2pK_2) = 4.6, and at the second equivalence point by (1/2pK_2 + 1/2pK_3) = 9.7; in the very weak third stage, the curve is very flat and no indicator is available for direct titration. The third equivalence pointmay be calculated approximately from the equation:

$$\mathrm{pH} = \tfrac{1}{2}\mathrm{p}K_w + \tfrac{1}{2}\mathrm{p}K_a - \tfrac{1}{2}\mathrm{p}c = 7.0 + 6.15 - \tfrac{1}{2}(1.6) = 12.35 \text{ for } 0.1M\ \mathrm{H_3PO_4}.$$

For the primary stage (phosphoric(V) acid as a monoprotic acid), methyl orange, bromocresol green, or Congo red may be used as indicators. The secondary stage of phosphoric) V) acid is very weak (see acid K_a = 1 x 10^{-7} in Fig. 2.3) and the only suitable simple indicator is thymolphthalein; with phenolphthalein the error may be several per cent. A mixed indicator composed of phenolphthalein (3 parts) and 1-naphtholphthalein (1 part) is very satisfactory for the determination of the end point of phosphoric) V) acid as a diprotic acid.

The experimental neutralization curve of 50 mL of 0.1*M* phosphoric(V) acid with 0.1*M*potassium hydroxide, determined by potentiometric titration, is shown in **Fig. 1.6**.There are a number of triprotic acids, e.g. citric acid with K_1 =9.2 x 10^{-4}, K_2 = 2.7 x 10^{-5}, K_3 = 1.3 x 10^{-6}, the three dissociation constants of which are too close together for the three stages to be differentiated easily. If K_3> ca 10^{-7}, all the replaceable hydrogen may be titrated; the indicator will be determined by the value of K_3.

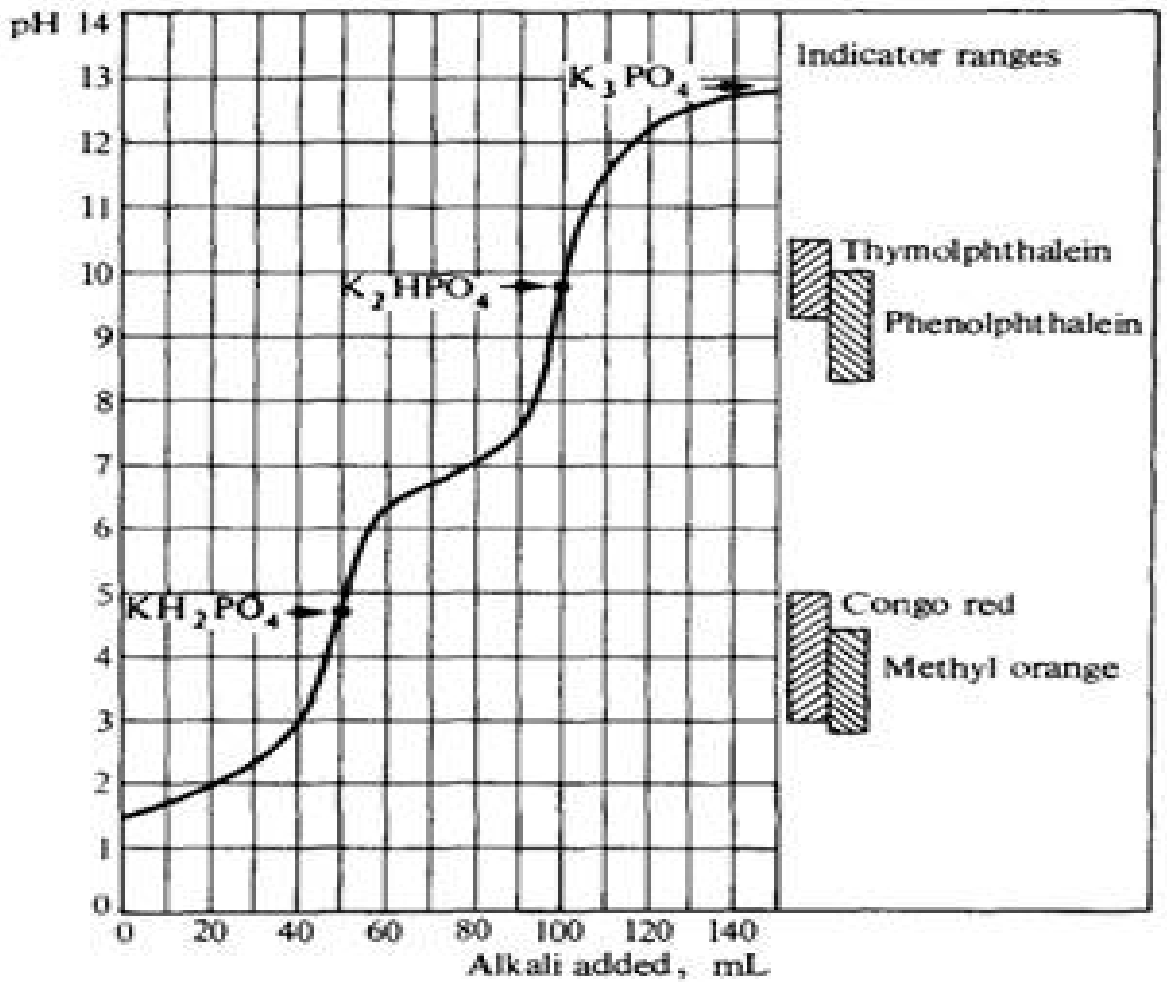

Figure 1.6: Titration of 50 mL of 0.1M H_3PO_4 with 0.1 KOH.

1.1.2.6) Titration of Anions of Weak Acids with Strong Acids:

Displacement Titrations:

So far, the titrations considered have involved a strong base, the hydroxide ion, but titrations are also possible with weaker bases, such as the carbonate ion, the borate ion, the acetate ion, etc. Formerly titrations involving these ions were regarded as titrations of solutions of hydrolysed salts, and the net result was that the weak acid was displaced by the stronger acid. Thus, in the titration of sodium acetate solution with hydrochloric acid the following equilibria were considered:

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + \bar{O}H \text{ (hydrolysis)}$$

$H^+ + OH^- = H_2O$ (strong acid reacts with OH^- produced by hydrolysis).

The net result thus appeared to be:

$$H^+ + CH_3COO^- = CH_3\text{-}COOH$$

$$\text{or } CH_3\text{-}COONa + HC1 = CH_3\text{-}COOH + NaCl$$

i.e. the weak acetic acid was apparently displaced by the strong hydrochloric acid, and the process was referred to as a **displacement titration**. According to the Bronsted-Lowry theory the so-called titration of solutions of hydrolysed salts is merely the titration of a weak base with a strong (highly ionized) acid. When the anion of a weak acid is titrated with a strong acid the titration curve is identical with that observed in the reverse titration of a weak acid itself with a strong base.

A few examples encountered in practice include the following:

a) Titration of borate ion with a strong acid:

The titration of the tetraborate ion with hydrochloric acid is similar to that described above. The net result of the displacement titration is given by:

$$B_4O_7^- + 2H^+ + 5H_2O = 4H_3BO_3$$

Boric acid behaves as a weak monoprotic acid with a dissociation constant of 6.4×10^{-10}. The pH at the equivalence point in the titration of 0.2*M* sodium tetraborate with 0.2 *M* hydrochloric acid is that due to 0.1 *M* boric acid, i.e. 5.6. Further addition of hydrochloric acid will cause a sharp decrease of pH and any indicator covering the pH range 3.7-5.1 (and slightly beyond this) may be used; suitable indicators are bromocresol green, methyl orange, bromophenol blue, and methyl red.

b) Titration of carbonate ion with a strong acid:

A solution of sodium carbonate may be titrated to the hydrogen carbonate stage (i.e. with one mole of hydrogen ions), when the net reaction is:

$$CO_3^{2-} + H^+ = HCO_3^-$$

The equivalence point for the primary stage of ionisation of carbonic acid is at pH = $(1/2pK_1 + 1/2pK_2) = 8.3$, and we have seen (Neutralization of a weak base with a strong acid) that thymol blue and, less satisfactorily, phenolphthalein, or a mixed indicator (Mixed indicators) may be employed to detect the end point.

Sodium carbonate solution may also be titrated until all the carbonic acid is displaced. The net reaction is then:

$$CO_3^{2-} + 2H^+ = H_2CO_3$$

The same end point is reached by titrating sodium hydrogen carbonate solution with hydrochloric acid:

$$HCO_3^- + H^+ = H_2CO_3$$

The end point with 100 mL of 0.2*M* sodium hydrogen carbonate and 0.2 *M* hydrochloric acid may be deduced as follows from the known dissociation constant and concentration of the weak acid. The end point will obviously occur when 100 mL of hydrochloric acid has been added, i.e. the solution now has a total volume of 200 mL.Consequently, since the carbonic acid liberated from the sodium hydrogen carbonate (0.02 moles) is now contained in a volume of 200 mL, its concentration is 0.1*M*. K_1, for carbonic acid has a value of 4.3×10^{-7}, and hence we can say:

$$[H^+] \times [HCO_3^-]/[H_2CO_3] = K_1 = 4.3 \times l0^{-7} molL^{-1}$$

and since

$$[H^+] = [HCO_3^-]$$

$$[H^+] = \sqrt{4.3 \times 10^{-7} \times 0.1} = 2.07 \times 10^{-4}$$

The pH at the equivalence point is thus approximately 3.7; the secondary ionisation and the loss of carbonic acid, due to any escape of carbon dioxide, have been neglected. Suitable indicators are therefore methyl yellow, methyl orange, Congo red, and bromophenol blue. The experimental titration curve, determined with the hydrogen electrode, for 100 mL of 0.1 *M* sodium carbonate and 0.1 *M* hydrochloric acid is shown in **Fig. 1.7.**

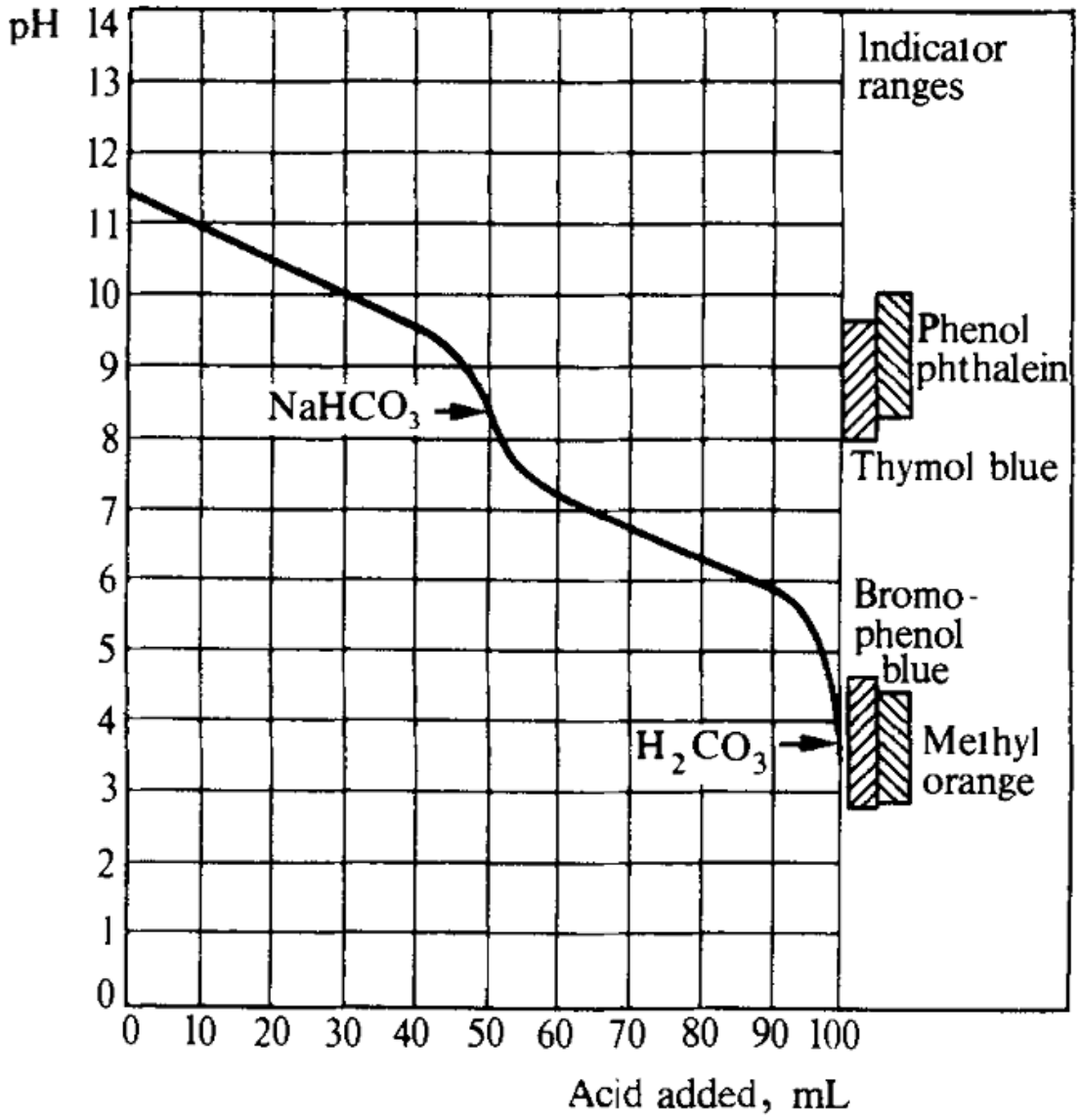

Figure 1.7: Titration of 100 mL of 0.1M Na_2CO_3 with 0.lM HCl.

Cations of weak bases (i.e. Bronsted acids such as the phenylammonium ion $C_6H_5NH_3^+$) may be titrated with strong bases, and the treatment is similar. These were formerly regarded as salts of weak bases (e.g. aniline (phenylamine), K_b = 4.0 x 10^{-10}) and strong acids: an example is aniline hydrochloride (phenylammonium chloride).

1.1.3) Redox Titrations (or) Oxidation-Reduction Titrations:

1.1.3.1) Change of the Electrode Potential during the Titration of a Reductant with an Oxidant:

In neutralization curves it is shown how the change in pH during acid-base titrations may be calculated, and how the titration curves thus obtained can be used (a) to ascertain the

most suitable indicator to be used in a given titration, and (b) to determine the titration error. Similar procedures may be carried out for oxidation-reduction titrations. Consider first a simple case which involves only change in ionic charge, and is theoretically independent of the hydrogen-ion concentration. A suitable example, for purposes of illustration, is the titration of 100 mL of 0.1 *M*iron(II) with 0.1 *M*cerium(IV) in the presence of dilute sulphuric acid:

$$Ce^{4+} + Fe^{2+} \rightleftharpoons Ce^{3+} + Fe^{3+}$$

The quantity corresponding to $[H^+]$ in acid-base titrations is the ratio [Ox]/[Red]. We are concerned here with two systems, the Fe^{3+}/Fe^{2+} ion electrode (1), and the Ce^{4+}/Ce^{3+} ion electrode (2).

For (1) at 25 °C:

$$E_1 = E_1^{\ominus} + \frac{0.0591}{1}\log\frac{[Fe^{3+}]}{[Fe^{2+}]} = +0.75 + 0.0591\log\frac{[Fe^{3+}]}{[Fe^{2+}]}$$

For (2) at 25 °C:

$$E_2 = E_2^{\ominus} + \frac{0.0591}{1}\log\frac{[Ce^{4+}]}{[Ce^{3+}]} = +1.45 + 0.0591\log\frac{[Ce^{4+}]}{[Ce^{3+}]}$$

The equilibrium constant of the reaction is given by:

$$\log K = \log\frac{[Ce^{3+}] \times [Fe^{3+}]}{[Ce^{4+}] \times [Fe^{2+}]} = \frac{1}{0.0591}(1.45 - 0.75) = 11.84$$

or

$$K = 7 \times 10^{11}$$

The reaction is therefore virtually complete.

During the addition of the cerium(IV) solution up to the equivalence point, its only effect will be to oxidise the iron(II) (since *K* is large) and consequently change the ratio $[Fe^{3+}]/[Fe^{2+}]$, When l0 mL of the oxidising agent have been added, $[Fe^{3+}]/[Fe^{2+}]$ = 10/90 (approx.) and

E_1 = 0.75 + 0.0591 log 10/90 = 0.75 - 0.056 = 0.69 volt

With 50 mL of the oxidising agent, $E_1 = E_1^{\emptyset}$ = 0.75 volt

With 90mL, E_1 = 0.75 + 0.0591 log90/10 = 0.81 volt

With 99mL, E_1= 0.75 = 0.0591 log99/1 = 0.87 volt

With 99.9 mL, E_1 = 0.75 + 0.0591 log99.9/0.1 = 0.93 volt

At the equivalence point (100.0 mL) $[Fe^{3+}] = [Ce^{3+}]$ and $[Ce^{4+}] = [Fe^{2+}]$,

and the electrode potential is given by:*

$$\frac{E_1^{\ominus} + E_2^{\ominus}}{2} = \frac{0.75 + 1.45}{2} = 1.10 \text{ volts}$$

The subsequent addition of cerium(IV) solution will merely increase the ratio $[Ce^{4+}]/[Ce^{3+}]$. Thus:

With 100.1 mL, E_2 = 1.45 + 0.059 1 log 0.1/100 = 1.27 volts

With 101 mL, E_2 = 1.45 + 0.059 1 log 1/100 = 1.33 volts

*For a deduction of this expression and a discussion of the approximations involved, see a textbook of electrochemistry. It can similarl$a\,\mathrm{Ox_I} + b\,\mathrm{Red_{II}} \rightleftharpoons b\,\mathrm{Ox_{II}} + a\,\mathrm{Red_I}$ be shown that for the reaction: the potential at the equivalence point is given by:

$$E_0 = \frac{b\,E_1^{\ominus} + a\,E_2^{\ominus}}{a + b}$$

Where $E_1^{\emptyset}$ refers Ox_I, Red_I, and $E_2^{\emptyset}$ to Ox_{II}, Red_{II}.

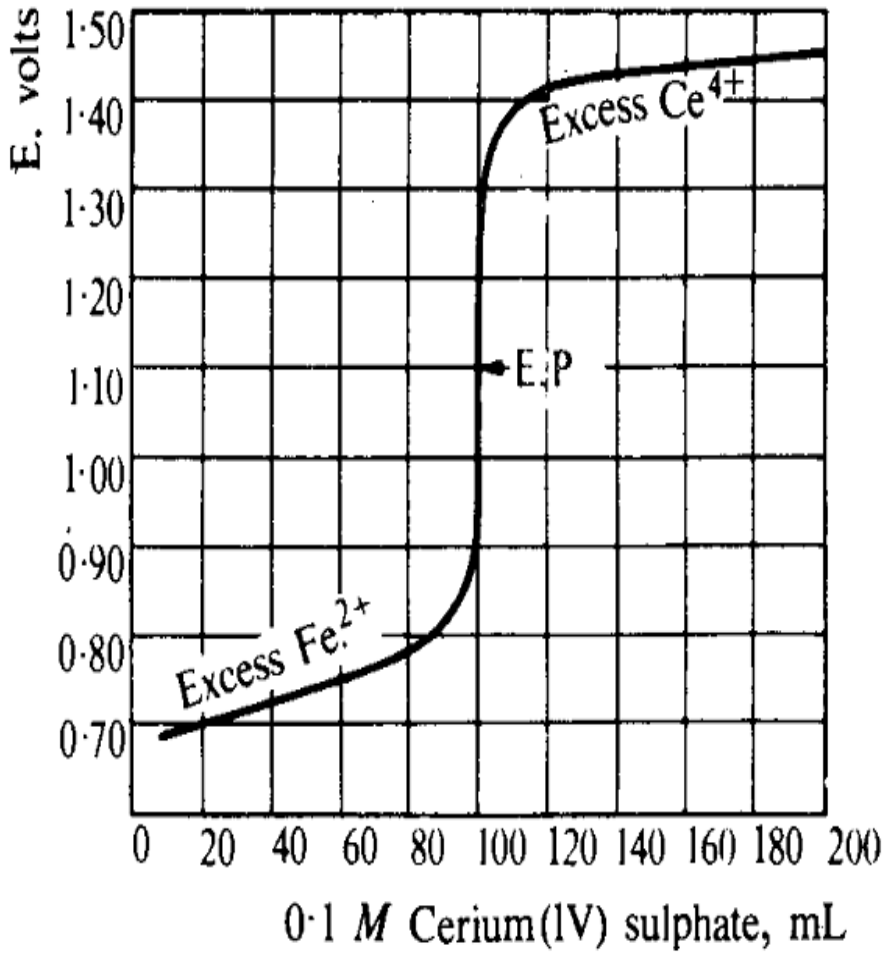

Figure 1.8: Titration of 100 mL of 0.1* M*iron(II) with 0.1* M *cerium(IV) sulphate (calculated)

With 110 mL, E_2 = 1.45 + 0.059 1 log 10/100 = 1.39 volts

With 190 mL, E_2 = 1.45 + 0.059 1 log 90/100 = 1.45 volts

These results are shown in **Fig. 1.8.**

It is of interest to calculate the iron(II) concentration in the neighbourhood of the equivalence point. When 99.9 mL of the cerium(IV) solution have been added, $[Fe^{2+}]$ = 0.1 x 0.1/199.9 = 5 x 10^{-5}, orpFe^{2+} = 4.3. The concentration at the equivalence point is given by:

$$[Fe^{3+}]/[Fe^{2+}] = \sqrt{K} = \sqrt{7 \times 10^{11}} = 8.4 \times 10^5$$

Now $[Fe^{3+}]$ = 0.05 *M*, hence $[Fe^{2+}]$ = 5 x 10^{-2}/8.4 x 10^5 = 6 x 10^{-8} *M*, or pFe^{2+}=7.2. Upon the addition of 100.1 mL of cerium(IV) solution, the reduction potential (see above)is 1.27 volts. The $[Fe^{3+}]$ is practically unchanged at 5 x 10^{-2}*M*, and we may calculate $[Fe^{2+}]$ with sufficient accuracy for our purpose from the equations:

$$E = E_1^{\ominus} + 0.0591 \log \frac{[Fe^{3+}]}{[Fe^{2+}]}$$

$$1.27 = 0.75 + 0.0591 \log \frac{5 \times 10^{-2}}{[Fe^{2+}]}$$

$$[Fe^{2+}] = 1 \times 10^{-10}$$

or

$$pFe^{2+} = 10$$

Thus pFe^{2+} changes from 4.3 to 10 between 0.1 per cent before and 0.1 per cent after the stoichiometric end point. These quantities are of importance in connection with the use of indicators for the detection of the equivalence point.

1.1.3.1) Detection of the End Point in Oxidation-Reduction Titrations:

a) Internal oxidation-reduction indicators. As discussed in neutralization curves, acid-base indicators are employed to mark the sudden change in pH during acid-base titrations. Similarly, an oxidation-reduction indicator should mark the sudden change in the oxidation potential in the neighbourhood of the equivalence point in an oxidation-reduction titration. The ideal oxidation- reduction indicator will be one with an oxidation potential intermediate between that of the solution titrated and that of the titrant, and which exhibits a sharp, readily detectable colour change.

An oxidation-reduction indicator (redox indicator) is a compound which exhibits different colours in the oxidised and reduced forms:

$$In_{Ox} + ne \rightleftharpoons In_{Red}$$

The oxidation and reduction should be reversible. At a potential £ the ratio of the concentrations of the two forms is given by the Nernst equation:

$$E = E_{In}^{\ominus} + \frac{RT}{nF} \ln a_{In.ox}/a_{In.Red}$$

$$E \approx E_{In}^{\ominus} + \frac{RT}{nF} \ln \frac{[In_{Ox}]}{[In_{Red}]}$$

where $E^{\ominus}_{In}$ is the standard (strictly the formal) potential of the indicator. If the colour intensities of the two forms are comparable a practical estimate of the colour-change interval corresponds to the change in the ratio $[In_{ox}]/[In_{Red}]$ from 10 to $\frac{1}{10}$, this leads to an interval of potential of:

$$E = E^{\ominus}_{In} \pm \frac{0.0591}{1} \text{ volts at } 25\,^{\circ}\text{C}$$

If the colour intensities of the two forms differ considerably the intermediate colour is attained at potential somewhat removed from $E^{\ominus}_{In}$, but the error is unlikely to exceed 0.06 volt. For a sharp colour change at the end point, $E^{\ominus}_{In}$ should differ by about at least 0.15 volt from the standard (formal) potentials of the other systems involved in the reaction.

One of the best oxidation-reduction indicators is the 1,10-phenanthroline- iron(II) complex. The base 1,10-phenanthroline combines readily in solution with iron(II) salts in the molecular ratio 3 base:liron(II) ion forming the intensely red l,10-phenanthroline-iron(II) complex ion; with strong oxidising agents the iron(III) complex ion is formed, which has a pale blue colour. The colour change is a very striking one:

$$\underset{\text{Pale blue}}{[Fe(C_{12}H_8N_2)_3]^{3+}} + e \rightleftharpoons \underset{\text{Deep red}}{[Fe(C_{12}H_8N_2)_3]^{2+}}$$

The standard redox potential is 1.14 volts; the formal potential is 1.06 volts in 1M hydrochloric acid solution. The colour change, however, occurs at about 1.12 volts, because the colour of the reduced form (deep red) is so much more intense than that of the oxidised form (pale blue). The indicator is of great value in the titration of iron(II) salts and other substances with cerium(IV) sulphate solutions. It is prepared by dissolving 1,10-phenanthroline hydrate (relative molecular mass = 198.1) in the calculated quantity of 0.02*M* acid-free iron(II) sulphate, and is therefore l,10-phenanthroline-iron(II) complex sulphate (known as **ferroin**). One drop is usually sufficient in a titration: this is equivalent to less than 0.01 mL of 0.05 *M*oxidising agent, and hence the indicator blank is negligible at this or higher concentrations.

It has been shown that the potential at the equivalence point is the mean of the two standard redox potentials. In Fig. 2.9, the curve shows the variation of the potential during the titration of 0.1 *M*iron(II) ion with 0.1 *M*cerium(IV) solution, and the equivalence point is at 1.10 volts. Ferroin changes from deep red to pale blue at a redox potential of 1.12 volts: the

indicator will therefore be present in the red form. After the addition of, say, a 0.1 per cent excess of cerium(IV) sulphate solution the potential rises to 1.27 volts, and the indicator is oxidised to the pale blue form. It is evident that the titration error is negligibly small.

The standard or formal potential of ferroin can be modified considerably by the introduction of various substituents in the 1,10-phenanthroline nucleus. The most important substituted ferroin is 5-nitro-l,10-phenanthroline iron(II) sulphate (nitroferroin) and 4,7-dimethyl-l,10-phenanthroline iron(II) sulphate (dimethylferroin). The former ($E^{\emptyset}$ = 1.25 volts) is especially suitable for titrations using Ce(IV) in nitric or perchloric acid solution where the formal potential of the oxidant is high. The 4,7-dimethylferroin has a sufficiently low formal potential ($E^{\emptyset}$ = 0.88 volt) to render it useful for the titration of Fe(II) with dichromate in 0.5 *M* sulphuric acid.

Mention should be made of one of the earliest internal indicators. This is a 1 per cent solution of diphenylamine in concentrated sulphuric acid, and was introduced for the titration of iron(II) with potassium dichromate solution. An intense blue-violet coloration is produced at the end point. The addition of phosphoric(V) acid is desirable, for it lowers the formal potential of the Fe(III)-Fe(II) system so that the equivalence point potential coincides more nearly with that of the indicator. The action of diphenylamine (I) (**Figure 1.9**) as an indicator depends upon its oxidation first into colourlessdiphenylbenzidine (II), which is the real indicator and is reversibly further oxidised to diphenylbenzidine violet (HI). Diphenylbenzidine violet undergoes further oxidation if it is allowed to stand with excess of dichromate solution; this further oxidation is irreversible, and red or yellow products of unknown composition are produced.

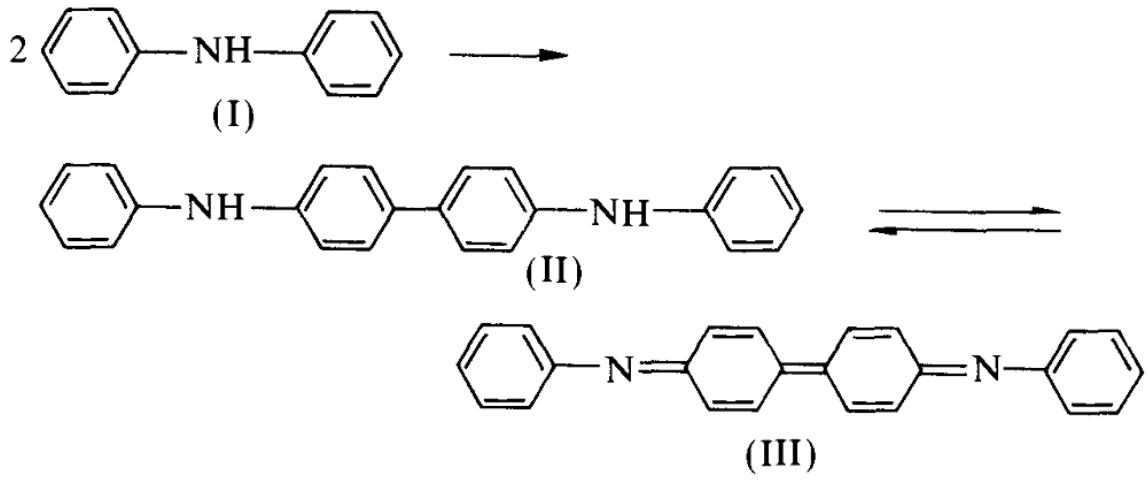

Figure 1.9: Diphenylamine Indicator Oxidative Reaction Progress

A solution of diphenylbenzidine in concentrated sulphuric acid acts similarly to diphenylamine. The reduction potential of the system II, III is 0.76 volt in 0.5-1 M sulphuric acid. It is therefore evident that a lowering of the potential of the Fe(III)-Fe(II) system is desirable, as already mentioned, in order to obtain a sharp colour change. The disadvantage of diphenylamine and of diphenylbenzidine is their slight solubility in water. This has been overcome by the use of the soluble barium or sodium diphenylaminesulphonate, which is employed in 0.2 per cent aqueous solution. The redox potential (E^0_{In}) is slightly higher (0.85 volt in 0.5 M sulphuric acid), and the oxidised form has a reddish-violet colour resembling that of potassium permanganate, but the colour slowly disappears on standing; the presence of phosphoric(V) acid is desirable in order to lower the redox potential of the system.

A list of selected redox indicators, together with their colour changes and reduction potentials in an acidic medium, is given in **Table 1.3.**

Table 1.3: Some Oxidation-Reduction Indicators

Indicator	Colour change		Formal potential at pH = 0 (volts)
	Oxidised form	Reduced form	
5-Nitro-1,10-phenanthroline iron(II) sulphate (nitroferroin)	Pale blue	Red	1.25
1,10-Phenanthroline iron(II) sulphate (ferroin)	Pale blue	Red	1.06
2,2′-Bipyridyl iron(II) sulphate	Faint blue	Red	1.02
5,6-Dimethylferroin	Pale blue	Red	0.97
N-Phenylanthranilic acid,	Purple red	Colourless	0.89
4,7-Dimethyl-1,10-phenanthroline iron(II) sulphate (4,7-dimethylferroin)	Pale blue	Red	0.88
Diphenylaminesulphonic acid	Red–violet	Colourless	0.85
Diphenylbenzidine	Violet	Colourless	0.76
Diphenylamine	Violet	Colourless	0.76
3,3′-Dimethylnaphthidine	Purplish-red	Colourless	0.71
Starch–I_3^-,KI	Blue	Colourless	0.53
Methylene blue	Blue	Colourless	0.52

At this stage reference may be made to potential mediators, i.e. substances which undergo reversible oxidation-reduction and reach equilibrium rapidly. If we have a mixture of two ions, say M^{2+} and M^{+}, which reaches equilibrium slowly with an inert electrode, and a very small quantity of cerium(IV) salt is added, then the reaction:

$$M^{+} + Ce^{4+} \rightarrow M^{2+} + Ce^{3+}$$

takes place until the tendency of M^+ to be oxidised to M^{2+} is exactly balanced by the tendency of Ce^{3+} to be oxidised to Ce^{4+}, that is, until the M^{2+}, M^+ and Ce^{4+}, Ce^{3+} potentials are equal. A platinum or other inert electrode rapidly attains equilibrium with the Ce(III) and Ce(IV) ions, and will soon register a stable potential which is also that due to the $M^{2+} + e \rightleftharpoons M^+$system. If the potential mediator is employed in small amount, then a negligible quantity of M^+ is converted into M^{2+} when equilibrium is reached, and the measured potential may be regarded as that of the original system. Potential mediators are, of course, useful in the measurement of the oxidation-reduction potentials of redox systems; in this connection mention may be made of the use of potassium iodide (≡ iodide-iodine system) in the arsenate-arsenite system in acid solution. It is evident that redox indicators (e.g. l,10-phenanthroline-iron(II) ion) may act as potential mediators.

b) Self-indicating Reagents:

This is well illustrated by potassium permanganate, one drop of which will impart a visible pink coloration to several hundred millilitres of solution, even in the presence of slightly coloured ions, such as iron(III). The colours of cerium(IV) sulphate and of iodine solutions have also been employed in the detection of end points, but the colour change is not so marked as for potassium permanganate; here, however, sensitive internal indicators (l,10-phenanthroline-iron(II) ion or *N*-phenylanthranilic acid and starch respectively) are available.

This method has the drawback that an excess of oxidizing agent is always present at the end point. For work of the highest accuracy, the indicator blank may be determined and allowed for, or the error may be considerably reduced by performing the standardization and determination under similar experimental conditions.

c) Potentiometric Methods:

This is a procedure which depends upon measurement of the e.m.f. between a reference electrode and an indicator (redox) electrode at suitable intervals during the titration, i.e. a potentiometric titration is carried out. The procedure is discussed fully in potentiometry chapter; let it suffice at this stage to point out that the procedure is applicable not only to those cases where suitable indicators are available, but also to those cases, e.g. coloured or very dilute solutions, where the indicator method is inapplicable, or of limited accuracy.

LESSON - 2

COMPLEXOMETRIC TITRATIONS & PRECIPITATION TITRATIONS

2.1 COMPLEXOMETRIC TITRATIONS:

This particular section is concerned with the way in which complexation reactions can be employed in titrimetry, especially for determining the proportions of individual cations in mixtures.

The vast majority of complexation titrations are carried out using multidentate ligands such as EDTA or similar substances as the complexone. However, there are other more simple processes which also involve complexation using monodentate or bidentate ligands and which also serve to exemplify the nature of this type of titration. This is demonstrated in the determination outlined below.

2.1.1) A Simple Complexation Titration:

A simple example of the application of a complexation reaction to a titration procedure is the titration of cyanides with silver nitrate solution. When a solution of silver nitrate is added to a solution containing cyanide ions (e.g. an alkali cyanide) a white precipitate is formed when the two liquids first come into contact with one another, but on stirring it re-dissolves owing to the formation of a stable complex cyanide, the alkali salt of which is soluble:

$$Ag^+ + 2CN^- \rightleftharpoons [Ag(CN)_2]^-$$

When the above reaction is complete, further addition of silver nitrate solution yields the insoluble silver cyanoargentate (sometimes termed insoluble silver cyanide); the end point of the reaction is therefore indicated by the formation of a permanent precipitate or turbidity.

The only difficulty in obtaining a sharp end point lies in the fact that silver cyanide, precipitated by local excess concentration of silver ion somewhat prior to the equivalence point, is very slow to re-dissolve and the titration is time-consuming. In the Deniges modification, iodide ion (usually as KI, ca 0.01 *M*) is used as the indicator and aqueous ammonia (ca 0.2*M*) is introduced to dissolve the silver cyanide.

The iodide ion and ammonia solution are added before the titration is commenced; the formation of silver iodide (as a turbidity) will indicate the end point:

$$[Ag(NH_3)_2]^+ + I^- \rightleftharpoons AgI + 2NH_3$$

During the titration any silver iodide which would tend to form will be kept in solution by the excess of cyanide ion always present until the equivalence point is reached:

$$AgI + 2CN^- \rightleftharpoons [Ag(CN)_2]^- + I^-$$

The method may also be applied to the analysis of silver halides by dissolution in excess of cyanide solution and back-titration with standard silver nitrate. It can also be utilised indirectly for the determination of several metals, notably nickel, cobalt, and zinc, which form stable stoichiometric complexes with cyanide ion. Thus, if a Ni(II) salt in ammoniacal solution is heated with excess of cyanide ion, the $[Ni(CN)_4]^{2-}$ ion is formed quantitatively; since it is more stable than the $[Ag(CN)_2]^-$ ion, the excess of cyanide may be determined by the Liebig-Deniges method. The metal ion determinations are, however, more conveniently made by titration with EDTA.

2.1.2) Titration of Cyanide with Silver Ion:

Silver halides can be dissolved in a solution of potassium tetracyanonickelate(II) in the presence of an ammonia-ammonium chloride buffer, and the nickel ion set free may be titrated with standard EDTA using murexide as indicator.

$$2Ag^+ + [Ni(CN)_4]^{2-} \rightleftharpoons 2[Ag(CN)_2]^- + Ni^{2+}$$

It can be shown from a consideration of the overall stability constants of the ions $[Ni(CN)_4]^{2-}(10^{27})$ and $[Ag(CN)_2]^-(10^{21})$ that the equilibrium constant for the above ionic reaction is 10^{15}, i.e. the reaction proceeds practically completely to the right. An interesting exercise is the analysis of a solid silver halide, e.g. silver chloride.

Procedure: Prepare the murexide indicator, and an ammonium chloride solution (1*M*) by dissolving 26.75 g ammonium chloride in de-ionised water in a 500 mL graduated flask.

The potassium tetracyanonickelate(II) which is required is prepared as follows. Dissolve 25 g of analytical grade $NiSO_4.7H_2O$ in 50 mL distilled water and add portion wise, with agitation, 25 g potassium cyanide. (**Caution**: use a fume cupboard.) A yellow solution forms and a white precipitate of potassium sulphate separates. Gradually add, with stirring, 100 mL of 95 per cent ethanol, filter off the precipitated potassium sulphate with suction, and

wash twice with 2mL ethanol. Concentrate the filtrate at about 70 °C - an infrared heater is convenient for this purpose. When crystals commence to separate, stir frequently. When the crystalline mass becomes thick (without evaporating completely to dryness), allow to cool and mix the crystals with 50 mL ethanol. Separate the crystals by suction filtration and wash twice with 5 mL portions ethanol. Spread the fine yellow crystals in thin layers upon absorbent paper, and allow to stand for 2-3 days in the air, adequately protected from dust. During this period the excess of potassium cyanide is converted into potassium carbonate. The preparation is then ready for use; it should be kept in a stoppered bottle.

Treat an aqueous suspension of about 0.072 g (accurately weighed) silver chloride with a mixture of 10 mL of concentrated ammonia solution and 10 mL of 1*M* ammonium chloride solution, then add about 0.2 g of potassium cyanonickelate and warm gently. Dilute to 100 mL with de-ionised water, add 50 mg of the indicator mixture and titrate with standard (0.01*M*) EDTA solution, adding the reagent dropwise in the neighbourhood of the end point, until the colour changes from yellow to violet.

1 mole EDTA = 2 moles Ag^+

2.2 PRECIPITATION TITRATIONS:

2.2.1 Precipitation Reactions:

The most important precipitation process in titrimetric analysis utilizes silver nitrate as the reagent (argentometric process). Discussion of the theory will, therefore, be confined to argentometric processes; the same principles can, of course, be applied to other precipitation reactions.

Consider the changes in ionic concentration which occur during the titration of 100 mL of 0.1 *M* sodium chloride with 0.1*M* silver nitrate. The solubility product of silver chloride at the laboratory temperature is 1.2×10^{-10}. The initial concentration of chloride ions, $[Cl^-]$, is 0.1 mol L^{-1}, or $pCl^- = 1$. When 50mL of 0.1 *M* silver nitrate have been added, 50 mL of 0.1 *M* sodium chloride remain in a total volume of 150mL: thus $[Cl^-] = 50 \times 0.1/150 = 3.33 \times 10^{-2}$, or $pCl^- = 1.48$. With 90mL of silver nitrate solution $[Cl^-] = 10 \times 0.1/190 = 5.3 \times 10^{-3}$, or pCl - =2.28.Now,

$$a_{Ag^+} \times a_{Cl^-} \approx [Ag^+] \times [Cl^-] = 1.2 \times 10^{-10} = K_{sol.\ AgCl}$$

or

$$pAg^+ + pCl^- = 9.92 = pAgCl$$

In the last calculation, $pCl^- = 1.48$, hence $pAg^+ = 9.92 — 1.48 = 8.44$. In this manner, the various concentrations of chloride and silver ions can be computed up to the equivalence point. At the equivalence point:

$$Ag^+ = Cl^- = \sqrt{K_{\text{sol. AgCl}}}$$
$$pAg^+ = pCl^- = \tfrac{1}{2}pAgCl = 9.92/2 = 4.96$$

and a saturated solution of silver chloride with no excess of silver or chloride ions is present.

With 100.1 Mlof silver nitrate solution, $[Ag^+] = 0.1 \times 0.1/200.1 = 5 \times 10^{-5}$, or $pAg^+ = 4.30$; $pCl^- = pAgCl - pAg^+ = 9.92 - 4.30 = 5.62$.*[1]

The values calculated in this way up to the addition of 110 mL of 0.1 *M* silver nitrate are collected in **Table 2.1.** Similar values for the titration of 100 mL of 0.1*M* potassium iodide with 0.1M silver nitrate are included in the same table ($K_{\text{sol.Ag1}} = 1.7 \times 10^{-16}$).

It will be seen by inspecting the silver-ion exponents in the neighborhood of the equivalence point (say, between 99.8 and 100.2 mL) that there is a marked change in the silver-ion concentration, and the change is more pronounced for silver iodide than for silver chloride, since the solubility product of the latter is about 106 larger than for the former. This is shown more clearly in the titration curve in **Fig. 2.1**, which represents the change of pAg^+ in the range between 10 per cent before and 10 per cent after the stoichiometric point in the titration of 0.1*M* chloride and 0.1*M* iodide respectively with 0.1*M* silver nitrate. An almost identical curve is obtained by potentiometric titration using a silver electrode; the pAg^+ values may be calculated from the e.m.f. figures as in the calculation of pH.

*This is not strictly true, since the dissolved silver chloride will contribute silver and chloride ions to the solution; the actual concentration is *ca* 1×10^{-5} g ions L^{-1}. If the excess of silver ions added is greater than 10times this value, i.e. $>10\sqrt{K_{\text{sol AgCl}}}$, the error introduced by neglecting the ionic concentration produced by the dissolved salt may be taken as negligible for the purpose of the ensuing discussion.

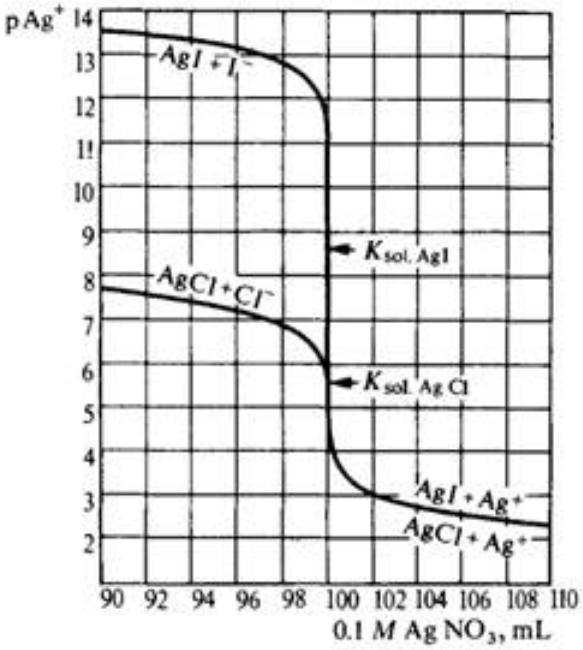

Figure 2.1: Titration curves of 100 mL of 0.1 M NaCl and 100 mL of 0.1 M KI respectively with 0.1M $AgNO_3$.

Table 2.1

Titration of 100 mL of 0.1 *M* NaCl and 100 mL of 0.1 *M* KI respectively with 0.l*M* $AgNO_3$ ($K_{sol.AgCl} = 1.2 \times 10^{-10}$; $K_{sol.AgI} = 1.7 \times 10^{-16}$)

Vol. of 0.1 *M* $AgNO_3$ (mL)	Titration of Chloride		Titration of Iodide	
	pCl^-	pAg^+	PI^-	pAg^+
0	1.0	-	1.0	-
50	1.5	8.4	1.5	14.3
90	2.3	7.6	2.3	13.5
95	2.6	7.3	2.6	13.2
98	3.0	6.9	3.0	12.8
99	3.3	6.6	3.3	12.5
99.5	3.7	6.2	3.7	12.1
99.8	4.0	5.9	4.0	11.8
99.9	4.3	5.6	4.3	11.5

100.0	5.0	5.0	7.9	7.9
100.1	5.6	4.3	11.5	4.3
100.2	5.9	4.0	11.8	4.0
100.5	6.3	3.6	12.2	3.6
101	6.6	3.3	12.5	3.3
102	6.9	3.0	12.8	3.0
105	7.3	2.6	13.2	2.6
110	7.6	2.3	13.5	2.4

2.2.2) Determination of End Points in Precipitation Reactions:

Many methods are utilized in determining end points in these reactions, but only the most important will be mentioned here.

(a) Formation of a Coloured Precipitate: This may be illustrated by the Mohr procedure for the determination of chloride and bromide. In the titration of aneutral solution of, say, chloride ions with silver nitrate solution, a small quantity of potassium chromate solution is added to serve as indicator. At the end point the chromate ions combine with silver ions to form the sparingly soluble, red, silver chromate.

The theory of the process is as follows. This is a case of fractional precipitation, the two sparingly soluble salts being silver chloride (K_{sol} 1.2 x 10^{-10}) and silver chromate (K_{sol}1.7 x 10^{-12}). It is best studied by considering an actual example encountered in practice, viz. the titration of, say, 0.1 *M* sodium chloride with 0.1*M* silver nitrate in the presence of a few millilitres of dilute potassium chromate solution. Silver chloride is the less soluble salt and the initial chloride concentration is high; hence silver chloride will be precipitated. At the first point where red silver chromate is just precipitated both salts will be in equilibrium with the solution. Hence:

$$[Ag^+] \times [Cl^-] = K_{sol.\ AgCl} = 1.2 \times 10^{-10}$$

$$[Ag^+]^2 \times [CrO_4^{2-}] = K_{sol.\ Ag_2CrO_4} = 1.7 \times 10^{-12}$$

$$[Ag^+] = \frac{K_{sol.\ AgCl}}{[Cl^-]} = \sqrt{\frac{K_{sol.\ Ag_2CrO_4}}{[CrO_4^{2-}]}}$$

$$\frac{[Cl^-]}{\sqrt{[CrO_4^{2-}]}} = \frac{K_{sol.\ AgCl}}{\sqrt{K_{sol.\ Ag_2CrO_4}}} = \frac{1.2 \times 10^{-10}}{\sqrt{1.7 \times 10^{-12}}} = 9.2 \times 10^{-5}$$

At the equivalence point $[Cl^-] = \sqrt{K_{sol.AgCl}} = 1.1 \times 10^{-5}$ if silver chromate is to precipitate at this chloride-ion concentration:

$$[CrO_4^{2-}] = \left(\frac{[Cl^-]}{9.2 \times 10^{-5}}\right)^2 = \left(\frac{1.1 \times 10^{-5}}{9.2 \times 10^{-5}}\right)^2 = 1.4 \times 10^{-2}$$

or the potassium chromate solution should be 0.014*M*. It should be noted that a slight excess of silver nitrate solution must be added before the red colour of silver chromate is visible. In practice, a more dilute solution (0.003-0.005*M*) of potassium chromate is generally used, since a chromate solution of concentration 0.01-0.02 *M* imparts a distinct deep orange colour to the solution, which renders the detection of the first appearance of silver chromate somewhat difficult. The error introduced can be readily calculated, for if $[CrO_4^{2-}]$ = (say) 0.003, silver chromate will be precipitated when:

$$[Ag^+] = \sqrt{\frac{K_{sol.\,Ag_2CrO_4}}{CrO_4^{2-}}} = \sqrt{\frac{1.7 \times 10^{-12}}{3 \times 10^{-3}}} = 2.4 \times 10^{-5}$$

If the theoretical concentration of indicator is used:

$$[Ag^+] = \sqrt{\frac{1.7 \times 10^{-12}}{1.4 \times 10^{-2}}} = 1.1 \times 10^{-5}$$

The difference is 1.3 x l0-5 molL-1. If the volume of the solution at the equivalence point is 150 mL, then this corresponds to 1.3 x 10-5 x 150 x 104/ 1000 = 0.02 mL of 0.1 M silver nitrate. This is the theoretical titration error, and is therefore negligible. In actual practice another factor must be considered, viz. the small excess of silver nitrate solution which must be added before the eye can detect the colour change in the solution; this is of the order of one drop or ca 0.05 mL of 0.1 *M* silver nitrate.

The titration error will increase with increasing dilution of the solution being titrated and is quite appreciable (*ca* 0.4* per cent) in dilute, say 0.01 *M*, solutions when the chromate concentration is of the order 0.003-0.005 *M*. This is most simply allowed for by means of an indicator blank determination, e.g. by measuring the volume of standard silver nitrate solution required to give a perceptible coloration when added to distilled water containing the same quantity of indicator as is employed in the titration. This volume is subtracted from the volume of standard solution used.

It must be mentioned that the titration should be carried out in neutral solution or in very faintly alkaline solution, i.e. within the pH range 6.5-9. In acid solution, the following reaction occurs:

$$2CrO_4^{2-} + 2H^+ \rightleftharpoons 2HCrO_4^- \rightleftharpoons Cr_2O_7^{2-} + H_2O$$

$HCrO_4^-$ is a weak acid; consequently, the chromate-ion concentration is reduced and the solubility product of silver chromate may not be exceeded. In markedly alkaline solutions, silver hydroxide (K_{sol} 2.3 x 10^{-8}) might be precipitated. A simple method of making an acid solution neutral is to add an excess of pure calcium carbonate or sodium hydrogen carbonate. An alkaline solution may be acidified with acetic acid and then a slight excess of calcium carbonate is added. The solubility product of silver chromate increases with rising temperature; the titration should therefore be performed at room temperature. By using a mixture of potassium chromate and potassium dichromate in proportions such as to give a neutral solution, the danger of accidentally raising the pH of an unbuffered solution beyond the acceptable limits is minimized; the mixed indicator has a buffering effect and adjusts the pH of the solution to 7.0 ± 0.1. In the presence of ammonium salts, the pH must not exceed 7.2 because of the effect of appreciable concentrations of ammonia upon the solubility of silver salts. Titration of iodide and of thiocyanate is not successful because silver iodide and silver thiocyanate adsorb chromate ions so strongly that a false and somewhat indistinct end point is obtained.

(b) Formation of a soluble coloured compound: This procedure is exemplified by Volhard's method for the titration of silver in the presence of free nitric acid with standard potassium thiocyanate or ammonium thiocyanate solution. The indicator is a solution of iron(III) nitrate or of iron(III) ammonium sulphate. The addition of thiocyanate solution produces first a precipitate of silver thiocyanate (K_{sol} 7.1 x 10^{-13}):

$$Ag^+ + SCN^- \rightleftharpoons AgSCN$$

When this reaction is complete, the slightest excess of thiocyanate produces a reddish-brown coloration, due to the formation of a complex ion:|

$$Fe^{3+} + SCN^- \rightleftharpoons [FeSCN]^{2+}$$

This method may be applied to the determination of chlorides, bromides, and iodides in acid solution. Excess of standard silver nitrate solution is added, and the excess is back-titrated with standard thiocyanate solution. For the chloride estimation, we have the following two equilibria during the titration of excess of silver ions:

$$Ag^+ + Cl^- \rightleftharpoons AgCl$$

$$Ag^{+} + SCN^{-} \rightleftharpoons AgSCN$$

The two sparingly soluble salts will be in equilibrium with the solution, hence:

$$\frac{[Cl^-]}{[SCN^-]} = \frac{K_{sol.\ AgCl}}{K_{sol.\ AgSCN}} = \frac{1.2 \times 10^{-10}}{7.1 \times 10^{-13}} = 169$$

When the excess of silver has reacted, the thiocyanate may react with the silver chloride, since silver thiocyanate is the less soluble salt, until the ratio $[Cl^-]/[SCN^-]$ in the solution is 169:

$$AgCl + SCN^{-} \rightleftharpoons AgSCN + Cl^{-}$$

This will take place before reaction occurs with the iron(III) ions in the solution, and there will consequently be a considerable titration error. It is therefore absolutely necessary to prevent the reaction between the thiocyanate and the silver chloride. This may be affected in several ways, of which the first is probably the most reliable:

1) The silver chloride is filtered off before back-titrating. Since at this stage the precipitate will be contaminated with adsorbed silver ions, the suspension should be boiled for a few minutes to coagulate the silver chloride and thus remove most of the adsorbed silver ions from its surface before filtration. The cold filtrate is titrated.
2) After the addition of silver nitrate, potassium nitrate is added as coagulant, the suspension is boiled for about 3 minutes, cooled and then titrated immediately. Desorption of silver ions occurs and, on cooling, re-adsorption is largely prevented by the presence of potassium nitrate.
3) An immiscible liquid is added to 'coat' the silver chloride particles and thereby protect them from interaction with the thiocyanate. The most successful liquid is nitrobenzene (*ca* 1.0 mL for each 50 mg of chloride): the suspension is well shaken to coagulate the precipitate before back-titration.

With bromides, we have the equilibrium:

$$\frac{[Br^-]}{[SCN^-]} = \frac{K_{sol.\ AgBr}}{K_{sol.\ AgSCN}} = \frac{3.5 \times 10^{-13}}{7.1 \times 10^{-13}} = 0.5$$

The titration error is small, and no difficulties arise in the determination of theend point. Silver iodide (K_{sol} 1.7 x 10^{-16}) is less soluble than the bromide; thetitration error is negligible, but the iron(III) indicator should not be added until excess of silver is present, since the dissolved iodide reacts with Fe^{3+} ions:

$$2Fe^{3+} + 2I^- \rightleftharpoons 2Fe^{2+} + I_2$$

(c) Use of adsorption indicators: K. Fajans introduced a useful type of indicator for precipitation reaction as a result of his studies on the nature of adsorption. The action of these indicators is due to the fact that at the equivalence point the indicator is adsorbed by the precipitate, and during the process of adsorption a change occurs in the indicator which leads to a substance of different colour; they have therefore been termed adsorption indicators. The substances employed are either acid dyes, such as those of the fluorescein series, e.g. fluorescein and eosin which are utilised as the sodium salts, or basic dyes, such as those of the rhodamine series (e.g. rhodamine 6G), which are used as the halogen salts.

The theory of the action of these indicators is based upon the properties of colloids. When a chloride solution is titrated with a solution of silver nitrate, the precipitated silver chloride adsorbs chloride ions (a precipitate has a tendency to adsorb its own ions); this may be termed the primary adsorbed layer. By a process known as secondary adsorption, oppositely charged ions present in solution are held around it (shown diagrammically in **Fig. 2.2a**). As soon as the stoichiometric point is reached, silver ions are present in excess and these now become primarily adsorbed; nitrate ions will be held by secondary adsorption (**Fig. 2.2b**). If fluorescein is also present in the solution, the negative fluorescein ion, which is much more strongly adsorbed than is the nitrate ion, is immediately adsorbed, and will reveal its presence on the precipitate, not by its own colour, which is that of the solution, but by the formation of a pink complex of silver and a modified fluorescein ion on the surface with the first trace of excess of silver ions. An alternative view is that during the adsorption of the fluorescein ion a rearrangement of the structure of the ion occurs with the formation of a coloured substance. It is important to notice that the colour change takes place at the Surface of the precipitate. If chloride is now added, the suspension remains pink until chloride ions are present in excess, the adsorbed silver ions are converted into silver chloride, which primarily adsorbs chloride ions. The secondary adsorbed fluorescein ions pass back into solution, to which they impart a greenish-yellow colour.

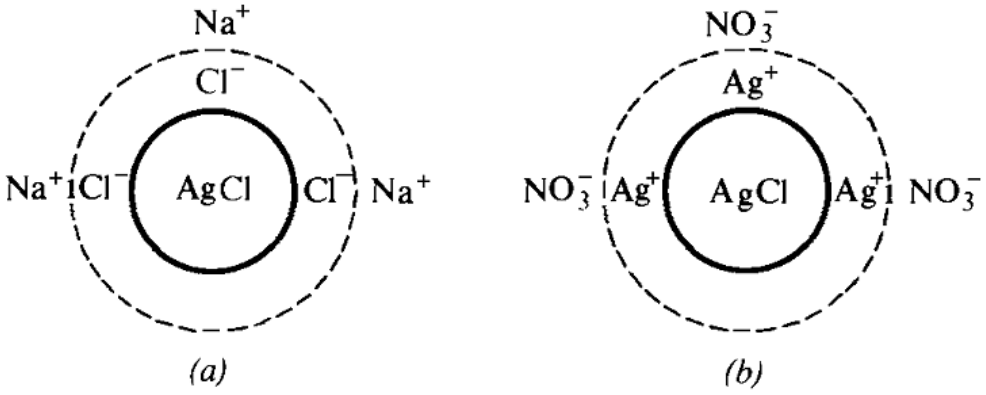

Figure 2.2: (a) AgCl precipitated in the presence of excess of Cl-;
(b) AgCl precipitated in the presence of excess of Ag+

The following conditions will govern the choice of a suitable adsorption indicator:

The precipitate should separate as far as possible in the colloidal condition. Large quantities of neutral salts, particularly of multicharged ions, should be avoided owing to their coagulating effect. The solution should not be too dilute, as the amount of precipitate formed will be small and the colour change far from sharp with certain indicators.

The indicator ion must be of opposite charge to the ion of the precipitating agent.

The indicator ion should not be adsorbed before the particular compound has been completely precipitated, but it should be strongly adsorbed immediately after the equivalence point. The indicator ion should not be too strongly adsorbed by the precipitate; if this occurs, e.g. eosin (tetrabromo - fluorescein) in the chloride-silver titration, the adsorption of the indicator ion may be a primary process and will take place before the equivalence point.

A disadvantage of adsorption indicators is that silver halides are sensitised to the action of light by a layer of adsorbed dyestuff. For this reason, titrations should be carried out with a minimum exposure to sunlight. When using adsorption indicators, only 2×10^{-4} to 3×10^{-3} mol of dye per mol of silver halide is added; this small concentration is used so that an appreciable fraction of the added indicator is actually adsorbed on the precipitate.

For the titration of chlorides, fluorescein may be used. This indicator is a very weak acid ($K_a = ca \text{ lx } 10^{-8}$); hence even a small number of other acids reduces the already minute ionisation, thus rendering the detection of the end point (which depends essentially upon the adsorption of the free anion) either impossible or difficult to observe. The optimum pH range is between 7 and 10. Dichlorofluorescein is a stronger acid and may be utilised in slightly acid solutions of pH greater than 4.4; this indicator has the further advantage that it is applicable in more dilute solutions.

Eosin (tetrabromofluorescein) is a stronger acid than dichlorofluorescein and can be used down to a pH of 1-2; the colour change is sharpest in an acetic acid solution (pH < 3). Eosin is so strongly adsorbed on silver halides that it cannot be used for chloride titrations; this is because the eosin ion can compete with chloride ion before the equivalence point and thereby gives a premature indication of the end point. With the more strongly adsorbing ions, Br^-, I^- and SCN^-, the competition is not serious and a very sharp end point is obtained in the titration of these ions, even in dilute solutions. The colour of the precipitate is magenta. Rose Bengal (dichlorotetraiodofluorescein) and dimethyldiiodo- fluorescein have been recommended for the titration of iodides.

Other dyestuffs have been recommended as adsorption indicators for the titration of halides and other ions. Thus, cyanide ion may be titrated with standard silver nitrate solution using diphenylcarbazide as adsorption indicator: the precipitate is pale violet at the end point. A selection of adsorption indicators, their properties and uses, is given in **Table 2.2**.

Table 2.2: Selected Adsorption Indicators: Properties and Uses

Indicator	Use
Fluorescein	Cl^-, Br^-, I^-, with Ag^+
Dichlorofluorescein	Cl^-, Br^-, BO_3^{3-}, with Ag^+
Tetrabromofluorescein (eosin)	Br^-, I^-, SCN^-, with Ag^+
Dichloro-tetraiodofluorescein (Rose Bengal)	I^- in presence of Cl^-, with Ag^+
Di-iodo-dimethylfluorescein	I^-, with Ag^+
Tartrazine	Ag^+, with I^- or SCN^-; $I^- + Cl^-$, with excess Ag^+, back-titration with I^-
Sodium alizarin sulphonate (alizarin red S)	$[Fe(CN)_6]^{4-}$, $[MoO_4]^{2-}$ with Pb^{2+}
Rhodamine 6G	Ag^+ with Br^-
Phenosafranine	Cl^-, Br^-, with Ag^+ Ag^+, with Br^-

* The colour change is as indicator passes from solution to precipitate, unless otherwise stated.

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LESSON - 3

INDICATORS

3.1 INDICATORS:

3.1.1 Neutralization Indicators:

The object of titrating, say, an alkaline solution with a standard solution of an acid is the determination of the amount of acid which is exactly equivalent chemically to the amount of base present. The point at which this is reached is the equivalence point, stoichiometric point, or theoretical end point; the resulting aqueous solution contains the corresponding salt. If both the acid and base are strong electrolytes, the solution at the end-point will be neutral and have a pH of 7; but if either the acid or the base is weak electrolyte, the salt will be hydrolysed to a certain degree, and the solution at the equivalence point will be either slightly alkaline or slightly acid. The exact pH of the solution at the equivalence point can readily be calculated from the ionization constant of the weak acid or the weak base and the concentration of the solution. For any actual titration the correct end-point will be characterized by a definite value of the hydrogen-ion concentration of the solution, the value depending upon the nature of the acid and the base and the concentration of the solution.

A large number of substances, called neutralization or acid-base indicators, change color according to the hydrogen-ion concentration of the solution. The chief characteristic of these indicators is that the change from predominantly ‘acid’ color to a predominantly ‘alkaline’ color is not sudden and abrupt, but takes place within a small interval of pH (usually about two pH units) termed the color change interval of the indicator. The position of the color change interval in the pH scale varies widely with different indicators. For most acid-base titrations it is possible to select an indicator which exhibits a distinct color change at a pH close to that corresponding to the equivalence point.

The first useful theory of indicator action was suggested by W. Ostwald based upon the concept that indicators in general use are very weak organic acids or bases.

The simple Ostwald theory of the color change of indicators has been revised, and the color changes are believed to be due to structural changes, including the production of quinonoid and resonance forms; these may be illustrated by reference to phenolphthalein, the changes of which are characteristic of all phthalein indicators: see the formula I-IV given in **Figure 3.1**.

In the presence of dilute alkali the lactone ring in I opens to yield II, and the triphenylcarbinol structure (II) under goes loss of water to produce the resonating ion III which is red. If phenolphthalein is treated with excess of concentrated alcoholic alkali the red color first produced disappears owing to the formation of IV.

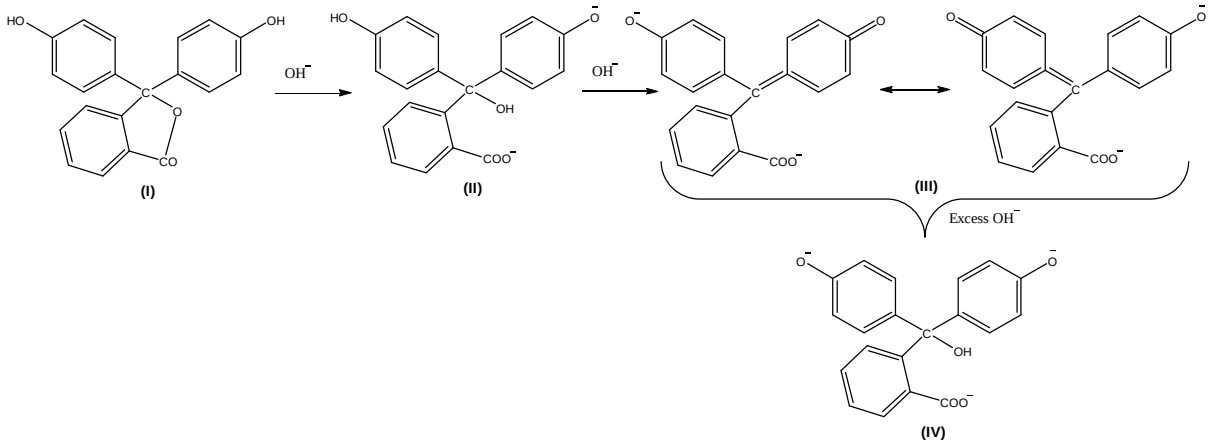


Figure 3.1: Phenolphthalein Color Changes as I to IV

The BrØnsted-Lowry concept of acids and bases makes it unnecessary to distinguish between acid and base indicators: emphasis is placed upon the charge types of acid and alkaline forms of indicator. The equilibrium between the acidic form In_A and basic form In_Bmay be expressed as:

$$In_A \rightleftharpoons H^+ + In_B \quad (1)$$

and the equilibrium constant as:

$$\frac{a_{H^+} \times a_{In_B}}{a_{In_A}} = K_{In} \quad (2)$$

The observed color of an indicator in solution is determined by the ratio of the concentrations of the acidic and basic forms. This is given by:

$$\frac{[In_A]}{[In_B]} = \frac{a_{H^+} \times y_{In_B}}{K_{In} \times y_{In_A}} \quad (3)$$

Where $y_{InA}$and y_{InB} are the activity coefficients of the acidic and basic forms of the indicator. Equation (3) may be written in the logarithmic form:

$$pH = -\log a_{H^+} = pK_{In} + \log\frac{[In_B]}{[In_A]} + \log\frac{y_{In_B}}{y_{In_A}} \quad (4)$$

The pH will depend upon the ionic strength of the solution (which is, of course, related to the activity coefficient). Hence, when making a color comparison for the determination of the pH of a solution, not only must the indicator concentration be the same in the two solutions but the ionic strength must also be equal or approximately equal. The equation incidentally provides an explanation of the so-called salt and solvent effects which are observed with indicators. The color-change equilibrium at any particular ionic strength (constant activity-coefficient term) can be expressed by a condensed form of equation (4):

$$pH = pK'_{In} + \log\frac{[In_B]}{[In_A]} \quad (5)$$

Where $pK`_{In}$is termed the apparent indicator constant.

The value of the ratio $[In_B]/[In_A]$ (i.e. [Basic form]/[Acidic form]) can be determined by a visual color comparison or, more accurately, by a spectrophotometric method. Both forms of the indicator are present at any hydrogen-ion concentration. It must be realized, however, that the human eye has a limited ability to detect either of two colors when one of them predominates. Experience shows that the solution will appear to have the 'acid' color i.e. of In_A, when the ratio of $[In_A]$ to $[In_B]$ is above approximately 10, and the 'alkaline' color i.e. ofIn_B, when the ratio of $[In_B]$ to $[In_A]$ is above approximately 10. Thus only the 'acid' color will be visible when $[In_A]/[In_B] > 10$; corresponding limit of pH given by equation (5) is $pH = pK'_{In}-1$. only the alkaline color will be visible when $[In_B]/[In_A] > 10$, and the corresponding limit of $pH = pK'_{In}+1$

The color change-interval is accordingly $pH = pK'_{In}\pm1$, i.e. over approximately two pH units. With in this range the indicator will appear to change from one color to the other. The change will be gradual, since it depends upon the ratio of the concentrations of the two colored forms (acidic form and basic form). When the pH of the solution is equal to the apparent dissociation constant of the pK'_{In}, the ratio $[In_A]$ to $[In_B]$ becomes equal to 1, and the indicator will have a color due to an equal mixture of the 'acid' and 'alkaline' forms. This is sometimes known as the 'middle tint' of the indicator. This applies strictly only if the two colors are of equal intensity. If one form is more intensely color than the other or if the eye is more sensitive to one color than the other, then the middle tint will be slightly displaced along the pH range of the indicator.

3.1.2 Mixed Indicators:

For some purposes it is desirable to have a sharp color change over a narrow and selected range of pH; this is not easily seen with an ordinary acid-base indicator, since the color change extends over two units of pH. The required result may, however, be achieved by the use of a suitable mixture of indicators; these are generally selected so that their pK'_{In} values are close together and the overlapping colors are completely at an intermediate pH value. A few examples will be given in some detail (**Table 3.1**).

(a) A mixture of equal parts of neutral red (0.1 percent solution in ethanol) and methylene blue (0.1 percent solution in ethanol) gives a sharp color change from violet-blue to green in passing from acid to alkaline solution at pH 7. This indicator may be employed to titrate acetic acid (ethanoic acid) with ammonia solution or vice versa. Both acid and base are approximately of the same strength, hence the equivalence point will be at a pH ≈ 7; owing to the extensive hydrolysis and the flat nature of the titration curve, the titration cannot be performed except with an indicator of very narrow range.

(b) A mixture of phenolphthalein (3 parts of a 0.1 percent solution in ethanol) and 1-naphtholphthalein (1 part of a 0.1 percent solution in ethanol) passes from pale rose to violet at pH = 8.9. The mixed indicator is suitable for the titration of phosphoric acid to the diprotic stage ($K_2 = 6.3 \times 10^{-8}$; the equivalence point at pH ≈ 8.7).

(c) A mixture of thymol blue (3 parts of a 0.1 percent aqueous solution of the sodium salt) and cresol red (1 part of a 0.1 percent aqueous solution of the sodium salt) changes from yellow to violet at pH = 8.3. it has been recommended for the titration of carbonate to the hydrogencarbonate stage.

Table 3.1: Some Mixed Indicators

Indicator mixture	pH	Colour change	Composition*
Bromocresol green; methyl orange	4.3	Orange → blue–green	1 p 0.1% (Na) in w; 1 p 0.2% in w
Bromocresol green; chlorophenol red	6.1	Pale green → blue violet	1 p 0.1% (Na) in w; 1 p 0.1% (Na) in w
Bromothymol blue; neutral red	7.2	Rose pink → green	1 p 0.1% in e; 1 p 0.1% in e
Bromothymol blue; phenol red	7.5	Yellow → violet	1 p 0.1% (Na) in w; 1 p 0.1% (Na) in w
Thymol blue; cresol red	8.3	Yellow → violet	3 p 0.1% (Na) in w; 1 p 0.1% (Na) in w
Thymol blue; phenolphthalein	9.0	Yellow → violet	1 p 0.1% in 50% e; 3 p 0.1% in 50% e
Thymolphthalein; phenolphthalein	9.9	Colourless → violet	1 p 0.1% in e; 1 p 0.1% in w

* Abbreviations: p = part, w = water, e = ethanol, Na = Na salt

The color change of a single indicator may also be improved by the addition of a pH-sensitive dyestuff to produce the complement of the one of the indicator colors. A typical example is the addition of xylene cyanol FF to methyl orange (1.0 g of methyl orange and 1.4 g of xylene cyanol FF in 500 mL of 50 percent ethanol): here the color change from the alkaline to the acid side is green → grey → magenta, the middle (grey) stage being at pH = 3.8. the above is an example of a screened indicator, and the mixed indicator solution is some times known as screened methyol orange. Another example is the addition of methyl green (2 parts of a 0.1 percent solution in ethanol); the former complements the red-violet basic color of the latter, and at a pH of 8.4-8.8 the color change is from grey to pale blue.

3.1.3 Universal (or) Multiple-Range Indicators:

By mixing suitable indicators together changes in colors may be obtained over a considerable portion of the pH range. Such mixtures are usually called 'universal indicators'. They are not suitable for quantitative titrations, but may be employed for the determination of the approximate pH of solution by the colorimetric method. One such universal indicator is prepared by dissolving 0.1 g of phenolphthalein, 0.2 g of methyl red, 0.3 g of methyl yellow, 0.4 g of bromothymol blue, and 0.5 g of thymol blue in 500 mL of absolute ethanol, and adding sodium hydroxide solution until the color is yellow. The color changes are: pH 2, red; pH 4, orange; pH 6, yellow; pH 8, green; pH 10, blue.

Another recipe for a universal indicator is as follows: 0.05 g methyl orange, 0.15 g of methyl red, 0.3 g of bromothymol blue, and 0.35 g of phenolphthalein in 1l of 66 percent ethanol. The color changes are: pH up to 3 red, pH 4, orange-red; pH 5, Orange; pH 6, Yellow; pH 7 Yellowish green; pH 8, greenish-blue; pH 9, blue, pH 10, violet; pH 11, reddish-violet. Several 'universal indicators' are available commercially as solution and as test papers.

3.1.4 Metal Ion Indicators:

General Properties: The success of an EDTA titration depends upon the precise determination of the end point. The most common procedure utilises metal ion indicators. The requisites of a metal ion indicator for use in the visual detection of end points include:

(a) The colour reaction must be such that before the end point, when nearly all the metal ion is complexed with EDTA, the solution is strongly.

(b) The colour reaction should be specific or at least selective.

(c) The metal-indicator complex must possess sufficient stability, otherwise, because of dissociation, a sharp colour change is not obtained. The metal-indicator complex must, however, be less stable than the metal-EDTA complex to ensure that, at the end point, EDTA removes metal ions from the metal indicator-complex. The change in equilibrium from the metal- indicator complex to the metal-EDTA complex should be sharp and rapid.

(d) The colour contrast between the free indicator and the metal-indicator complex should be such as to be readily observed.

(e) The indicator must be very sensitive to metal ions (i.e. to pM) so that the colour change occurs as near to the equivalence point as possible.

(f) The above requirements must be fulfilled within the pH range at which the titration is performed.

Dyestuff's which form complexes with specific metal cations can serve as indicators of pM values; 1:1-complexes (metal: dyestuff= 1:1) are common, but 1:2-complexes and 2:1-complexes also occur. The metal ion indicators, like EDTA itself, are chelating agents; this implies that the dyestuff- molecule possesses several ligand atoms suitably disposed for coordination with a metal atom. They can, of course, equally take up protons, which also produces a colour change; metal ion indicators are therefore not only pM but also pH indicators.

Theory of the Visual Use of Metal Ion Indicators:

Discussion will be confined to the more common 1:1-complexes. The use of a metal ion indicator in an EDTA titration may be written as:

$$\mathbf{M\text{-}In + EDTA \rightarrow M\text{-}EDTA + In}$$

This reaction will proceed if the metal-indicator complex M-In is less stable than the metal-EDTA complex M-EDTA. The former dissociates to a limited extent, and during the titration the free metal ions are progressively complexed by the EDTA until ultimately the metal is displaced from the complex M-In to leave the free indicator (In). The stability of the metal-indicator complex may be expressed in terms of the formation constant (or indicator constant) K_{In}:

$$\boldsymbol{K_{In} = [M\text{-}In]/[M][In]}$$

The indicator colour change is affected by the hydrogen ion concentration of the solution, and no account of this has been taken in the above expression for the formation constant. Thussolochrome black, which may be written as H_2In^-, exhibits the following acid-base behaviour:

$$\underset{\text{Red}}{H_2In^-} \xrightleftharpoons[5.3-7.3]{pH} \underset{\text{Blue}}{HIn^{2-}} \xrightleftharpoons[10.5-12.5]{pH} \underset{\text{Yellow-orange}}{In^{3-}}$$

In the pH range 7-11, in which the dye itself exhibits a blue colour, many metal ions form red complexes; these colours are extremely sensitive, as is shown, for example, by the fact that 10^{-6}- 10^{-7} molar solutions of magnesium ion give a distinct red colour with the indicator. From the practical viewpoint, it is more convenient to define the apparent indicator constant K'_{In}, which varies with pH, as:

$$K'_{In} = [MIn^-]/[M^{n+}][In]$$

where

$[MIn^-]$ = concentration of metal-indicator complex,

$[M^{n+}]$ = concentration of metallic ion, and

[In] = concentration of indicator not complexed with metallic ion.

(This, for the above indicator, is equal to $[H_2In^-] + [HIn^{2-}] + [In^{3-}]$.) The equation may be expressed as:

$$\log K'_{In} = pM + \log [MIn^-]/[In];$$

$\log K'_{In}$ gives the value of pM when half the total indicator is present as the metal ion complex. Some values for $\log K'_{In}$ for $CaIn^-$ and $MgIn^-$ respectively (where H_2In^- is the anion of solochrome black) are: 0.8 and 2.4 at pH = 7; 1.9 and 3.4 at pH = 8; 2.8 and 4.4 at pH = 9; 3.8 and 5.4 at pH = 10; 4.7 andat pH = 11; 5.3 and 6.8 at pH = 12. For a small titration error K'_{In} should be large ($> 10^4$), the ratio of the apparent stability constant of the metal-EDTA complex K'_{MY} to that of the metal-indicator complex K'_{In} should be large ($> 10^4$), and the ratio of the indicator concentration to the metal ion concentration should be small ($<10^{-2}$).

The visual metallochromic indicators discussed above form by far the most important group of indicators for EDTA titrations and the operations subsequently described will be confined to the use of indicators of this type; nevertheless, there are certain other substances which can be used as indicators.

3.1.5 Some Examples of Metal Ion Indicators:

Numerous compounds have been proposed for use as pM indicators; a selected few of these will be described. Where applicable, *Colour Index* (C.I.) references are given.[12] It has

been pointed out by West,[11] that apart from a few miscellaneous compounds, the important visual metallochromic indicators fall into three main groups: (a) hydroxyazo compounds; (b) phenolic compounds and hydroxy-substituted triphenylmethane compounds; (c) compounds containing an aminomethyldicarboxymethyl group: many of these are also triphenylmethane compounds.

Note. In view of the varying stability of solutions of these indicators, and the possible variation in sharpness of the end point with the age of the solution, it is generally advisable (if the stability of the indicator solution is suspect), to dilute the solid indicator with 100-200 parts of potassium (or sodium) chloride, nitrate or sulphate (potassium nitrate is usually preferred) and grind the mixture well in a glass mortar. The resultant mixture is usually stable indefinitely if kept dry and in a tightly stoppered bottle.

Murexide (C.I. 56085):

This is the ammonium salt of purpuric acid, and is of interest because it was probably the first metal-ion indicator to be employed in the EDTA titration. Murexide solutions are reddish violet up to pH = 9 (H_4D^-), violet from pH 9 to pH 11 (H_3D^{2-}), and blue-violet (or blue) above pH 11 (H_2D^{3-}). These colour changes are due to the progressive displacement of protons from imido groups; since there are four such groups, murexide may be represented as H_4D^-. Only two of these four acidic hydrogens can be removed by adding an alkali hydroxide, so that only two pK values need be considered; these are pK_4 = 9.2 ($H_2D^- \rightarrow H_3D^{2-}$) and p$K_3$ = 10.5 ($H_3D^{2-} \rightarrow H_2D^{3-}$). The anion H_4D^- can also take up a proton to yield the yellow and unstable purpuric acid, but this requires a pH of about 0.

Murexide forms complexes with many metal ions: only those with Cu, Ni, Co, Ca and the lanthanides are sufficiently stable to find application in analysis. Their colours in alkaline solution are orange (copper), yellow (nickel and cobalt), and red (calcium); the colours vary somewhat with the pH of the solution.

Murexide may be employed for the direct EDTA titration of calcium at pH = 11; the colour change at the end-point is from red to blue-violet, but is far from ideal. The colour change in the direct titration of nickel at pH 10-11 is from yellow to blue-violet.

Aqueous solutions of murexide are unstable and must be prepared each day. The indicator solution may be prepared by suspending 0.5 g of the powdered dyestuff in water, shaking thoroughly, and allowing the undissolved portion to settle. The saturated supernatant liquid is used for titrations. Every day the old supernatant liquid is decanted and the residue

treated with water as before to provide a fresh solution of the indicator. Normally it is better to prepare a mixture of the indicator with pure sodium chloride in the ratio 1:500, and employ 0.2 - 0.4 g in each titration.

Solochrome black-T (Eriochrome black T):

This substance is sodium 1-(1- hydroxy-2-naphthylazo)-6-nitro-2-naphthol-4-sulphonate, and has the Colour Index reference C.I. 14645. In strongly acidic solutions the dye tends to polymerise to a red-brown product, and consequently the indicator is rarely applied in titrations of solutions more acidic than pH = 6.5.

The sulphonic acid group gives up its proton long before the pH range of 7-12, which is of immediate interest for metal-ion indicator use. Only the dissociation of the two hydrogen atoms of the phenolic groups needs therefore be considered, and so the dyestuff may be represented by the formula H_2D^-. The two p*K* values for these hydrogen atoms are 6.3 and 11.5 respectively. Below pH = 5.5, the solution of solochrome black is red (due to H_2D^-), between pH 7 and 11 it is blue (due to HD^{2-}), and above pH = 11.5 it is yellowish-orange (due to D^{3-}). In the pH range 7-11 the addition of metallic salts produces a brilliant change in colour from blue to red:

$$\mathbf{M^{2+} + HD^{2-}\ (blue) \rightarrow MD^-\ (red) + H^+}$$

This colour change can be observed with the ions of Mg, Mn, Zn, Cd, Hg, Pb, Cu, Al, Fe, Ti, Co, Ni, and the Pt metals. To maintain the pH constant (*ca* 10) a buffer mixture is added, and most of the above metals must be kept in solution with the aid of a weak complexing reagent such as ammonia or tartrate. The cations of Cu, Co, Ni, Al, Fe(III), Ti(IV), and certain of the Pt metals form such stable indicator complexes that the dyestuff can no longer be liberated by adding EDTA: direct titration of these ions using solochrome black as indicator is therefore impracticable, and the metallic ions are said to ‘block’ the indicator. However, with Cu, Co, Ni, and Al a back-titration can be carried out, for the rate of reaction of their EDTA complexes with the indicator is extremely slow and it is possible to titrate the excess of EDTA with standard zinc or magnesium ion solution.

Cu, Ni, Co, Cr, Fe, or Al, even in traces, must be absent when conducting a direct titration of the other metals listed above; if the metal ion to be titrated does not react with the cyanide ion or with triethanolamine, these substances can be used as masking reagents. It has been stated that the addition of 0.5-1 mL of 0.001 *Mo*-phenanthroline prior to the EDTA

titration eliminates the 'blocking effect' of these metals with solochrome black and also with xylenol orange (see below).

The indicator solution is prepared by dissolving 0.2 g of the dyestuff in 15 mL of triethanolamine with the addition of 5 mL of absolute ethanol to reduce the viscosity; the reagent is stable for several months. A 0.4 per cent solution of the pure dyestuff in methanol remains serviceable for at least a month.

Patton and Reeder's indicator:

The indicator is 2-hydroxy-l-(2-hydroxy-4-sulpho-l-naphthylazo)-3-naphthoic acid; the name may be abbreviated to HHSNNA. Its main use is in the direct titration of calcium, particularly in the presence of magnesium. A sharp colourchange from wine red to pure blue is obtained when calcium ions are titrated with EDTA at pH values between 12 and 14. Interferences are similar to those observed with solochrome black, and can be obviated similarly. This indicator may be used as an alternative to murexide for the determination of calcium.

The dyestuff is thoroughly mixed with 100 times its weight of sodium sulphate, and 1 g of the mixture is used in each titration. The indicator is not very stable in alkaline solution.

Solochrome Dark Blue or Calcon (C.I. 15705):

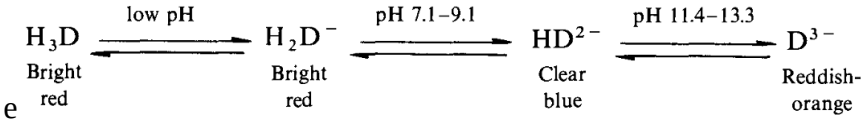
This is sometimes referred to as Eriochrome blue black RC; it is in fact sodium l-(2-hydroxy-l-naphthylazo)-2-naphthol-4-sulphonate. The dyestuff has two ionisable phenolic hydrogen atoms; the protons ionise stepwise with p*K* values of 7.4 and 13.5 respectively. An important application of the indicator is in the complexometric titration of calcium in the presence of magnesium; this must be carried out at a pH of about(obtained, for example, with a diethylamine buffer: 5 mL for every 100 mL of solution) in order to avoid the interference of magnesium. Under these conditions magnesium is precipitated quantitatively as the hydroxide. The colour change is from pink to pure blue.

The indicator solution is prepared by dissolving 0.2 g of the dyestuff in 50 mL of methanol.

Calmagite:

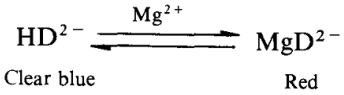
This indicator, l-(l-hydroxyl-4-methyl-2-phenylazo)-2-naphthol-4-sulphonic acid, has the same colour change as solochrome black, but the colour change is somewhat clearer and sharper. An important advantage is that aqueous solutions of the indicator are stable almost

indefinitely. It may be substituted for solochrome black without change in the experimental procedures for the titration of calcium plus magnesium. Calmagite functions as an acid-base indicator:



e

The hydrogen of the sulphonic acid group plays no part in the functioning of the dye as a metal ion indicator. The acid properties of the hydroxyl groups are expressed by pK_1 = 8.14 and pK_2 = 12.35. The blue colour of calmagite at pH = 10 is changed to red by the addition of magnesium ions, the change being reversible:



This is the basis of the indicator action in the EDTA titration. The pH of 10 is attained by the use of an aqueous ammonia-ammonium chloride buffer mixture.

The combining ratio between calcium or magnesium and the indicator is 1:1; the magnesium compound is the more stable. Calmagite is similar to solochrome black in that small amounts of copper, iron, and aluminium interfere seriously in the titration of calcium and magnesium, and similar masking agents may be used. Potassium hydroxide should be employed for the neutralisation of large amounts of acid since sodium ions in high concentration cause difficulty.

The indicator solution is prepared by dissolving 0.05 g of calmagite in 100 mL of water. It is stable for at least 12 months when stored in a polythene bottle out of sunlight.

Calcichrome:

This indicator, cyclotris-7-(l-azo-8-hydroxynaphthalene-3,6-disulphonic acid), is very selective for calcium. It is in fact not very suitable as an indicator for EDTA titrations because the colour change is not particularly sharp, but if EDTA is replaced by CDTA, then the indicator gives good results for calcium in the presence of large amounts of barium and small amounts of strontium.

Fast sulphon black F (C.1.26990):

This dyestuff is the sodium salt of 1-hydroxy-8-(2-hydroxynaphthylazo)-2-(sulphonaphthylazo)-3,6-disulphonic acid. The colour reaction seems virtually specific for

copper ions. In ammoniacal solution it forms complexes with only copper and nickel; the presence of ammonia or pyridine is required for colour formation. In the direct titration of copper in ammoniacal solution the colour change at the end point is from magenta or [depending upon the concentration of copper (II) ions] pale blue to bright green. The indicator action with nickel is poor. Metal ions, such as those of Cd, Pb, Ni, Zn, Ca, and Ba, may be titrated using this indicator by the prior addition of a reasonable excess of standard copper(II) solution. The indicator solution consists of a 0.5 percent aqueous solution.

Bromopyrogallol Red:

This metal ion indicator is dibromopyrogallolsulphon- phthalein and is resistant to oxidation; it also possesses acid-base indicator properties. The indicator is coloured orange-yellow in strongly acidic solution, claret red in nearly neutral solution, and violet to blue in basic solution. The dyestuff forms coloured complexes with many cations. It is valuable for the determination, for example, of bismuth (pH = 2-3. nitric acid solution; endpoint blue to claret red).

The indicator solution is prepared by dissolving 0.05 g of the solid reagent in 100 mL of 50 per cent ethanol.

Xylenolorange:

This indicator is 3,3'-bis[iV-di(carboxymethyl)aminomethyl]-*o*-cresolsulphonphthalein; it retains the acid-base properties of cresol red and displays metal indicator properties even in acid solution (pH = 3-5). Acidic solutions of the indicator are coloured lemon-yellow and those of the metal complexes intensely red.

Direct EDTA titrations of Bi, Th, Zn, Cd, Pb, Co, etc., are readily carried out and the colour change is sharp. Iron(III) and, to a lesser extent, aluminum interfere. By appropriate pH adjustment certain pairs of metals may be titrated successfully in a single sample solution. Thus, bismuth may be titrated at pH = 1-2, and zinc or lead after adjustment to pH = 5 by addition of hexamine.

The indicator solution is prepared by dissolving 0.5 g of xylenol orange in 100 mL of water. For storage it is best kept as a solid mixture with potassium nitrate.

Thymolphthalein Complexone (thymolphthalexone):

This is thymolphthaleindi (methyliminediacetic acid); it contains a stable lactone ring and reacts only in an alkaline medium. The indicator may be used for the titration of calcium;

the colour change is from blue to colourless (or a slight pink). Manganese and also nickel may be determined by adding an excess of standard EDTA solution, and titrating the excess with standard calcium chloride solution; the colour change is from very pale blue to deep blue.

The indicator solution consists of a 0.5 per cent solution in ethanol. Alternatively, a finely ground mixture (1:100) with potassium nitrate may be used.

Methylthymol Blue (Methylthymol Blue Complexone):

This compound is very similar in structure to the preceding one from which it is derived by replacement of the lactone grouping by a sulphonic acid group. By contrast, however, it will function in both acidic and alkaline media, ranging from pH = 0, under which condition bismuth may be titrated with a colour change from blue to yellow, to pH = 12; where the alkaline earths may be titrated with a colour change from blue to colourless. At intermediate pH values a wide variety of doubly charged metal ions may be titrated; of particular interest is its use as an indicator for the titration of Hg(II), an ion for which very few indicators are available. It is also suitable for determining calcium in the presence of magnesium provided that the proportion of the latter is not too high, and is therefore of value in determining the hardness of water. The indicator does not keep well in solution and is used as a solid mixture: 1 part to 100 of potassium nitrate.

Zincon:

This is l-(2-hydroxy-5-sulphophenyl)-3-phenyl-5-(2-carboxyphenyl) formazan, which is a specific indicator for zinc at pH 9-10. Its most important use, however, is as indicator for titration of calcium in the presence of magnesium, using the complexone EGTA; the magnesium-EGTA complex is relatively weak and does not interfere with the calcium titration. Calcium and magnesium do not give coloured complexes with the indicator, and the procedure is to add a little of the zinc complex of EGTA. The titration is carried out in a buffer at pH 10, and under these conditions' calcium ions decompose the Zn-EGTA complex, liberating zinc ions which give a blue colour with the indicator. As soon as all the calcium has been titrated, excess EGTA reconverts the zinc ions to the EGTA complex, and the solution acquires the orange colour of the metal-free indicator.

Variamine blue (C.I. 37255):

The end point in an EDTA titration may sometimes be detected by changes in redox potential, and hence by the use of appropriate redox indicators. An excellent example is

variamine blue (4-methoxy-4'-aminodiphenylamine), which may be employed in the complexometric titration of iron (III). When a mixture of iron (II) and (III) is titrated with EDTA the latter disappears first. As soon as an amount of the complexing agent equivalent to the concentration of iron (III) has been added, pFe (III) increases abruptly and consequently there is a sudden decrease in the redox potential; the end point can therefore be detected either potentiometrically or with a redox indicator (10.91). The stability constant of the iron(III) complex FeY^- (EDTA = Na_2H_2Y) is about 10^{25} and that of the iron(II) complex FeY^{2-} is 10^{14}; approximate calculations show that the change of redox potential is about 600 millivolts at pH = 2 and that this will be almost independent of the concentration ofiron (II) present. Thejump in redox potential will also be obtained if no iron (II) salt is actually added, since the extremely minute amount of iron (II) necessary is always present in any 'pure' iron (III) salt.

The visual detection of the sharp change in redox potential in the titration of an iron(III) salt with EDTA is readily made with variamine blue as indicator. The almost colourlessleuco form of the base passes upon oxidation into the strongly coloured indamine. When titrating iron (III) at a pH of about 3 and the colourless hydrochloride of the leuco base is added, oxidation to the violet-blue indamine occurs with the formation of an equivalent amount of iron (II). At the end point of the EDTA titration, the small amount of iron (II) formed when the indicator was introduced is also transformed into the Fe(III)-EDTA complex FeY^-, whereupon the blue indamine is reduced back to the leucobase. The indicator solution is a 1 per cent solution of the base in water.

Dr. K. Bala Murali Krishna

LESSON - 4

PRIMARY AND SECONDARY STANDARDS

4.1 PRIMARY STANDARDS:

In titrimetry certain chemicals are used frequently in defined concentrations as reference solutions. Such substances are referred to as primary standards or secondary standards. A primary standard is compound of sufficient purity form which a standard solution can be prepared by direct weighing of a quantity of it, followed by dilution to give a defined volume of solution. The solution produced is then a primary standard solution. A primary standard should satisfy the following requirements.

- It must be easy to obtain, to purify, to dry (preferably at 110-120 ° C), and to preserve in a pure state. (This requirement is not usually met by hydrated substances, since it is difficult to remove surface moisture completely without effecting partial decomposition.)
- The substance should be unaltered in air during weighing; this condition implies that it should not by hygroscopic, oxidized by air, or affected by carbon dioxide. The standard should maintain an unchanged composition during storage.
- The substance should be capable of being tested for impurities by qualitative and other tests of known sensitivity. (The total amount of impurities should not, in general, exceed 0.01-0.02 per cent.)
- It should have a high relative molecular mass so that the weighing errors may be negligible. (The precision in weighing is ordinarily 0.1-0.2 mg; for an accuracy of 1 part in 1000, it is necessary to employ samples weighing at least about 0.2 g.)
- The substance should be readily soluble under the conditions in which it is employed.
- The reaction with the standard solution should be stoichiometric and practically instantaneous. The titration error should be negligible, or easy to determine accurately by experiment.

In practice, an ideal primary standard is difficult to obtain, and a compromise between the above ideal requirements is usually necessary. The substances commonly employed as primary standards are indicated below.

(a) Acid-Base Reactions: Sodium carbonate Na_2CO_3, sodium tetraborate $Na_2B_4O_7$, potassium hydrogenphthalate $KH(C_8H_4O_4)$, constant boiling point hydrochloric acid, potassium hydrogeniodate $KH(IO_3)_2$, benzoic acid (C_6H_5COOH).

(b) Complex Formation Reactions: silver, silver nitrate, sodium chloride, various metals (e.g. spectroscopically pure zinc, magnesium, copper and manganese) and salts, depending upon the reaction used.

(c) Precipitation Reactions: silver, silver nitrate, sodium chloride, potassium chloride, and potassium bromide.

(d) Oxidation-Reduction Reactions: Potassium dichromate $K_2Cr_2O_7$, potassium bromate K_2BrO_3, Potassium iodate (KIO_3), potassium hydrogen iodate $KH(IO_3)_2$, sodium oxalate $Na_2C_2O_4$, arsenic(III) oxide As_2O_3 and pure iron.

Hydrated salts, as a rule, do not make good standards because of the difficulty of efficient drying. However, those salts which do not effloresce, such as sodium tetraborate $Na_2B_4O_7.10H_2O$, and copper sulphate $CuSO_4.5H_2O$, are found by experiment to be satisfactory secondary standards.

4.2 SECONDARY STANDARDS:

A secondary standard is a substance which may be used for standardizations, and whose content of the active substance has been found by comparison against a primary standard. It follows that secondary standard solution is a solution in which the concentration of dissolved solute has not been determined from the weight of the compound dissolved but by reaction (titration) of a volume of the solution against a measured volume of a primary standard solution.

Dr. K. Bala Murali Krishna

LESSON - 5

ERRORS

5.1 INTRODUCTION:

when a quantity is measured with the greatest exactness that the instrument, method and observer are capable of, it is found that the results of successive determinations differ among themselves to a greater or lesser extent' At the same time we cannot consider that all the values obtained are correct within the reasonable limits of measurements. The average value of a series of measurements is accepted as the most probable value. However, it should be noted that the average value may not always be the true value. At times the difference may betoo small, but in case of others it may be so large that the result cannot be accepted. The reliability of the result depends upon the magnitude of the difference between the average value and the true value.

5.2 ERRORS:

Error is defined as the numerical difference between a measured value and the absolute or true value of an analytical determination. The absolute or true value of a quantity is, however, never known. All that we can use is only an Accepted Value. The value for any quantity is 'accepted' when the only uncertainty in this value is less than the uncertainty in some other quantity with which the other quantity is to be compared.

Error may be represented in the following two ways:

i. Absolute Error, the absolute error E in a measurement is expressed as:

$$E = x_i - x_t$$

Where, x_i = Measured value.

x_t = True value (accepted) for given measurement

ii. Relative Error, the relative error E_r in a measurement is expressed as:

$$E_r = \frac{x_i - x_t}{x_t}$$

where x_i, x_t have the same significance as mentioned above.

Relative error may also be expressed as percent or as parts per thousand (ppt) Thus,

$$E_r = \frac{x_i - x_t}{x_t} \times 100\ \%$$

$$E_r = \frac{x_i - x_t}{x_t} \times 1000\ \text{ppt}$$

5.3 CLASSIFICATION OF ERRORS:

The various types of errors that usually occur in measurements can be classified into two broad categories, i.e.,

I) Determinate (or) Systematic Errors

II) indeterminate (or) Random Errors

I) Determinate Errors: Determinate errors have a finite source which can be identified. A given determinate error is generally unidirectional with respect to the true value and thus makes measured value either lower or higher than the true value. These errors would evidently, render the results of all the replicate measurements either low or high.

Examples of Sources of Determinate Errors.

a) In correct weights,

b) A poorly calibrated burette

c) An impurity in a reagent.

d) An appreciable solubility in precipitate.

e) A side reaction in a titration and

f) Heating a sample at a very high temperature

Determinate errors can be further divided into following types:

i) Instrument Errors: These errors arise from the imperfections in measuring device. For instance, measuring devices such as pipettes, burettes, measuring flasks, etc., deliver volumes that are slightly different from those indicated by their graduations. There can be several reasons for these difference like the use of the glassware at a temperature which is significantly different from the temperature at which glassware was calibrated, errors in the original calibration etc.

Instruments powered by electricity are susceptible to determinate errors because of the fall in voltage of battery operated instruments or increased resistance in circuit due to unclean electrical contacts. But these errors can be easily detected and corrected.

ii) **Method Errors:** These errors generally arise from the non-ideal behaviour of reagents and reactions involved. The non-ideality originates from slowness of reactions, incompleteness of reactions, instability of reactions or non-specificity of reagents etc. These errors cannot be easily detected and corrected.

iii) **Personal Errors**. These errors arise from incorrect personal judgement. Many experimental measurements, such as the estimation of the position of pointer between two scale divisions. Judgement of the colour of solution at the end point in a titration, judgement of level of a liquid with respect to graduation on a burette or a pipette are sources of personal errors.

Determinate errors may also be classified into constant errors and proportional errors.

i) **Constant Errors:** The magnitude of constant error is independent of the size of the sample or size of the quantity that is being measured. It is also independent of the concentration of the substance being analysed. For example, in volumetric analysis, the excess of the titrant (say, 1 drop) that has to be added to bring about a change of colour at the end point remains the same whether we titrate 5 ml or 25 ml of the solution.

Relative error would increase five times if we use a 5 ml pipette in place of a 25 ml pipette, i.e., if we take 5 ml of the solution for titration in place of 25 ml of the solution.

It follows from the above that the effect of constant error can be reduced to minimum by increasing the size of the sample to maximum within the permissible limits.

ii) **Proportional Errors:** Proportional errors take place due to the presence of interfering impurities in the sample. The magnitude of such an error depends upon the fraction of the impurity and is independent of the size of the sample.

Correction of Determinate Errors: The determinate instrument errors are detected and corrected by periodic calibration of the instruments. We observe that response of most of the Instrument's changes with time because of wear, corrosion or mistreatment. A periodic calibration in therefore a must.

Determinate personal errors can be reduced to a minimum by. care and self discipline. It would be certainly desirable to develop a habit of checking instruments readings. Most important requisite of avoiding personal error is to keep away from pre-conceptions.

II) Indeterminate (Or) Random Errors:

These are random or accidental errors whose sources cannot be positively identified. As a result of these errors, the data from replicate measurements fluctuate randomly around the mean of the set. Most frequently, the deviation from the mean is verysmall. Also, there is almost equal probability of the occurrence of positive and negative errors with the result that overall magnitude of indeterminate errors becomes almost insignificant.

They can be classified into two classes:

i) Variations within Determinate Errors: A determinate error will arise when the knit-e edge of balance has become worn out. But when the errorvaries owing to load it becomes an indeterminate error.

Similarly, temperature changes and variation in humidity in a balance room give rise to determinate errorbut if they are not controlled, they become indeterminate.

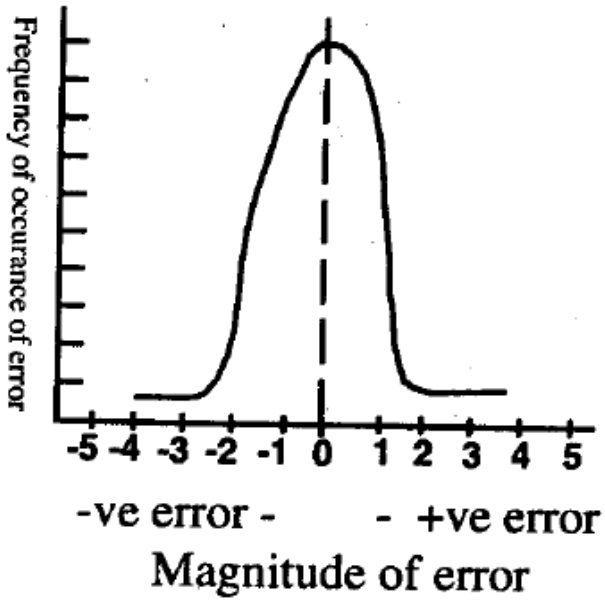
ii) Erratic Errors: It is very difficult to notice them.

a) Fluctuations in balance room can cause erratic errors in weighing.

b) Accidental loss of materials during analysis.

A numerical relationship exists between the magnitude of a random error and the frequency of its occurrence.

The relationship is shown in the figure below. This is known as Normal Distribution Curve.



A statistical analysis of random errors reveals that

a) Random errors of frequent occurrence are those of small magnitude.

b) large errors are not likely to occur at all.

c) Positive and negative differences are equally likely to occur.

The form of the error curve indicates the relative precision of the measurements made.

A narrow peaked curve with steep slopes indicates a relatively a high degree of precision. A broad curve indicates a relatively row degree of precision.

5.4 MINIMISATION OF ERRORS:

As discussed earlier determinate errors can be minimized by one of the following methods:

i) Calibration of apparatus and application of corrections.

ii) Running a blank determination.

iii) Running a control determination and correction canbe applied as

$$\frac{\text{Result for standard}}{\text{Result for unknown}} = \frac{\text{Weight of the constituent in standard}}{x}$$

Where 'x' is the constituent in the unknown.

The standards useful for this purpose are:

a) British chemical standards (BCS);

b) Bureau of analyticalsamples (BAS);

c) US Bureau of standards (US BS) and

d) Analytical samples for students. (ASS)

iv) Usingindependentmethodsofanalysis.

v) Running parallel determinations (precision).

vi) Standard addition methods.

vii) Isotopic dilution.

LESSON - 6

ACCURACY AND PRECISION

6.1 ACCURACY:

Accuracy of a measurement denotes closeness of an experimental value or the mean value of a set of measurements to the true value.

In other words, *it is the difference between the experimental value or the mean value of a set of measurements and the true value.*

Accuracy = Mean value - True value

We can say, smaller the difference between the mean value and the true value, larger is the accuracy.

Suppose a sample contains 20.50 per cent of sulphur. The chemical analysis of the sample by one method gives the mean value of 20.65 per cent of sulphur.

Then,

Accuracy of first method = 20.40 - 20.50 = 0.10% (Neglecting the negative sign)

Accuracy of second method = 20.65 - 20.50 = 0.15%

Thus, the first method gives more accurate determination of the percentage of sulphur than the second method.

However, it may be realised that in certain cases, the true value of a quantity is not known. In such cases, it becomes difficult to calculate the accuracy of the measurement. We measure precision of the measurement in such situations.

6.2 PRECISION:

The degree of agreement between two or more replicate measurements made on a sample in an identical manner is known as the precision of the measurement. Precision reflects the closeness among replicate measurements of the same quantity. For illustration, let us suppose that the percentages of an element in an alloy determined by one analyst are 2.63, 2.61 and 2.62 while those determined by another analyst are 2.70, 2.75, 2.80.

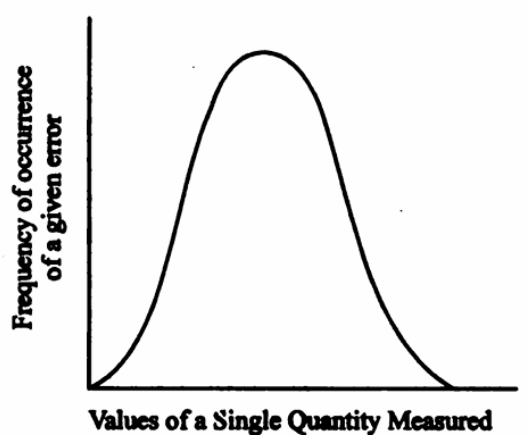


Fig 6.1: Error Distribution Curve

Evidently, the precision of the first set of results is better that of the second If we make a large number of observations of single quantity and then plot the number of times a given value occurs against the value of the quantity itself, we obtain a curve known as Error Distribution Curve as shown in Fig. 6.1

These curves have two useful qualitative features, viz., the height of the peak of the distribution curve and the spread of the distribution curve (also called dispersion).

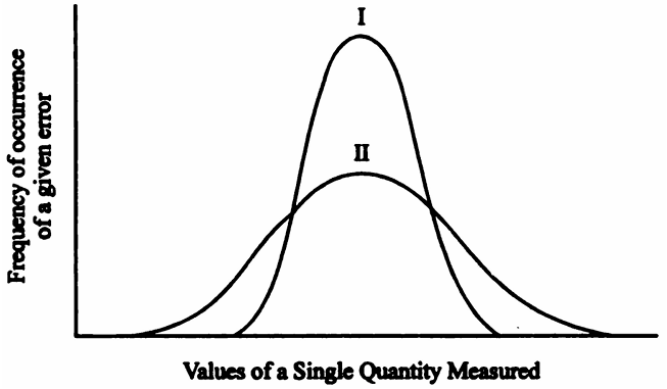


Fig. 6.2: Characteristics of Less Precise and more Precise Result

The precision of two sets of measurements of the same quantity can thus be easily compared with the help of their error distribution curves. Thus, in Fig. 6.2, the curve I with lesser spread and higher peak, is characteristic of more precise measurements as compared to the curve II which represents less precise measurement.

6.3 EXPRESSION OF ACCURACY - EXPLANATION:

For example, a volume of twenty five milli litres carefully measured in cylinder should not be expressed as 25.0 mL, as cylinder is graduated in a milli to estimate the fraction of such units closer than tenths of milli litres.

On the other hand, the same volume measured in a fifty milli litres burette may be expressed as 25.00 mL, ashere the apparatus is graduated directly in tenths of milli litres and the hundredth place is capable of possible estimation. The accuracy of measurement with burette is greater than with the graduated cylinder.

Likewise, a ten gram weight when measured on a side shelf balance may be expressed as 10.00 g but on analytical balance as 10.0000 g.

Thus, in each case, the accuracy of measurement is limited by the nature of the instrument used and the skill of the observer in making the observation.

The difference between the numerical values can be expressed asthe absolute difference or as the relative difference (generally relative difference will be expressed in parts per thousand. i.e. ppt)

For example: 3.042, 3.031 are two numerical values.

The absolute difference of these two values will be 0.011, while the relative difference will be

$$\frac{0.011}{3.042} X\ 1000 = 3.616\text{ppt}$$

Now, we know that absolute error of a determination is the difference between the observed or measured value and the true or most probable value.

In the case of above example, if 3.042 is regarded as the true value, the absolute error of the value 3.031is 0.011, the relative error is the absolute error divided by the true or most probable value. Thus, the relative error is 3.616 ppt. in the case of value 3.031.

Deviations in parts per thousand (ppt) may be readily computed between any two numbers of similar magnitude by comparison of such difference without regard to the decimal point.

Ex: The difference between 6.3 and 6.4 is

One part in about 64 (or)

1bn parts in about 640 (or)

100 parts in about 6400 (or)

$1\ x\frac{1000}{64}$ = 16 (15.625) ppt but it should be expressed as 16 ppt.

LESSON - 7

STATISTICAL APPROACH

The mean (or average) deviation or the relative mean deviation is a measure of the precision'

7.1 ARITHMETIC MEAN (OR) AVERAGE:

The mean is the numerical value obtained by dividing the sum of a set of measurements by the number of individual results in the set. It is also called the arithmetic mean or average.

Explanation:

Data	Individual deviations from average
0.973	0.001
0.976	0.002
0.971	0.003
0.975	0.001
Average = 3.895/4= 0.973	**0.007 =mean Deviation**

Thus, the mean 'm' is given by $m = \frac{\Sigma Mn}{n}$

Where, M is the individual measurement and n is the total number of measurements.

7.2 MEAN DEVIATION:

The agreement between a series of results is measured by computing their mean deviations. This is evaluated by determining the arithmetical mean of the results, then calculating the deviation of each individual measurement from the mean and finally dividing the sum of the deviations, regardless of the sign by the number of measurements.

The *relative mean deviation* is the mean deviation divided by the mean. This may be expressed in terms of percentage or in parts per thousand.

Example:

The percentages of a constituent Ain a compound AB were found to be 48.32, 48.36, 48.23, 48.11, 48.38 percent. Calculate the mean deviation and the relative mean deviation.

Results	**Deviations**
48.32	0.04
48.36	0.08
48.23	0.05
48.11	0.17
48.38	0.10
= 241.40/5 **Mean = 48.28**	**= Relative** Mean Deviation = **0.44/5** **Mean Deviation = 0.088**

Relative Mean Deviation = $\frac{0.088 \times 100}{48.28}$ = 0.1822 % = 1.8 parts per thousand (ppt)

If we consider a series of observations arranged in an ascending order of magnitude

$$x_1, x_2, x_3, \ldots x_{n-1}, x_n$$

The Arithmetic mean is given by $x = \frac{X1+X2+\cdots+Xn-1+Xn}{n}$

7.3 STANDARD DEVIATION:

The term standard deviation is commonly called in statistics as a measure of precision. This quantity is obtained by the summation of the squares of the individual deviations from the mean, dividing the sum by N-1 where N is the number of Measurements and then taking the square root. The standard deviation S is thus expressed mathematically as

$$S = \sqrt{\frac{\sum_{i=1}^{N} (x_i - \bar{x})^2}{N-1}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(i)}$$

The divisor (N-1), in fact, represents the degree of freedom for the set of N measurements. It indicates that there can be (N-1) independent deviations from the mean.

By definition, the mean x of the set N measurements is given by

$$\bar{x} = \sum_{i=1}^{N} x_i / N \qquad \text{.....(ii)}$$

Mathematically, the numerator under the square root in eq. (ii) may be expressed as follows:

$$\sum_{i=1}^{N} (x_i - \bar{x})^2 = \sum_{i=1}^{N} x_i^2 - \left(\sum_{i=1}^{N} x_i \right)^2 / N$$

Substituting this value in eq. (i),

$$S = \sqrt{\frac{\sum_{i=1}^{N} x_i^2 - \left(\sum_{i=1}^{N} x_i \right)^2 / N}{N-1}}$$

This equation is, more convenient to use than eq. (1).

For titrating 10 ml of a solution with the help of micro burette the volumes ofthe titrant used are 9.98, 9.99, 9.98, 9.95, 10.00 and 10.20 ml. Calculate the standard deviation.

Trial	x_i	x_i^2
1	9.98	99.6004
2	9.99	99.8001
3	9.98	99.6004
4	9.95	99.0025
5	10.00	100.0000

$$\Sigma x_i = 49.90,\ \Sigma x_i^2 = 498.0034$$

$$\frac{(\Sigma x_i)^2}{N} = \frac{(49.90)^2}{5} = 498.0020$$

$$S = \sqrt{\frac{498.0034 - 498.0020}{5-1}}$$

$$= \sqrt{\frac{.0014}{4}} = \sqrt{0.00035} = 0.0187$$

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LESSON - 8

ANALYSIS OF RESULTS

Analysis of results can be made by two different ways.

They are:

i) Comparison of results

ii) Reliability of results

Comparison of sets of values with either true value or with another set of values gives us the trick to determine whether the sets of values or the analytical procedure is accurate of precise. There are two common methods

a) Student's t -test

b) Variance ration test or F –test

8.1 The t –test or Student's t –test:

Student's t –test is used for small samples. It can also be used to test the difference between the mean of two sets of data's ($\bar{x_1}$ and $\bar{x_2}$). The purpose of the test is to compare the mean of samples with some standard value and to express some level of confidence in the significance of comparison.

The t –test is obtained as

One-Sample T-Test

$$t = \frac{\bar{x} - \mu}{\frac{s}{\sqrt{n}}}$$

$\bar{x}$ = obersved mean of the sample
μ = assumed mean
s = standard deviation
n = sample size

Two-Sample T-Test

$$t = \frac{(\bar{x}_1 - \bar{x}_2)}{\sqrt{\frac{s_1^2}{n_1} + \frac{s_2^2}{n_2}}}$$

$\bar{x}_1$ = observed mean of 1st sample
$\bar{x}_2$ = observed mean of 2nd sample
s_1 = standard deviation of 1st sample
s_2 = standard deviation of 2nd sample
n_1 = sample size of 1st sample
n_2 = sample size of 2nd sample

These calculated values are then compared with the sets of values obtained for different *probabilities and degree of freedom* from the given table 8.1.

(Degree of freedom: It may be defined as the number of individual observations that could be allowed to vary under the condition that $\bar{x}$and s, once determined, be held constant)

Table 8.1: Some Values of Students 't'

NUMBER OF OBSERVATIONS N	NUMBER OF DEGREES OF FREEDOM, N-1	PROBABILITY LEVELS t 50%	t 90%	t 95%	t 99%
2	1	1.000	6.314	12.706	63.66
3	2	0.816	2.920	4.303	9.925
4	3	0.765	2.353	3.182	5.841
5	4	0.741	2.132	2.776	4.604
6	5	0.727	2.015	2.571	4.032
7	6	0.718	1.943	2.447	3.707
8	7	0.711	1.895	2.365	3.500
9	8	0.706	1.860	2.306	3.355
10	9	0.703	1.833	2.262	3.250
11	10	0.700	1.812	2.228	3.169
21	20	0.687	1.725	2.086	2.845
μ	μ	0.674	1.645	1.960	2.576

may be found in statistical compilations.

Degree of freedom is one less than n, (n- l) the number of observations.

The values of 't' are given in **Table 8.2**

Confidence Interval of Mean:

By rearranging the equation of student's t test, we obtain the confidence interval of the mean, or confidence limits.

$$\pm t = (\bar{x} - \mu)\frac{\sqrt{n}}{s}$$

We obtain the confidence internal of the mean, or confidence limits.

$$\mu = \bar{x} \pm \frac{ts}{\sqrt{n}}$$

This equation may be used to estimate the probability, that the population mean μ, lies within a certain region, canteredat x, the experimental mean of measurements.

Value of 't' is essential for calculation confidence internal of mean.

It is observed that the't' values increase with decrease in 'n' values (or)'t' values decrease with increase in 'n' values.

This is reasonable, since the smaller 'n' becomes, the less information is available for estimating the population parameter. Increase in 't' exactly compensate for the lessing of information.

In some cases where analyses have been repeated extensively, a chemist may have a reliable estimate of the population standard deviation 'o'. In such case there is no uncertainty in the value of σ and the confidence interval is given by

$$\mu = \bar{x} \pm \frac{z\sigma}{\sqrt{n}}$$

where 'z' is simply the value of 't' at $n = \infty$

when $n = \infty$, then

$$\mu = \bar{x} \pm C_n \cdot \frac{\sigma}{\sqrt{n}}$$

$$= \bar{x} \pm 1.96 \frac{\sigma}{\sqrt{n}} \text{ for 95\% confidence}$$

and $\mu = \bar{x} \pm 2.58 \frac{\sigma}{\sqrt{n}}$ for 99% confidence

Precision of the Mean:

For mean x, of n measurements, the population mean m lies within the limits.

$$= \bar{x} \pm 1.96 \frac{\sigma}{\sqrt{x}} \text{ for 95\% confidence}$$

and $\mu = \bar{x} \pm 2.58 \frac{\sigma}{\sqrt{n}}$ for 99% confidence

It is possible to calculate a confidence interval from the range 'R' of a series of measurements using the relationship.

$$\mu = \bar{x} \pm C_n R$$

[Where 'R' is range that is difference between maximum value and minimum value. Example Range (R) of: 26.28, 26.33, 26.36, 26.24; R =26.36 -26.24=0. 12]

Values of C_n for various number of observations are based upon estimates of 's' obtained from the range.

Table 8.3

Some Values of C_n for Calculating Confidence Intervals from the Range

No. of observations	Probability Levels 95%	99%
2	6.353	31.828
3	1.304	3.008
4	0.717	1.316
5	0.507	0.843
6	0.399	0.628

Precision of Standard Deviation:

To obtain a measure of the precision of a standard deviation, we calculate a value 'q'.

$$q = \sqrt{\frac{s^2(n-1)}{n}} = \sqrt{\frac{\Sigma(x_i - \bar{x})^2}{n}}$$

Example: Ten replicate measurements of nitrogen in soil samples gave a mean of 0.1362% with a standard deviation of 0.0072%.Calculate the95% confidence interval of the mean and the standard deviation.

Answer: Degrees of freedom = 9

t value for 95% = 2.262 (from table)

(t-value will be given along with the question during examination)

$\bar{x} = 0.1362$

$s = 0.0072$

$\mu = \bar{x} \pm \frac{ts}{\sqrt{n}}$

The 95% confidence interval of the mean

$= 0.1362 \pm 2.262 \times \frac{0.0072}{\sqrt{10}}$

$= 0.1414$ to 0.1311

For standard deviation : $q = \frac{\sqrt{s^2(n-1)}}{n}$

$q = \sqrt{\frac{(0.0072)^2 .9}{10}} = 0.0068$

The 95% confidence interval for the standard deviation.

$= 0.0072 - (0.66 \times q)$ and $+(1.77 \times q)$

The values 0.66 and 1.77 are the values to be used with q for n degrees of freedom for various levels of the highest desity regions. (Whenever necessary such values will be given in the question paper)

$$= 0.0072 - (0.66 \times 0.0068) \text{ or}$$
$$= 0.0072 + (1.77 \times 0.0068)$$
$$= 0.0027 \text{ to } 0.0192$$

Criteria for rejection of an observation:

When one of the results in a set of replicate measurements seems to be out of line with others. Then one must be able to decide whether to exclude this result from further consideration or not.

The frequency will be lessened with experience and practice.

It is not correct to reject results which were subject to known errors when they appear to be not in agreement with others. The only way to avoid unconscious introduction of bias into the measurements is to reject every result where an error was known to be made regardless of its agreement with others.

When the number of replicate values is large, the question of rejecting one value is not an important one. 'Since first, a single value will have only a small effect upon the mean and second, statistical considerations give a clear answer regarding the probability that the suspected result is a member of the same population as others.

The real dilemma arises when the number of replicate measurements is too small. The divergent result exerts a significant effect on the mean.

But there will be insufficient data to present real statistical analysis.

However, the question of rejecting or retaining one divergent value from a small sample really cannot satisfactorily be answered.

It is to be just decided, how large the difference between the suspected result and the other data before the result is to be rejected (discarded).

If the minimum difference is made too small, valid data may be rejected too frequently. This is an error of first kind.

On the other hand, setting minimum difference too high leads to errors of second kind that is too frequent retention of highly erroneous values.

8.2 F - TEST:

This test is based on measurements of standard deviation, S. The various steps involved in this test are as follows:

i) Determination of standard deviation by employing the standard deviation S method. The standard deviation is determined with the following equation:

$$S = \sqrt{\frac{\Sigma (x_i - \bar{x})^2}{N-1}} \quad \text{..... (i)}$$

Where N - 1 gives the number of degrees of freedom which is less than the number N of the results. The value of N is sufficiently large. The deviation obtained by standard method is denoted by S_{std}.

ii) Determination of standard deviation by employing the newly developed method. The degree of freedom (or number of results) used in this determination is small, generally less than20. Let the standard deviation obtained by the new method be denoted by S_n.

iii) Determination of F-value with the help of the expression

$$F = S_{std.}^{\ 2} / S_n^{\ 2} \quad \text{..... (ii)}$$

The square of standard deviation is also known as variance.

iv) Tabulation of critical values of F determined statistically at appropriate levels of the confidence by extending the degrees of freedom (N value) to infinity both for the determination of S_{std} and S_n.

v) Comparison of the value of F as obtained from eq.(ii) with the critical value of F corresponding to N as infinity.

If the value of F < critical value, there is no significant difference in the precision of the new method and the standard method.

Test for Significance:

(i) Comparison of Two Means:

Suppose that a sample is analysed by two methods each being repeated several times and the mean values are different from each other. in such circumstances statistics cannot say which one is the right value.

It can only say whether the difference between the two values is significant or not. The statical approach to this problem is so called *null hypothesis.*

This hypothesis states in the present case that the two means are identifical. The test 't' gives yes or no answer to the correctness of null hypothesis with a certain confidence such as 95% to 99%.

Explanation:

Suppose a sample has been analysed by two different methods, yielding means $\bar{x}1$ and $\bar{x}2$ at and standard deviations s_1 and s_2, n_1 and n_2 are the number of individual results obtained by two methods.

The first step is to calculate 't' value using the formula.

$$t = \frac{|\bar{x}_1 - \bar{x}_2|}{s} \sqrt{\frac{n_1 n_2}{n_1 + n_2}}$$

Treating s_1 and s_2 as same which will be tested later. Then we have to go to table for 't' values at a degree of freedom ($n_1 + n_2 - 2$) and at desired probability level.

If the value of t, in the table is greater than the calculated 't' from the data, the null hypothesis is substantiated i.e. $\bar{x}1$ and $\bar{x}2$ and il are same with certain probability.

If 't' value in table is less than the calculated 't', we can say that null hypothesis is incorrect.

ii) Comparison of two standard deviations:

'F' test: (named after R.A. Fisher)

If s_1 and s_2 are really different, much more complicated procedure is to be used.

A test is available for deciding whether the difference between s_1 and s_2, is significant or not.

This is the variance-ratio test or F test. The procedure involves calculation of ratio of $S_1^2$and S_2^2.

$$\text{i.e. } F = \frac{s_1^2}{s_2^2} = \frac{v_1}{v_2}$$

V_1 and v_2 are variances placing the larger 's' value in the numerator such that F>1, then go to table of F values.

Table 8.4

F Values at the 95% Probability Level

n-1 for Smaller s^2	n-1 For Larger s^2					
	3	4	5	6	10	20
3	9.28	9.12	9.01	8.94	8.79	8.66
4	6.59	6.39	6.26	6.16	5.96	5.80
5	5.41	5.19	5.05	4.95	4.74	4.56
6	4.76	4.53	4.39	4.28	4.06	3.87
10	3.71	3.48	3.33	3.22	2.98	2.77
20	3.10	2.87	2.71	2.60	2.35	2.12

If the F value in table is less than the calculated F value then the two standard deviations are significantly different, otherwise they are not.

8.3 THE GAUSSIAN OR NORMAL DISTRIBUTION:

The Gaussian or normal distribution plays a central role in all of statistics and is the most ubiquitous distribution in all the sciences. Measurement errors, and in particular, instrumental errors are generally described by this probability distribution. Moreover, even in cases where its application is not strictly correct, the Gaussian often provides a good approximation to the true governing distribution.

The Gaussian is a continuous, symmetric distribution whose density is given by

$$P(x) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left(-\frac{(x-\mu)^2}{2\sigma^2}\right)$$

$$\mu = E[x] = \int x\, P(x)\, dx$$

$$\sigma^2 = E[(x-\mu)^2] = \int (x-\mu)^2\, P(x)\, dx$$

The two parameters μ and σ can be shown to correspond to the mean and variance of the distribution by applying the above equations.

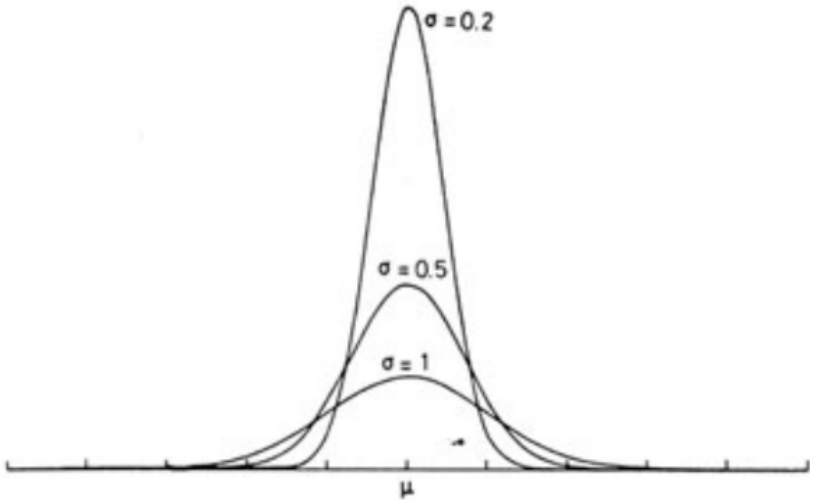


Fig. 8.1: The Gaussian distribution for various σ (sigma). The standard deviation determines the width of the distribution

The shape of the Gaussian is shown in Fig. 8.1 which illustrates this distribution for various σ. The significance of σ as a measure of the distribution width is clearly seen. As can be calculated from (19), the standard deviation corresponds to the half width of the peak at about 60% of the full height. In some applications, however, the full width at half maximum (FWHM) is often used instead. This is somewhat larger than and can easily be shown to be

$$\mathrm{FWHM} = 2\sigma\sqrt{2\ln 2} = 2.35\sigma$$

This is illustrated in Fig. 8.2. In such cases, care should be taken to be clear about which parameter is being used. Another width parameter which is also seen in the Literature is the full-width at one-tenth maximum (FWTM)

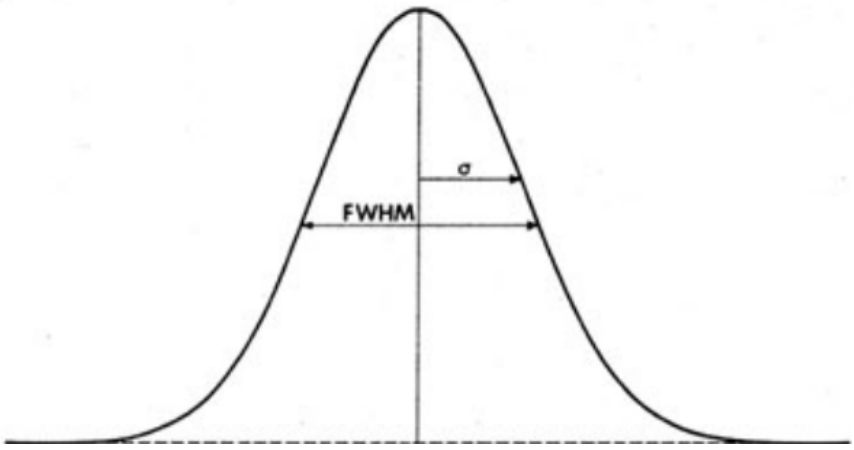


Fig. 8.2: Relation between the Standard Deviation a and the Full Width at Half-Maximum (FWHM)

The integral distribution for the Gaussian density, unfortunately, cannot be calculated analytically so that one must resort to numerical integration. Tables of integral values are readily found as well. These are tabulated in terms of a reduced Gaussian distribution with $\mu=0$ and $\sigma^2 = 1$. All Gaussian distributions may be transformed to this reduced form by making the variable transformation

$$z = \frac{x - \mu}{\sigma}$$

where μ andσ are the mean and standard deviation of the original distribution. It is a trivial matter then to verify that z is distributed as a reduced Gaussian.

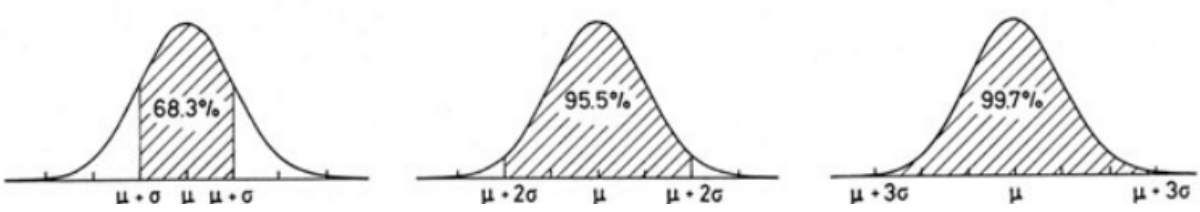


Fig. 8.3: The area contained between the limits μ ± 1 , μ ± 2 and μ ± 3 in a Gaussian distribution

An important practical note is the area under the Gaussian between integral intervals of σ. This is shown in figure 8.3. These values should be kept in mind when interpreting measurement errors. The presentation of a result as x ±σ signifies, in fact, that the true value has ≈ 68% probability of lying between the limits x - and x + or a 95% probability of lying between x-2σ and x + 2σ, etc. Note that for a 1σ interval, there is almost a 1/3 probability that the true value is outside these limits! If two standard deviations are taken, then, the probability of being outside is only ≈ 5%, etc.

LESSON - 9

REACTIVE INTERMEDIATES

9.1 REACTIVE INTERMEDIATES:

It was indicated earlier that organic reactions proceed step-wise. The step-wise process is known to take place through intermediates. The intermediates are usually very short-lived. They may not even be insoluble at times and detected by trap π ng experiments. Yet their study is important to have an overall idea of the complete nature of the reaction. Intermediates formed are prone to transform to stable molecules. The six types of intermediate carbon species are

a) Carbocations (Carbonium ions)

b) Carbon anions (Carbanions)

c) Carbine

d) Free radical

e) Nitrene

f) Benzyne

A glance at the structures of the above species brings to light the variation in the valency of carbon.

Nitrenes R-N are the analogues of carbenes.

In the coming pages an attempt is made to infuse into the minds of the students, the generation, structure stability and reactivity of the above-mentioned species.

9.2 CARBOCATION (OR) CARBONIUM IONS:

Suppose the bond C-X suffers a heterolytic cleavage to give a positively charged carbon residue. This carbon cation (1) is called carbonium ion. The remaining three valencies assume sp^2 hybridised state and the carbonium ion assumes a planar configuration (2).

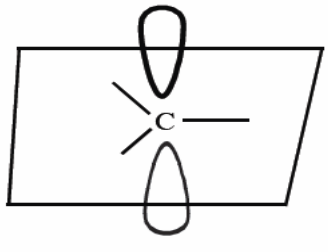
Formation of carbonium is unlikely if the planarity is prevented by structural or steric factors.

$$-C-X \rightarrow -C^{+} + X^{-}$$

(1)

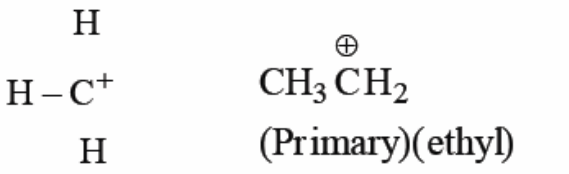
120^{o} C^{+} C –

(2)

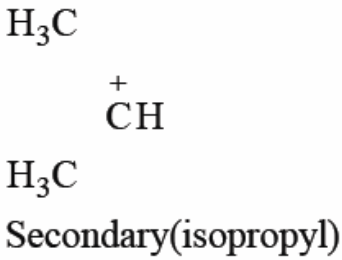


(2)

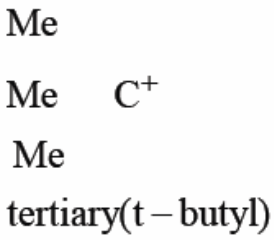
Following are some typical examples:



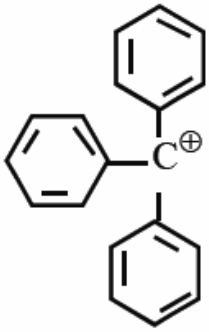
(Primary)(ethyl)



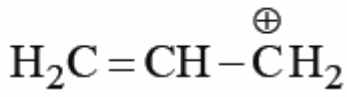
Secondary(isopropyl)



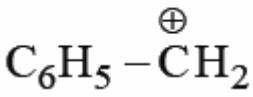
tertiary(t – butyl)



Triphenyl methyl



allyl



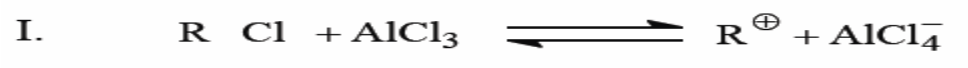
Benzyl

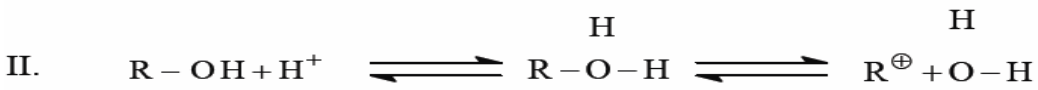
These carbonium ions are unstable, usually identified in solution half-life period around fraction of a second. Following is some of the crystalline salts.

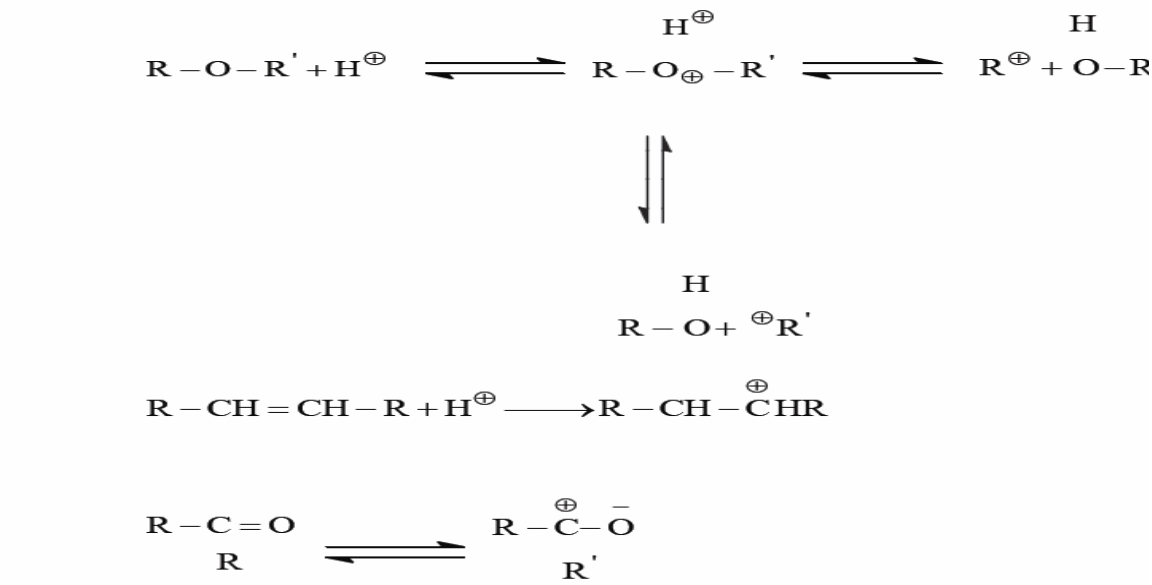
$$(C_6H_5)_3C^+AlCl_4^-,\ (C_6H_5)_3C^+ClO_4^-,(CH_3)_3C^+SbF_6^-$$

9.2.1 Generation:

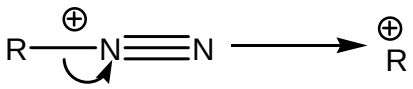
1) Alkyl halides, alcohols, ethers and unsaturated systems like olefins and carbonyl compounds are some of the sources.







2) By the decomposition of azo compounds gives carbocations at room temperature.



3) From alcohols

$$R\text{-}OH + H^+ \rightarrow R\text{-}OH_2^+ \rightarrow R^+$$

9.2.2 Structure of Carbocation:

The shape of a carbocation depends on the number of atoms attached to the positively charged carbon. Here's a breakdown:

1. Methyl Carbocation (CH_3^+) & Primary Carbocations ($R\text{-}CH_2^+$)

- Shape: Trigonal planar
- Hybridization: sp^2
- Bond Angles: ~120°
- Reason: The positively charged carbon has three sigma bonds and an empty p-orbital, making it adopt a planar structure to minimize electron repulsion.

2. Secondary Carbocations (R_2CH^+)

- Shape: Trigonal planar
- Hybridization: sp^2
- Bond Angles: ~120°

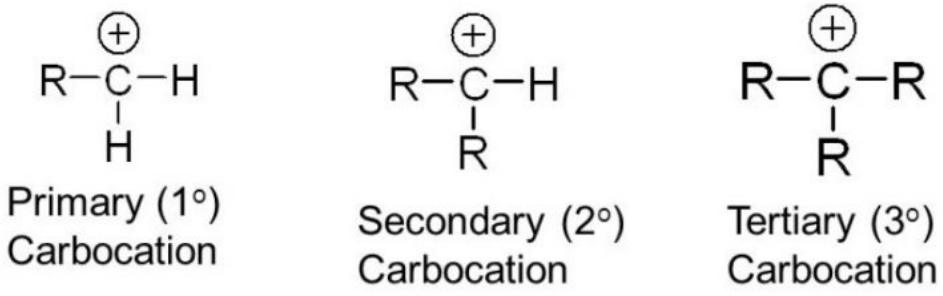
- Reason: Similar to primary carbocations, it maintains planarity due to the empty p-orbital.

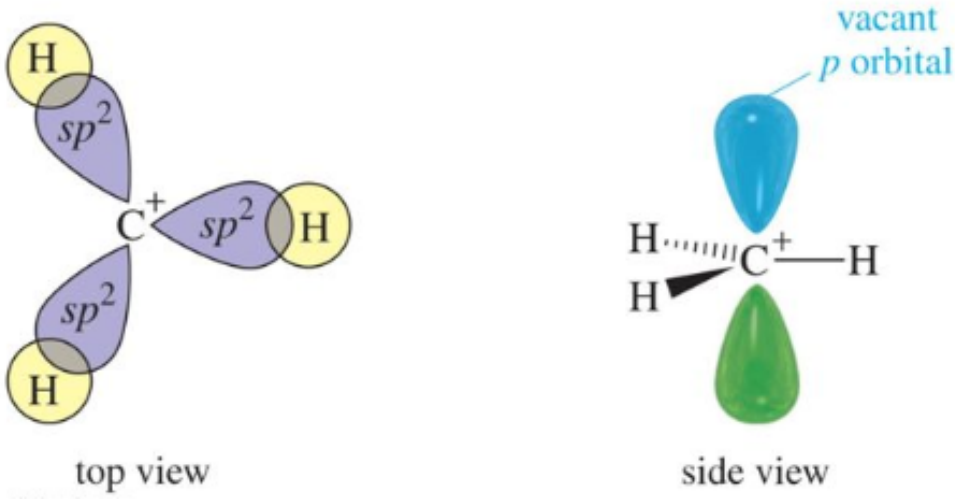
3. Tertiary Carbocations (R_3C^+)

- Shape: Trigonal planar
- Hybridization: sp^2
- Bond Angles: ~120°
- Reason: The carbon has three alkyl groups donating electron density via the inductive effect and hyperconjugation, but the planarity is maintained.

4. Non-Classical Carbocations (e.g., Norbornyl Cation)

- Shape: Bridged structure
- Hybridization: Delocalized bonding
- Reason: Some carbocations have delocalized electrons over multiple atoms, leading to a non-planar or bridged structure.





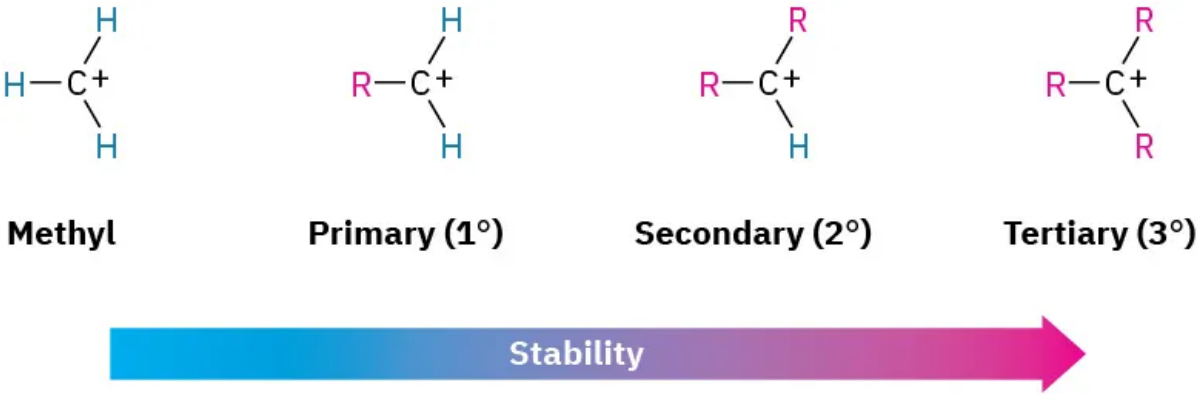
Shape of Carbocation

9.2.3 Stability:

The readiness with which a carbonium is formed depends on its stability. The stability in turn relates to its generation.

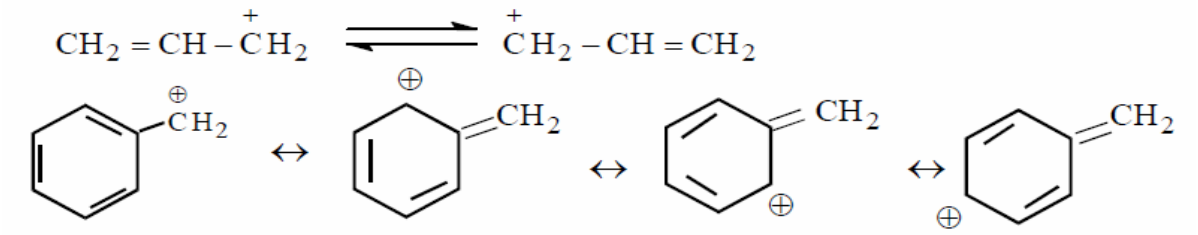
The relative rate of formation of carbonium ion as also its stability follows the order

tertiary > secondary > primary > CH_3



The resonance energies of *t*-butyl, *iso*propyl and ethyl carbonium ions are 84, 66 and 36 k.cal/mole respectively. Stability of t-butyl carbonium ion is attributed to the nine different possible hyper conjugation structures.

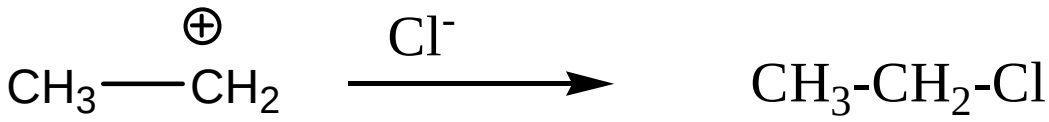
In allylic and benzylic cations, the charge on the carbon is quickly delocalised within the ion



Canonical forms of Benzylic Cations

Diaryl and triaryl methyl cations are more stable than the benzylic carbonium ions. Stability is further increased when the electron donating substituents are in *o*-or *p*-positions.

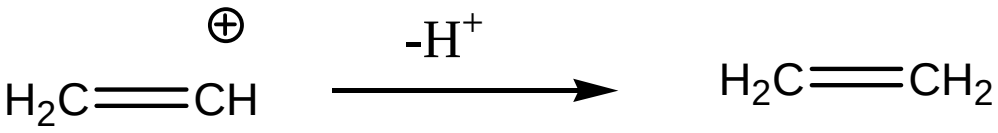
Hetero atoms like halogens, nitrogen, oxygen and sulphur lend the lone pair of electrons and stabilise the carbonium ion. In the process, a cyclic system arises.



9.2.4 Reactivity of Carbocations:

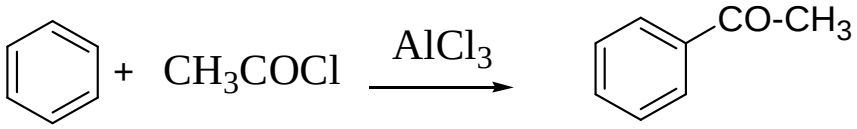
1) Nucleophilic Additions:

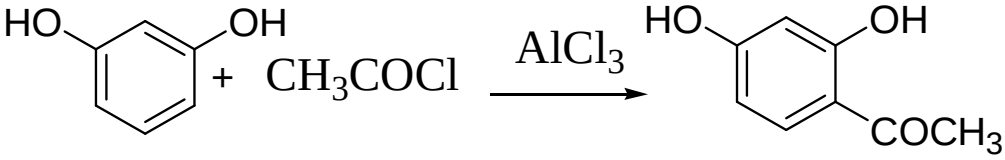
Carbocations which is electron deficient easily attacks nucleophile.



The α-carbon atoms must which contain one α-H atom.

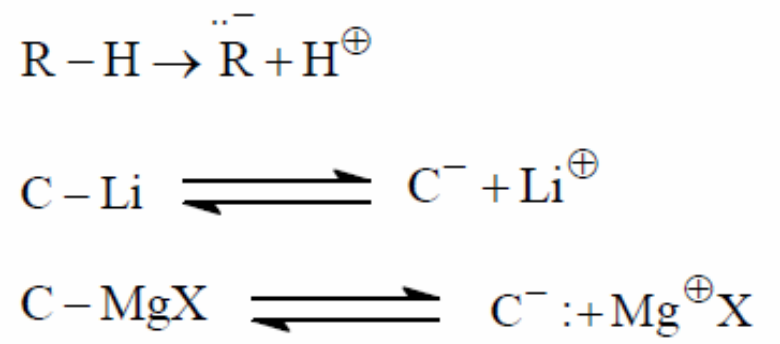
2) Friedel-Crafts reaction useful for introducing $COCH_3$ group in an aromatic ring (acylation) and alkyl group (alkylation).



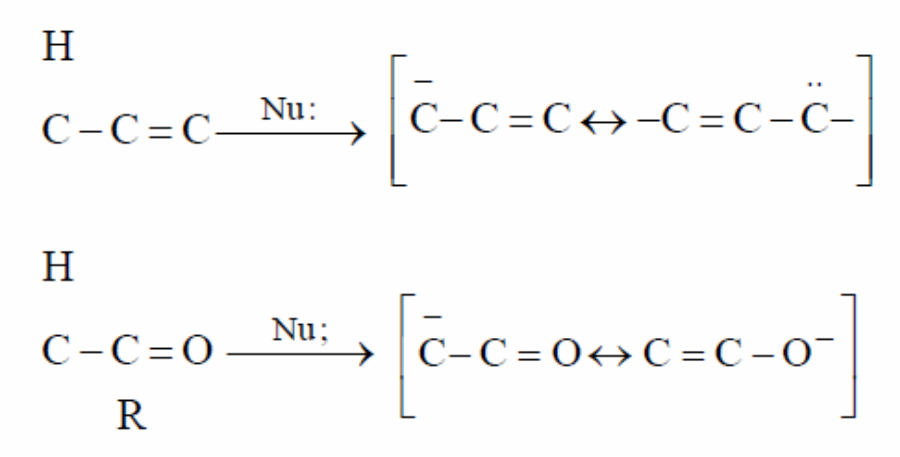


9.3 CARBANIONS:

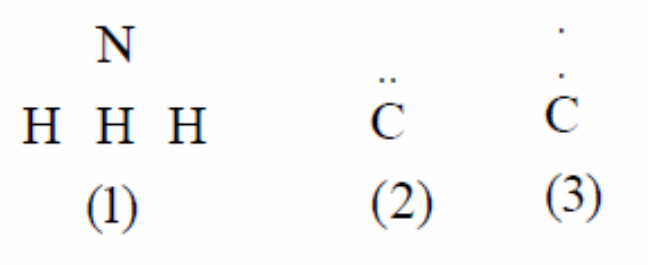
Carbanions are negatively charged ions. They possess an unshared pair of electrons and hence basic in nature. They are produced by the cleavage of carbon-hydrogen or carbon-metal bonds, (under the impact of a nucleophile) metal alkyls, Grignard reagents.



Loss of proton to a nucleophile (Nu:) from methyls of alkyl and carbonyl compounds results in the formation of carbanions.



Its molecular picture resembles that of ammonia (1). It assumes the formation of a pyramid. The central carbon is sp3 hybridised in its tetrahedral form. The unshared pair of electrons occupies one apex of the tetrahedron.



9.3.1 Generation of Carbanions:

Carbanion is an anionic species where a carbon atom has a negative charge, resulting from the gain of an electron or the loss of a proton. Carbanions are important intermediates in organic chemistry, particularly in nucleophilic reactions and organometallic chemistry.

Methods of Carbanion Generation:

1) Deprotonation of Hydrocarbons:

Carbanions are most commonly generated by removing a proton (H^+) from a carbon atom using a strong base. The stability of the carbanion depends on factors like resonance, inductive effects, and hybridization.

- **Using Strong Bases:**
  - Alkali metal amides (e.g., $NaNH_2$, LDA - lithium diisopropylamide)
  - Alkyl lithium reagents (e.g., n-BuLi, MeLi)
  - Grignard reagents (RMgX, although they are more nucleophilic than purely carbanionic)

Example:

$$CH_3C{\equiv}CH + NaNH_2 \rightarrow CH_3C{\equiv}C{-}Na^+ + NH_3$$

(Sodium acetylide formation)

2. Metal-Halogen Exchange Reactions:

A carbanion-like species can be generated by reacting an organohalide (R-X) with an alkali metal such as lithium or magnesium.

Example: $R{-}Br + 2Li \rightarrow R{-}Li^+$

(Formation of an organolithium reagent)

3. Reduction of Organic Compounds:

Certain organic compounds can be reduced to generate carbanions.

- **Reduction with Sodium in Liquid Ammonia (Birch Reduction)**
  - Used for aromatic ring reduction or alkyne transformations.
- **Reduction of Carbonyl Compounds**
  - Organometallic reductions can lead to enolate anions, which are resonance-stabilized carbanions.

4. Decarboxylation of Carboxylates

Carbanions can also be generated by decarboxylation (loss of CO_2) from carboxylate salts**.**

Example: $R{-}COO^- \rightarrow R^- + CO_2$

5. α-Deprotonation of Carbonyl Compounds (Enolate Formation)

Ketones, aldehydes, and esters can form carbanionic enolates when treated with a base.

Example: $\mathbf{CH_3COCH_3 + LDA \rightarrow CH_2^-COCH_3 + LDAH}$

9.3.2 Factors Affecting Carbanion Stability:

1) Resonance: Delocalization stabilizes the negative charge.
2) Inductive Effect: Electronegative groups (e.g., $-NO_2$, -CN) increase stability.
3) Hybridization: sp-hybridized carbanions (e.g., alkynyl anions) are more stable than sp^3.

4) Solvation Effects: Polar solvents stabilize carbanions through solvation.

Carbanions play a crucial role in organic synthesis, particularly in nucleophilic substitution (SN^2), aldol reactions, and organometallic reactions.

9.3.3 Structure of Carbanion:

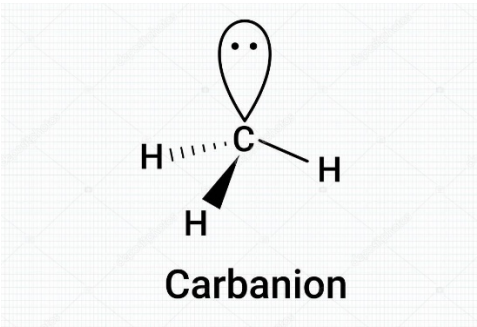
A carbanion is an anion in which a carbon atom bears a negative charge. It is typically formed when a carbon atom gains an extra electron, making it negatively charged.

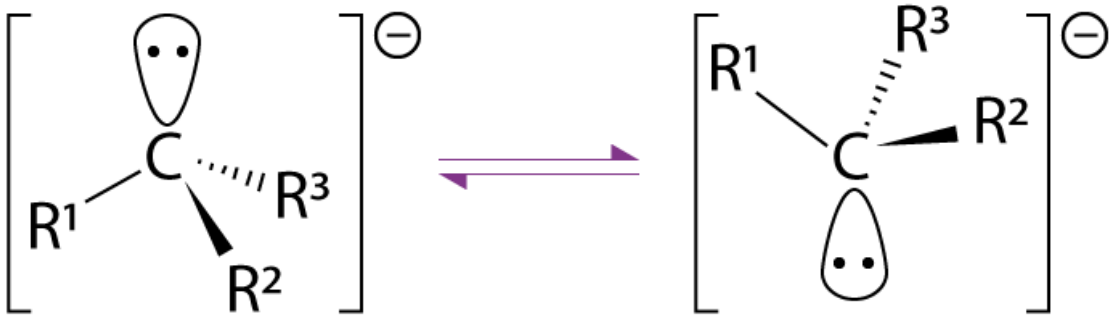
Structure of Carbanion:

1) **Geometry:**
   - A carbanion adopts a trigonal pyramidal geometry due to the presence of a lone pair on the negatively charged carbon.
   - This structure is similar to ammonia (NH_3) because both have a lone pair, causing sp^3 hybridization with a tetrahedral electron geometry but a pyramidal molecular shape.
2) **Hybridization:**
   - The negatively charged carbon in a carbanion is usually sp^3 hybridized.
   - However, in some cases (e.g., vinyl or aryl carbanions), the carbanion may exhibit sp^2 hybridization due to resonance.
3) **Bond Angle:**
   - The bond angle in a carbanion is slightly less than 109.5° (typical of sp^3 hybridization) due to lone pair-bond pair repulsion, which pushes the bonded atoms closer together.
4) **Stability Factors:**
   - Inductive Effect: Electron-withdrawing groups stabilize the negative charge by dispersing it.
   - Resonance: If the negative charge is delocalized (e.g., in benzyl or allyl carbanions), the structure is more stable.
   - Hybridization: Carbanions with sp^2 or sp hybridization are more stable than sp^3 due to increased s-character, which holds the negative charge closer to the nucleus.

Examples of Carbanions:

- Methyl Carbanion (CH_3^-) → Highly reactive due to lack of stabilization.
- Benzyl Carbanion ($C_6H_5CH_2^-$) → Stabilized by resonance.
- Allyl Carbanion ($CH_2=CH-CH_2^-$) → Stabilized by resonance.





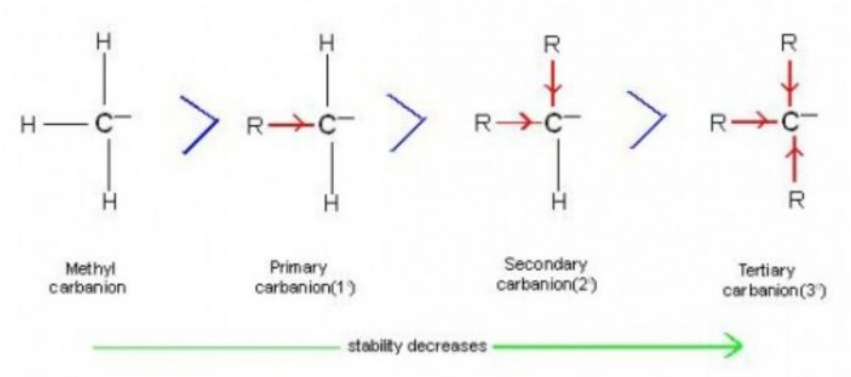
Structure of Carbanion

9.3.4 Stability:

More reactive unsaturated group such as carbonyl, nitrile etc. activate adjacent C-H bonds by higher conjugation. carbanions derived from them are more stable than those derived from the alkyl group.

The stability order among alkyl carbanions is

methyl > ethyl > isopropyl > t-butyl.



With the increase of electron donating alkyl groups -ve charge on carbanion increases thereby decreasing the stability.

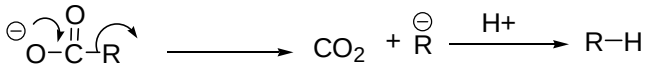
If the carbanion is in conjugation with carbon-oxygen or carbon-nitrogen multiple bonds, the stability would be even more. This is obviously influenced adversely if carbonyl is attained to an electron releasing group and the case of formation of carbanion decreases in the order aldehydes ketones esters and free carboxylic acids.

In compounds where the methylene group is flanked by two polar groups such as malonic eser, acetoacetic ester, cyanoacetic ester, cyclic diones such as cyclopentadiene etc, the carbanion formed is a resonance hybrid of three or more forms and hence possess greater stability.

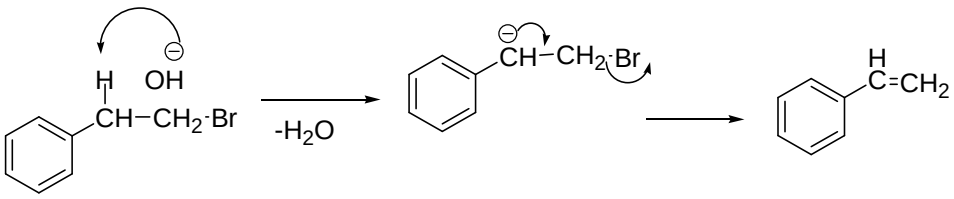
9.3.5 Reactions of Carbanions:

Carbanions are reactive nucleophiles. They take part in nucleophilic displacements.

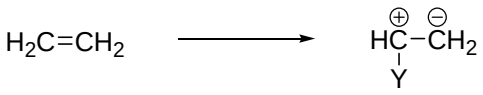
1. Carbanions undergo Nucleophilic addition reactions at multiple bonds. Carbonyls give more preferrable because O^- acts as nucleophile.



2. Elimination reactions: On ethyl phenyl bromide on dehydrogenation followed by dehalogenation to form styrene.



3. Polymerization:



Further several Additions and rearrangements reactions are followed with carbanion intermediate. Those are:

a) Aldol condensation

b) Perkins reaction

c) Claisen condensation and related types

d) Michael addition

e) Knoevenagel reaction etc.

Rearrangements:

a) Stevens,

b) Wittig,

c) Favorskie,

d) Sommelet rearrangements etc.

Dr. K. Chandra Mohan

LESSON - 10

FREE RADICALS

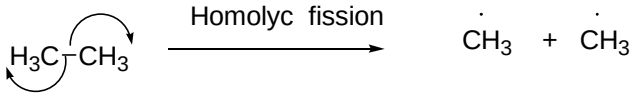
10.1 FREE RADICALS:

When a bond is broken homolytically, each fragment carries one electron called free-radicals or radicals in short. They are unstable and reactive. The weak bonds like O-O as in organic peroxides or C-C bonds influenced by steric factors are vulnerable for this type of fission.

$$A - B \rightarrow A^{\circ} + {}^{\circ} B$$

$$- O - O - \rightarrow - O^{\circ} + {}^{\circ} O -$$

$$C - C \rightarrow C^{\cdot} + C^{\cdot} -$$



The term Free radical used for Spectroscopy which being unpaired e^{-}s.

Characteristics of Free Radicals:

- Possess an unpaired electron, making them unstable and highly reactive.
- Can form as intermediate species in chemical reactions.
- React quickly with other molecules to achieve stability.

Formation of Free Radicals:

Free radicals can be formed through various natural and artificial processes, including:

1) **Biological Processes:**
   - Cellular respiration
   - Immune responses
2) **Environmental Factors:**
   - UV radiation
   - Pollution and cigarette smoke

3) Chemical Reactions:

- Breakdown of peroxides
- High-energy reactions in combustion

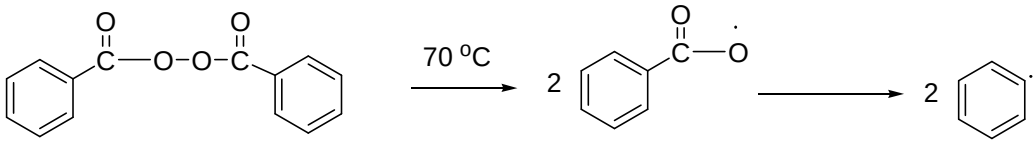
10.1.1 Generation of Free Radicals in Organic Reactions:

Free radicals can be generated through various methods, depending on the reaction conditions and the desired outcome. The primary ways of generating free radicals include:

1) Homolytic Bond Cleavage (Homolysis):

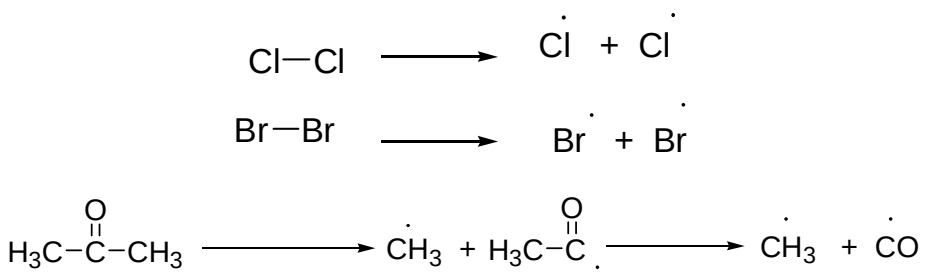
Homolytic cleavage occurs when a covalent bond breaks evenly, with each fragment retaining one electron. This process is usually facilitated by heat (thermal initiation) or light (photochemical initiation).

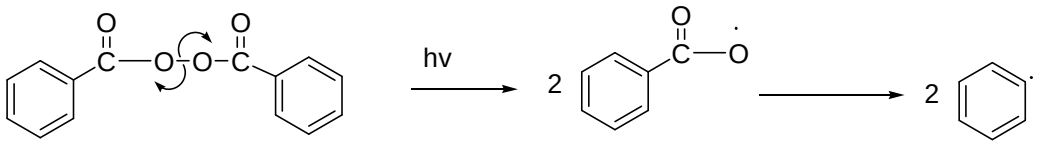
- **Thermal Initiation:**
  - High temperatures provide the necessary energy to break bonds homolytically.
  - Example: Decomposition of diacyl peroxides (Benzyl Peroxides) to generate acyloxy radicals.



Benzyl Peroxide
(Diacyl peroxides)

- **Photochemical Initiation:**
  - UV light or visible light can break bonds, forming radicals.
  - Example: The photo dissociation of halogens (e.g., $Cl_2 \rightarrow 2Cl\bullet$) in halogenation reactions.





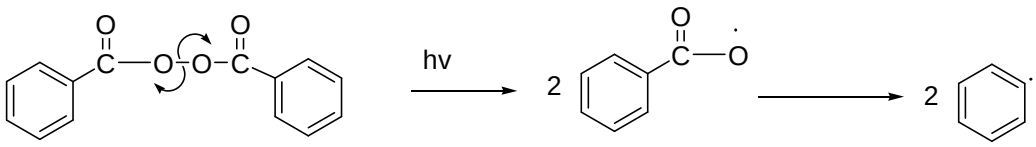
Benzyl Peroxide
(Diacyl peroxides)

2. Radical Initiators:

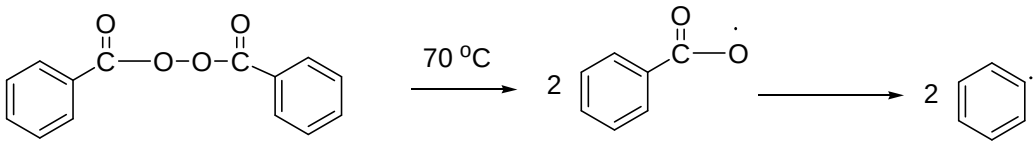
Certain compounds decompose easily to generate radicals and are used as initiators in radical reactions.

- **Peroxides (R-O-O-R):**

Example: Benzoyl peroxide decomposes to benzoyl radicals



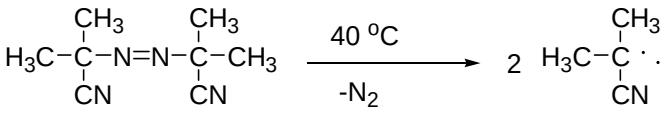
Benzyl Peroxide
(Diacyl peroxides)



Benzyl Peroxide
(Diacyl peroxides)

- **Azo Compounds (R-N=N-R'):**

Example: Azobisisobutyronitrile (AIBN) decomposes to form isobutyronitrile radicals.



Azabisisobutyro Nitrile
(AIBN)

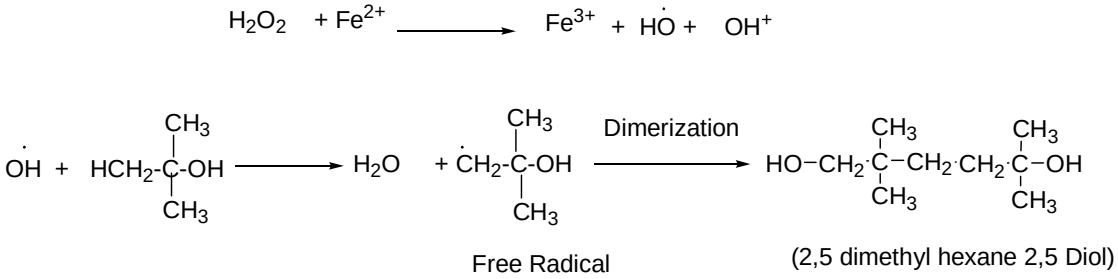
Isobutyro Nitrile radicals

3. Redox Reactions:

Radicals can also form through electron transfer processes in redox reactions.

- **Metal-catalyzed Radical Generation:**
    - Transition metals (Fe^{2+}, Cu^{+}) can reduce peroxides or halides to form radicals.

Example: Fenton's reagent (Fe^{2+}/H_2O_2) produces hydroxyl radicals.



Electrochemical Reduction:

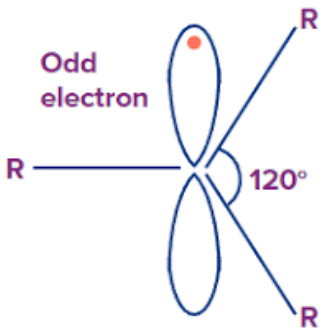
- Involves applying an electric current to reduce molecules and form radicals.

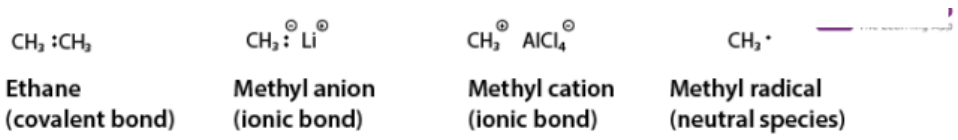
4. Reactions with Radical Chain Propagation

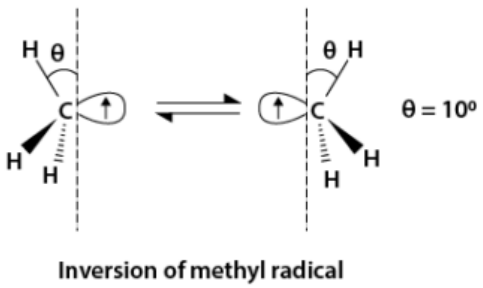
Once radicals are formed, they participate in chain reactions, which include three stages:

1) **Initiation:** Formation of free radicals.
2) **Propagation:** Radicals react with stable molecules, creating new radicals.
3) **Termination**: Two radicals combine, forming a stable product and ending the reaction.

10.1.2 Structure of Free Radicals:







Inversion of methyl radical

Free radicals are atoms, molecules, or ions that contain an unpaired electron, making them highly reactive. Their structure depends on the type of free radical and the nature of the atom or molecule involved.

1. General Characteristics of Free Radicals:

- Contain an odd number of electrons
- Typically formed by homolytic bond cleavage
- Highly reactive and unstable
- Can exist in different hybridization states (sp^3, sp^2, sp)

2. Geometry and Hybridization of Free Radicals:

Type of Radical	Example	Hybridization	Geometry
Alkyl Radicals	CH_3• (Methyl radical)	sp^2 (partial sp^3 character)	Trigonal planar/slightly pyramidal
Aryl Radicals	C_6H_5• (Phenyl radical)	sp^2	Planar
Vinyl Radicals	CH_2=CH•	sp^2	Planar
Acyl Radicals	CH_3CO•	sp^2	Planar
Oxygen Radicals	OH• (Hydroxyl radical)	sp^2	Bent

3. Structural Explanation:

- Alkyl Radicals: The carbon radical is mostly sp^2 hybridized, with slight pyramidal distortion due to repulsion from the unpaired electron.
- Aryl Radicals: Highly stabilized by resonance; the unpaired electron is delocalized across the benzene ring.
- Vinyl Radicals: The unpaired electron remains localized on the sp^2-hybridized carbon, making it less stable.
- Oxygen-based Radicals: Such as hydroxyl (OH•) and superoxide ($O_2^{\bullet -}$), have different bond angles due to oxygen's lone pairs.

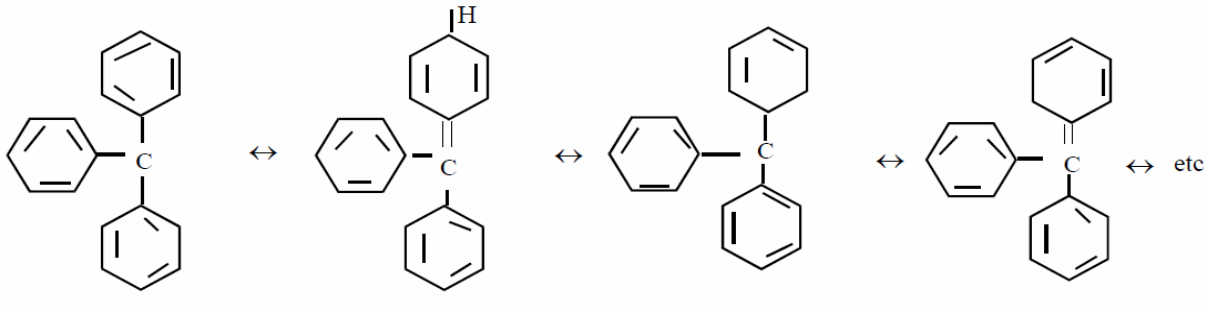
10.1.3 Stability:

The stability of free radicals follows this order:

Benzyl > Allyl > 3° (tertiary) > 2° (secondary) > 1° (primary) > Methyl

- Resonance and hyperconjugation increase stability.
- Inductive effects play a role in radical stabilization.

As in carbonium ions and cations, the radicals are also stabilised through extensive delocalisation of the free electrons. Thus, triphenyl methyl radial is greatly stabilised by resonance [*note:* 9 resonance structures can be drawn (as in the accompanying structures)].

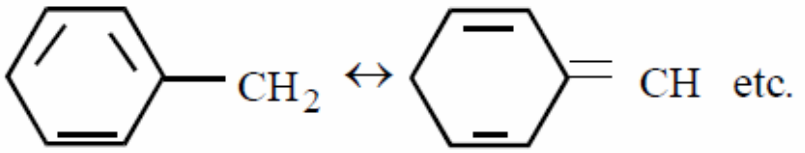


In the case of methyl or ethyl radicals, delocalisation is not feasible hence less stable and thereby dimerise to form stable products.

The higher the bond dissociation energy value less stable the radical R will be. The D value for the bond CH_3 H is 102 K.cal/mole at 25 ^oC while that of $(C_6H_5)_3$ C $C(C_6H_5)_3$ is 11 k.cal/mole.

The stability of allyl and benzyl free radicals over simple alkyl radicals is also attributed to resonance.

$$CH_2 = CH - CH_2 \leftrightarrow CH - CH = CH_2$$



Structure simple allyl radicals might have sp^2 or sp^3 bonding. In the former, the radical has a planar structure with the odd electron in the p-orbital. In the latter, the radical can assume a pyramidal structure with the odd electron in a sp^3 orbital. Further proof for the

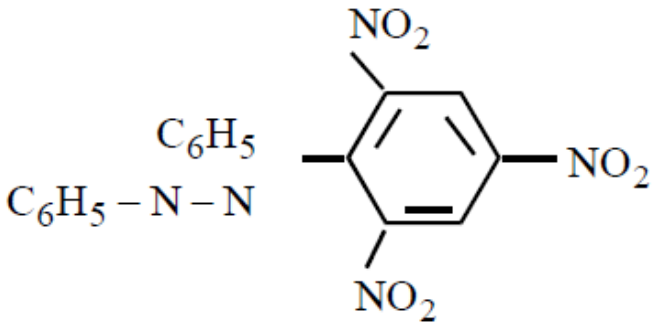
planar structure was obtained from kinetic evidence from iodine exchange reaction and the evidence from the ESR spectra. In short simple alkyl free-radicals prefer planar structure. The radicals are which the carbon is connected to atoms of high electronegativity.

Ex: CF_3 radical prefer pyramidal shape.

Electron with drawing groups like $-NO_2$ in a phenyl cause powerful delocalisation generating stable free-radicals with long life.

Some radicals, in which the unpaired electron is on a heteroatom are still more stable.

Ex: Diphenyl picryl hydrazyl (DPPH) is a solid that can be kept for several years.



10.1.4 Reactions of Free Radical:

1) Halogenation of Alkanes (e.g., Chlorination of Methane)
   - $CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$ (via a radical mechanism)
2) Polymerization of Alkenes
   - Initiated by radical initiators like benzoyl peroxide.
3) Radical Addition Reactions
   a. Example: Anti-Markovnikov addition of HBr to alkenes in the presence of peroxides.
4) Recombination

   The free alkyl radicals may recombine to form hydrocarbons.

$$CH_3^{\cdot} + CH_3^{\cdot} \rightarrow CH_3\text{-}CH_3$$

Methyl radical Ethane

$$2CH_3\text{-}CH_2^{\cdot} \rightarrow CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_3$$

Ethyl radical Butane

5) Reaction with Olefines

The alkyl radicals react with olefines to form a new free radical.

$$CH_3^{\cdot} + CH_2=CH_2 \rightarrow CH_3\text{-}CH_2\text{-}CH_2^{\cdot}$$

The newly formed free radical further adds onto another molecule of olefin.

$$CH_3\text{-}CH_2\text{-}CH_2^{\cdot} + CH_2=CH_2 \rightarrow CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2^{\cdot}$$

10.2 CARBENES:

Carbenes are highly reactive Parent species methylene is a short lived and bivalent carbon compound.

Types of Carbenes:

It exists in two different forms, spectrally designated as singlet and triplet methylenes.

1) **Singlet Carbene** – The two nonbonded electrons are paired (sp^2 hybridized, bent structure).
2) **Triplet Carbene** – The two nonbonded electrons are unpaired (sp hybridized, linear structure).

They have the general formula **R–C:–R'**, where the carbon is divalent (has a valency of two) and has a formal charge of zero.

10.2.1 Generation of Carbenes:

Carbenes can be generated through:

1) Thermal or photochemical decomposition of diazo compounds

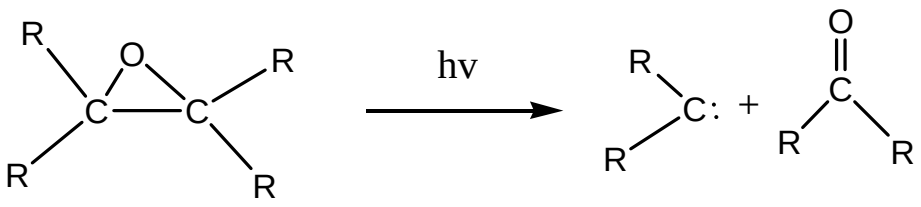
$$R_2C=N_2 \rightarrow R_2C: + N_2$$

2) Alpha elimination of haloforms

$$CHX_3 + \text{Strong base} \rightarrow C: HX + X^-$$

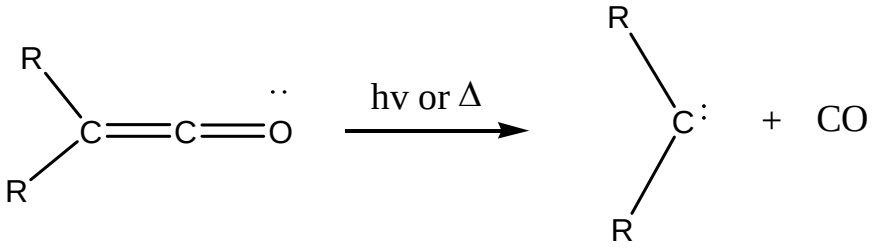
3) From epoxides

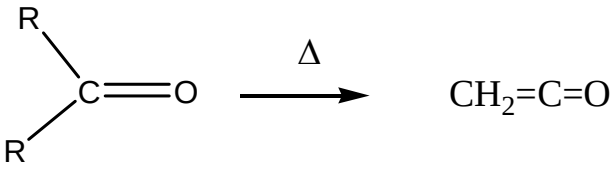
Photolytic decomposition epoxides generate carbenes.



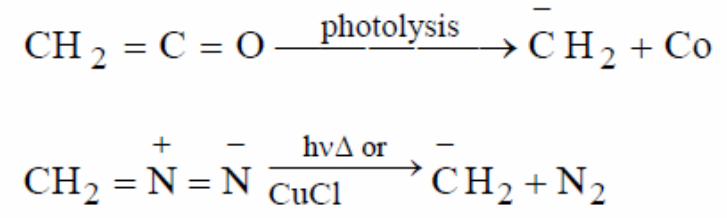
4) From ketenes

Ketenes are decomposed thermally of photochemically to generate carbenes.





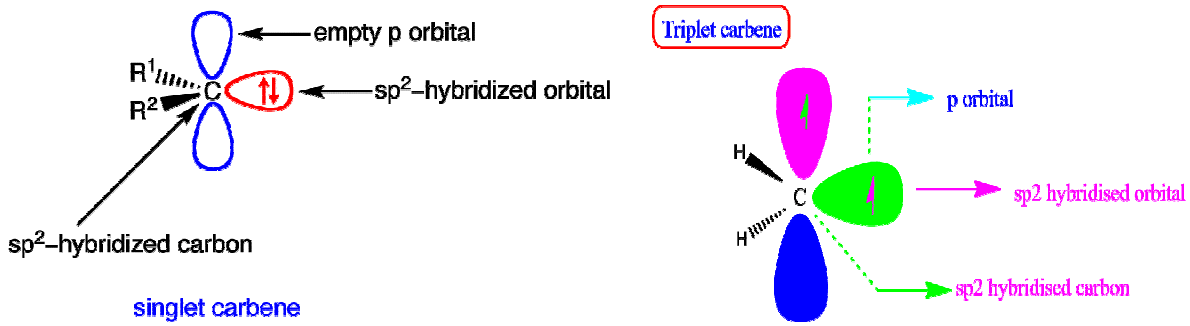
Depending on how the carbenes are generated, some of them react as singlets, some as triplets and some others as singlets or triplets. The triplet is more stable than the singlet by about 20 K.cal/mole^{-1}. Disintegration of compounds like ketones and diazomethanes give carbenes.



10.2.2 Structure of Carbene:

Carbenes exists as singlet or triplet.

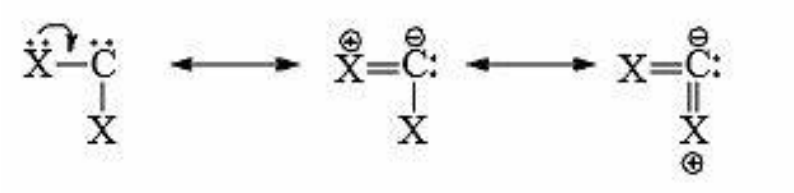
The carbene is singlet having antiparallel spin & there is no magnetic moment. The 2 electrons in different orbits, they have parallel spins (unpaired) & it having magnetic moment (triplet)



In singlet state the 'C' atom is sp2 hybridized two of sp2 hybrid orbitals are bonded to 2H atoms and 3rd contains a lone pair of electrons, which is diamagnetic in nature. The unhybrid p orbital is parallel to the plane. The bond angle is 130^o & C-H bond length is 1.12 A^o. In triplet carbene the C' atom is SP hybridized. The 2 sp hybrid orbitals are bonded to 2H atoms & 2 unhybridized p-orbitals having one electron. The carbene having bent shape with the bond angle od 136^o & C-H bond length 1.03 A^o which is paramagnetic in nature.

Stability:

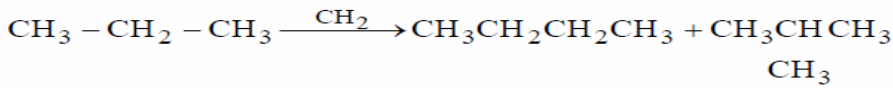
Carbenes in which 'C' attached to 2 atoms having lone pair of electrons are more stable due to resonance.



10.2.3 Reactions of Carbenes:

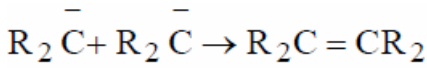
Carbenes are unstable but very reactive intermediate.

1) Insertion reaction occur mainly in the C- H bonds and have little relevance since a mixture of products formed.



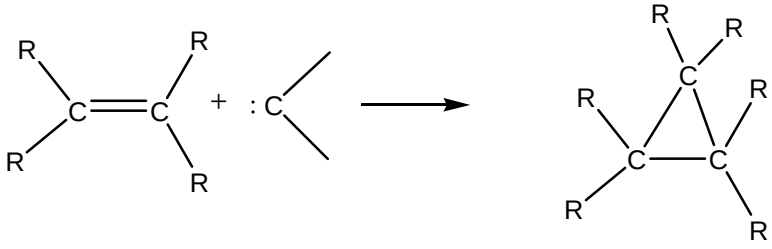
Dihalo carbenes, however, do not give insertion reaction and are used to formylate aromatic rings. Riemer-Tiemann reaction is a very good example.

2) Dimerize:



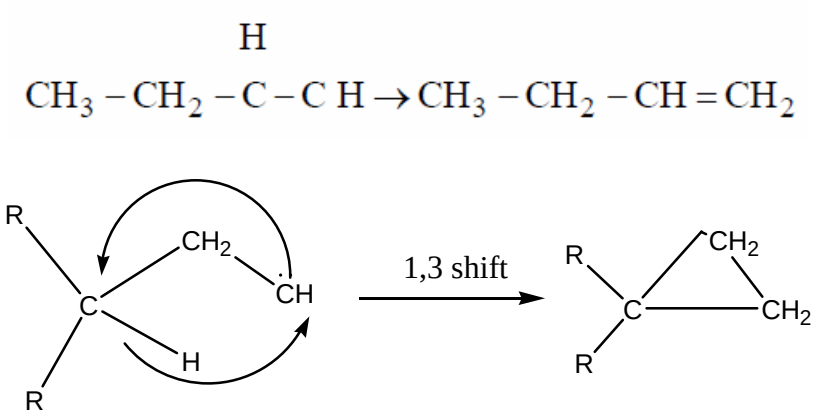
3) **Cycloaddition Reactions** – Carbenes react with alkenes to form cyclopropanes.

Carbenes used for ring expansion.



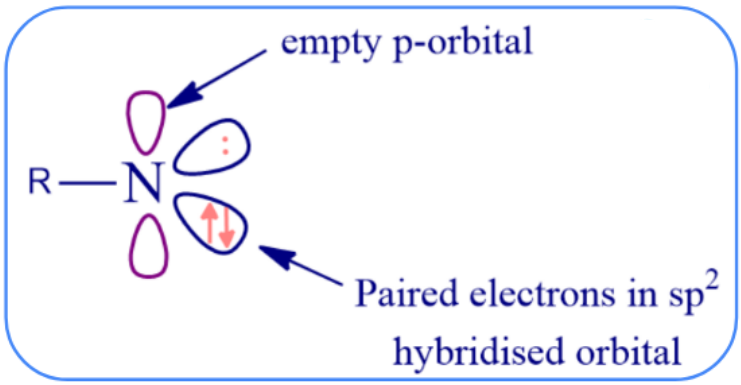
cyclopropyl derivative

4) Rearrangement: Alkyl carbenes undergo rearrangement.

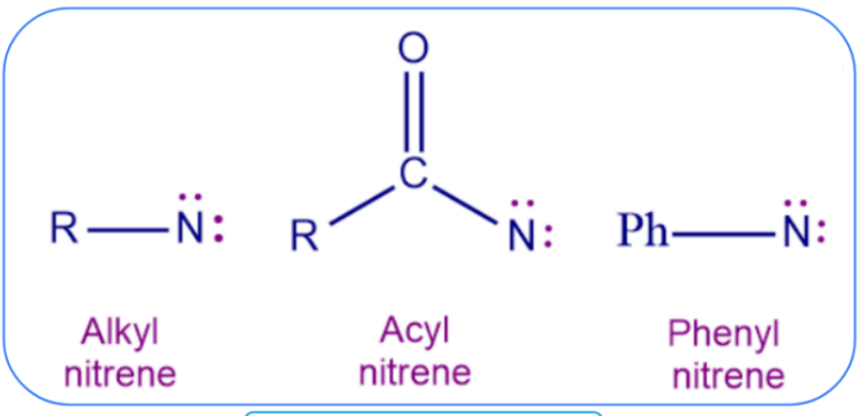


10.3 NITRENES:

The species that can exist with sextet of electrons on a nitrogen atom are called nitrenes. They are the nitrogen analogues (R-N) of carbenes. They are too reactive to be isolated under ordinary condition nitrenes can be generated in singlet $(R\text{-}N)^{*}$ and triplet states $(R\text{-}N)^{*3}$.



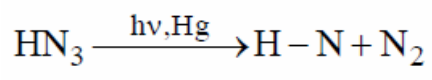
Singlet Nitrene



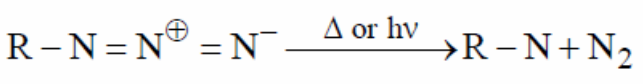
Common nitrene derivatives

10.3.1 Generation:

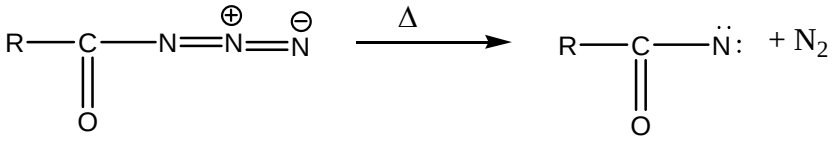
1. Photolysis of hydrazoic acid.



2. Pyrolytic or thermal decomposition of azides.

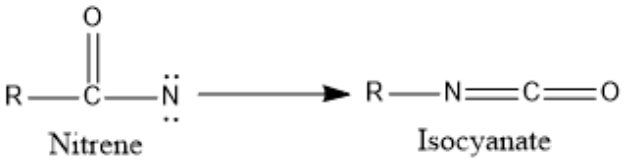


3. Decomposition of acyl azides to acyl nitrenes.

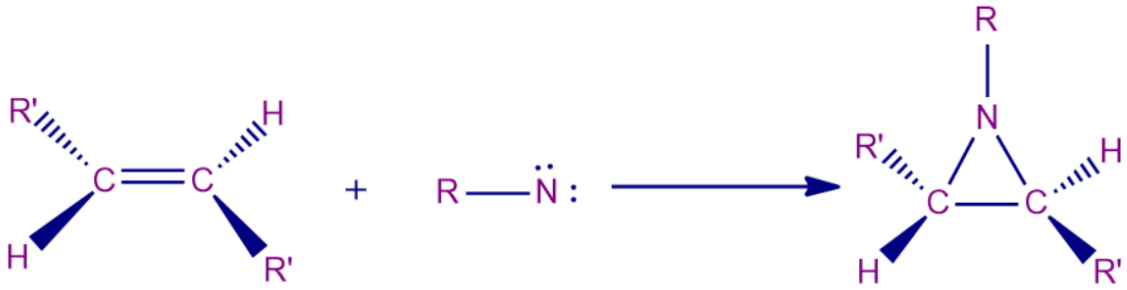


10.3.2 Stability:

Nitrenes are very reactive species and can't be isolated.



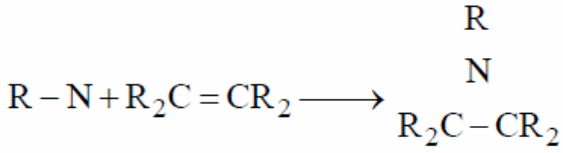
Nitrenes also trapped in presence of ethylene.



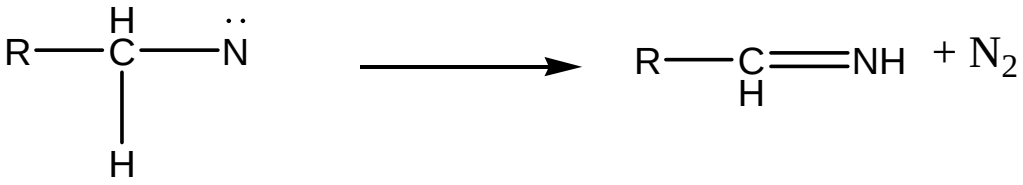
10.3.3 Reactions are like Nitrenes:

1. Addition to C=C bonds

Like carbenes undergoes addition with C=C bond is stereospecific with singlet & non-stereospecific with triplet nitrenes.



2. Rearrangement: In the case of alkyl nitrene, the rearrangement is very rapid and the formation of Nitrene and migration are simultaneous.



3. Dimerization: Formation of azobenzene from aryl nitrenes.

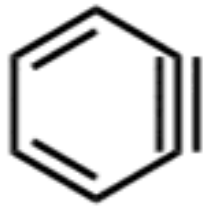
$$2Ar-N\longrightarrow ArN=NAr$$

Nitrenes can also add to aromatic rings to give expansion products (as in carbenes). Schmidt degradation and curtius, Hofmann, Neber rearrangements proceed through nitrene intermediates.

10.4 BENZYNE:

In recent years, the interpretation of the rearrangements which sometimes occur in substitution reactions of non-activated aromatic halides with strong bases has gone through such a cycle. A rationalization of the pattern for this type of rearrangement was provided by postulation of an elimination-addition mechanism involving 'benzyne' intermediates.

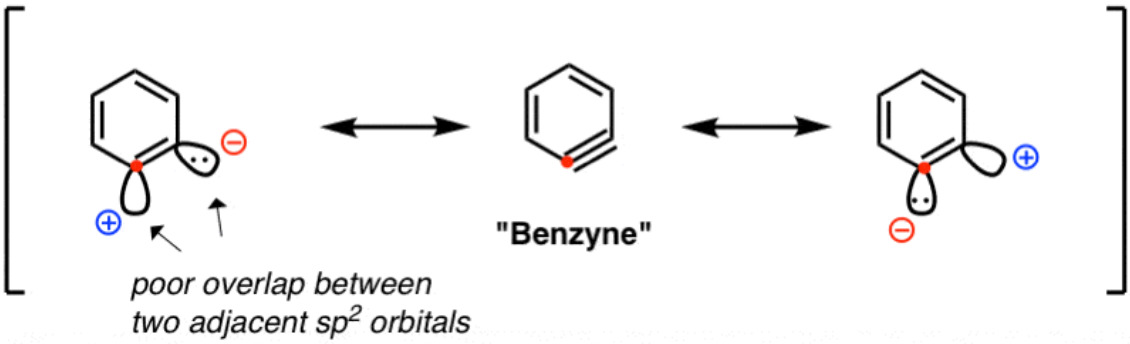
Benzyne has a hexagonal planar structure in which 6 π-electrons are found above and below the ring, which are delocalized and two additional electrons are found in the extra π-bond outside the ring formed as a result of the lateral overlap of two sp 2 hybrid orbitals.



"Benzyne"

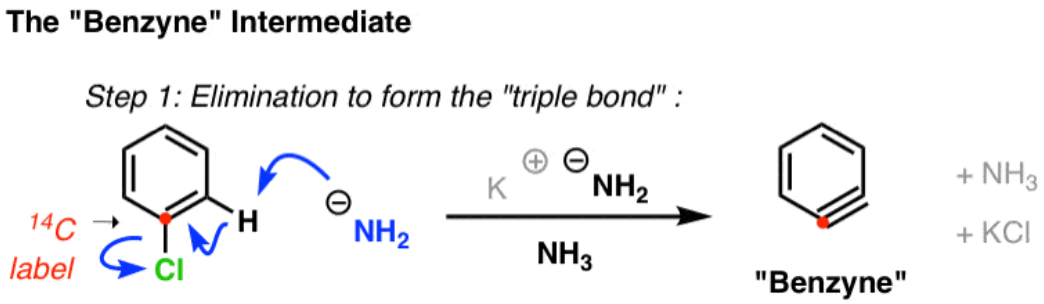
An intuitive way to think about it is to imagine the involvement of two resonance structures (far left and far right, below) that make strong (and equal) contributions to the overall resonance hybrid, such that both carbons can be considered “electrophilie”.

Sometimes helpful to think of the triple-bonded form as being in resonance with two "charged" forms:

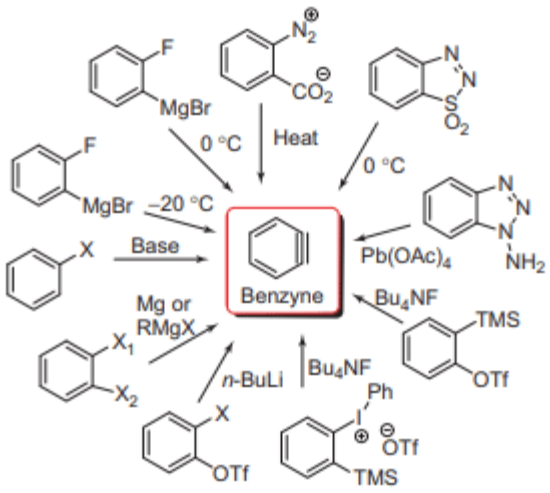


10.4.1 Generation of Benzyne:

1) From alkyl halides: Aryl halides react with strong base like KNH_2, C_6H_5Li.



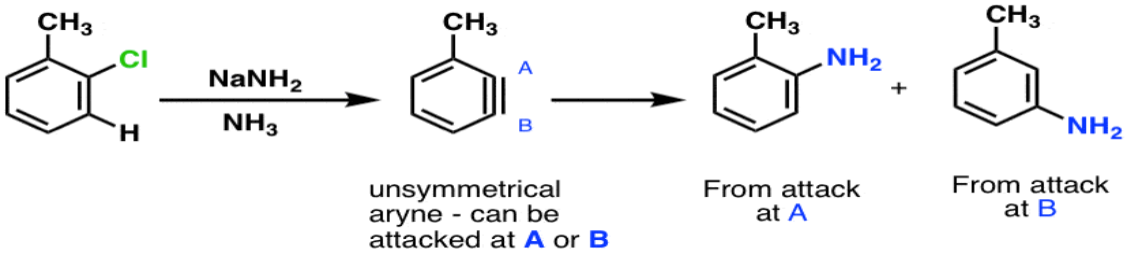
2) More Ways to Form of Benzyne:



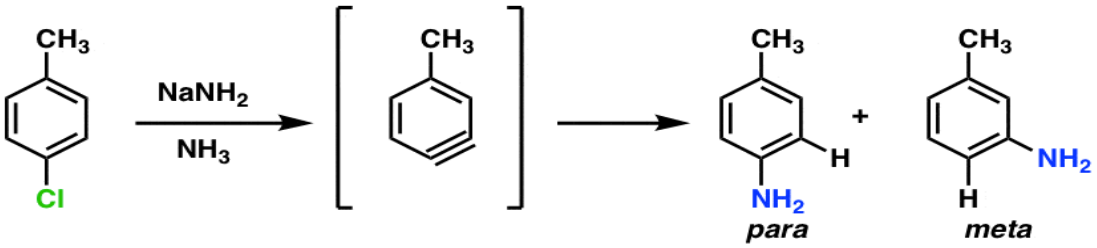
10.4.2 Reactions of Benzyne:

1. Benzyne is reactive species and generated insitu for obtaining various products.

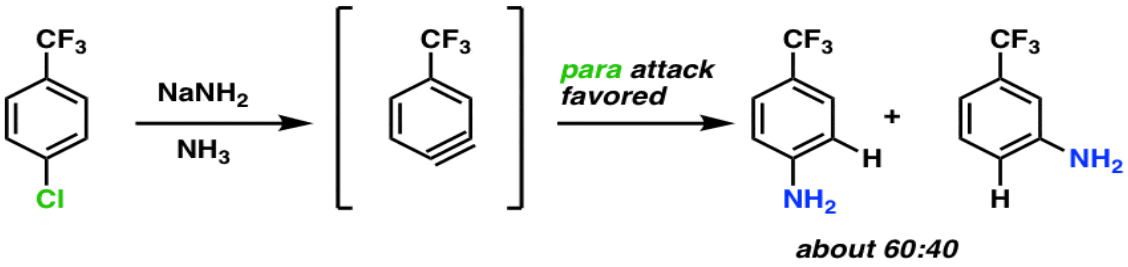
Substituted benzynes ("arynes") can produce multiple products



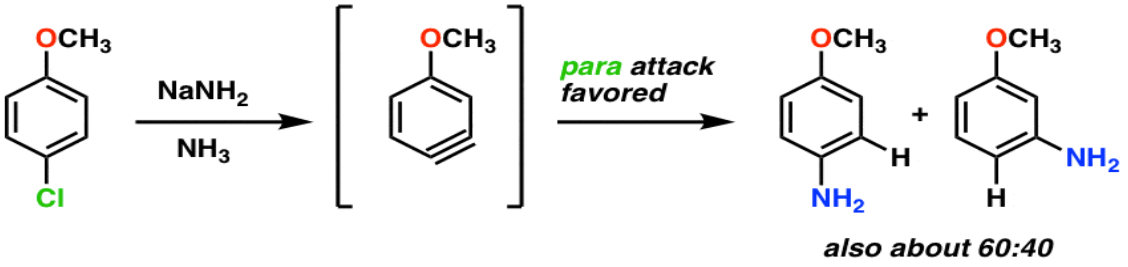
***para*-chlorotoluene gives a mixture of *meta* and *para* products:**



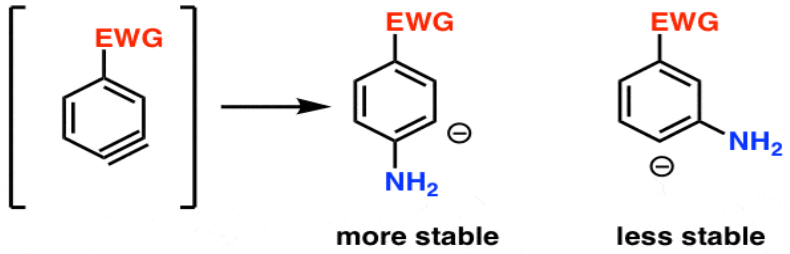
When an electron-withdrawing substituent is used instead of CH_3, more of the *para* product is formed.



OCH_3 gives about the same product ratio as CF_3 !



Attack at the *para* position places the negative charge on the intermediate closer to the electron-withdrawing group



10.5 ELECTROPHILES ("ELECTRON-LOVING") AND NUCLEOPHILES (NUCLEOLUS -LOVING):

10.5.1 Electrophiles ("Electron-Loving"):

An electrophile is a species that accepts electrons. It is electron-deficient and seeks to gain electrons to complete its octet. Electrophiles are usually positively charged or partially positive due to polarization. They are typically electron-deficient species and are attracted to electron-rich areas (nucleophiles).

Characteristics of Electrophiles:

- Electron-deficient (positively charged or partially positive)
- Accept electron pairs
- React with nucleophiles
- Can be cations, neutral molecules, or even polarized bonds

Examples of Electrophiles:

1) Cations (Positively Charged Species):

- H^+ (Proton) – Highly reactive, found in acid-base reactions
- NO_2^+ (Nitronium ion) – Important in nitration reactions
- Carbocations (R^+) – Reactive intermediates in organic reactions, such as SN1

2) Neutral Molecules with Electron Deficiency:

- BF_3 (Boron trifluoride) – Used in Lewis acid catalysis
- $AlCl_3$ (Aluminum chloride) – Common in Friedel-Crafts reactions
- SO_3 (Sulfur trioxide) – Involved in sulfonation reactions

3) Polarized Molecules (Partial Positive Charge):

- CH_3COCl (Acetyl chloride) – Used in acylation reactions
- Carbonyl compounds (C=O group in aldehydes & ketones) – The carbonyl carbon is electrophilic
- RX (Alkyl halides, e.g., CH_3Cl) – Undergo nucleophilic substitution reactions

10.5.2 Nucleophiles ("Nucleus-Loving"):

A nucleophile is a species that donates electrons. It is electron-rich and seeks to donate electrons to electrophiles. Nucleophiles are usually negatively charged or electron-rich due to lone pairs or π-electrons.

Characteristics of Nucleophiles:

- Have a negative charge or lone pairs of electrons.
- Can form bonds by donating electrons to an electrophile.
- Often participate in substitution (SN1, SN2) and addition reactions.
- Reactivity depends on factors like charge, electronegativity, steric hindrance, and solvent effects.

Examples of Nucleophiles:

1) Strong Nucleophiles (Usually Charged):

- Hydroxide ion (OH^-)
- Alkoxide ions (RO^-) (e.g., CH_3O^-, $C_2H_5O^-$)
- Cyanide ion (CN^-)
- Halide ions (I^-, Br^-, Cl^-)
- Thiolate ions (RS^-)
- Carbanions (R^-, e.g., CH_3^-)

2) Moderate Nucleophiles (Neutral Molecules with Lone Pairs):

- Water (H_2O)
- Alcohols (ROH)
- Ammonia (NH_3)
- Amines (RNH_2, R_2NH, R_3N)
- Phosphines (PR_3)

3) Weak Nucleophiles:

- Fluoride ion (F^-)
- Carboxylic acids (RCOOH)
- Nitrites (NO_2^-)

Nucleophilicity Trend:

- Across a Period: Decreases (e.g., $C^- > N^- > O^- > F^-$).
- Down a Group: Increases in polar protic solvents (e.g., $I^- > Br^- > Cl^- > F^-$).
- Charged nucleophiles are stronger than neutral ones (e.g., $OH^- > H_2O$).

Key difference between Electrophiles and Nucleophiles:

Property	Electrophile	Nucleophile
Electron Affinity	Electron-deficient (wants electrons)	Electron-rich (donates electrons)
Charge	Positive or partially positive	Negative or has lone pairs
Role in Reaction	Accepts electrons	Donates electrons
Example	H^+, NO_2^+, BF_3	OH^-, NH_3, C=C

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LESSON - 11

NATURE OF BONDING IN ORGANIC MOLECULES

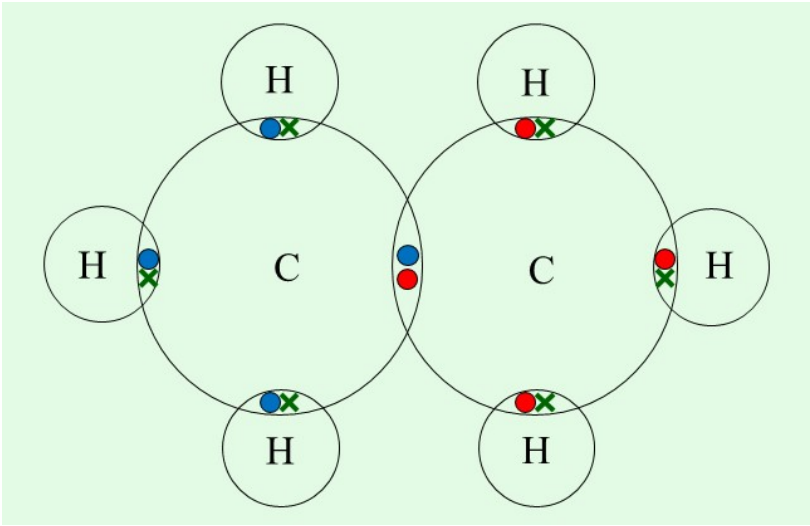
11.1 LOCALISED AND DELOCALIZED COVALENT BONDS:

Covalent bonds can be classified as localized or delocalized based on how electrons are distributed in a molecule.

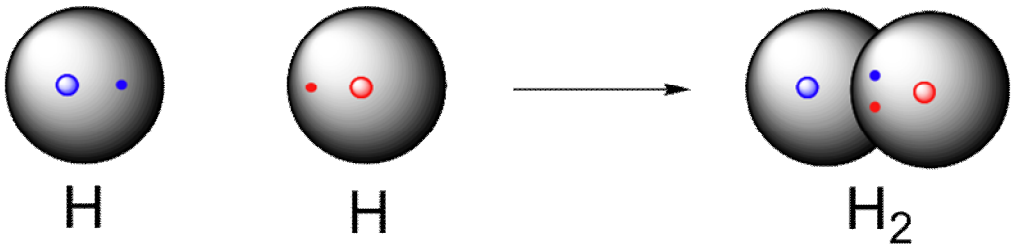
11.1.1 Localized Covalent Bonds:

- Electrons in these bonds are confined between two specific atoms.
- These bonds do not participate in resonance.
- Found in molecules where there is no need for electron delocalization to stabilize the structure.

Example 1: The C-H or C-C bonds in ethane (C_2H_6) are localized. Ethane is formed when two methyl group. i.e. 2 CH3 group combine with each other by a single bond. As carbon has 4 valency therefore it combines with 3hydrogen and one carbon which can be seen clearly in the diagram given below.

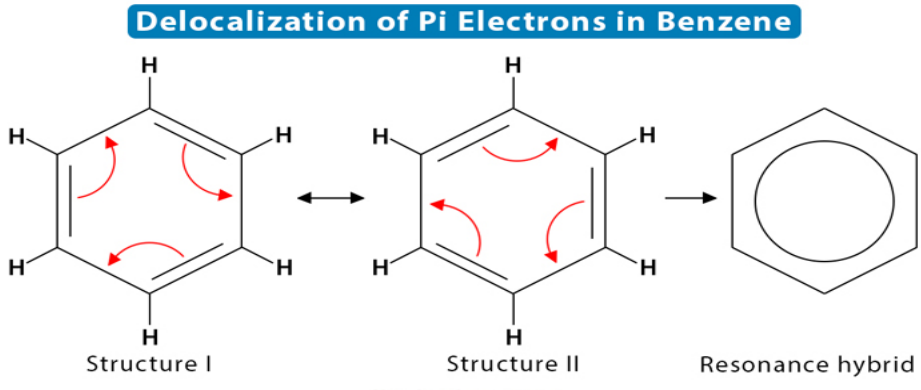


Example 2: The hydrogen molecule, H_2. the two electrons from each of the hydrogen atoms are shared to form a covalent bond between the two atoms. The two spherical 1*s* orbitals overlap, allowing the two electrons to form a pair within the two overlapping orbitals. In simple terms, both electrons now spend more time *between* the two nuclei and thus hold the atoms together. The two electrons must now occupy a *shared orbital space*. This will be the essential principle of valence bond theory.



11.1.2 Delocalized Covalent Bonds:

- Electrons in these bonds are spread out over multiple atoms.
- These bonds contribute to resonance structures.
- Often found in conjugated systems, such as benzene (C_6H_6) and carboxylate ions (COO^-).
- Example: In benzene, the π-electrons are shared among all six carbon atoms, leading to delocalization. Molecules with two or more resonance structures can have bonds that eztend over more than two bonded atoms. Electrons in pi (π) bonds that extend over more than two atoms are said to be delocalized



Differences between localized and delocalized bonds

Feature	Localized Bonds	Delocalized Bonds
Electron Position	Fixed between two atoms	Spread across multiple atoms
Resonance	Not involved	Involved
Stability	Less stable	More stable due to resonance
Example	Ethane (C_2H_6)	Benzene (C_6H_6)

11.2 DELOCALIZED CHEMICAL BONDING:

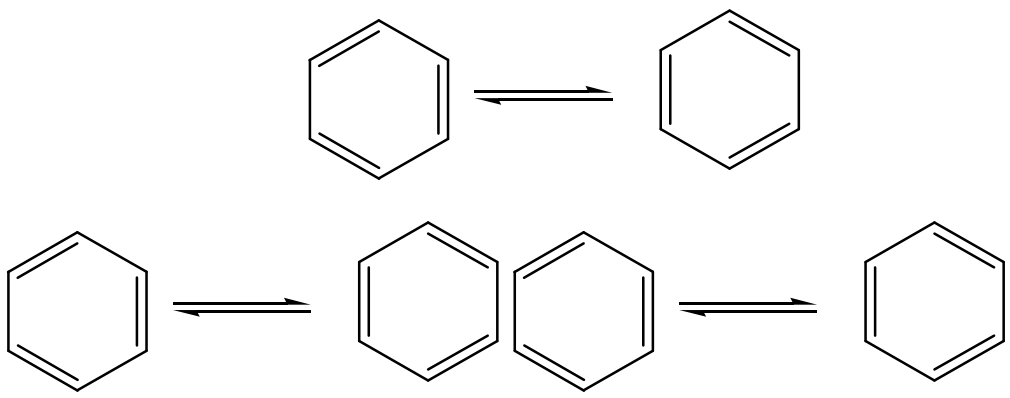
Some compounds contain one or more bonding orbitals that are not restricted to two atoms, but that are spread out over three or more. Such bonding is said to be delocalized bonding. This delocalised chemical bonding can be explained by Valence bond method and Molecular orbital method.

In the valence bond method, several Lewis structures or canonical forms are drawn and the molecule taken to be a weighted average of them.

$$C_1\ _1 \quad C_2\ _2 \quad .....$$

In this equation each represents one of these structures. This representation of a real structure as a weighted average of two or more canonical forms is called resonance.

Ex: Benzene

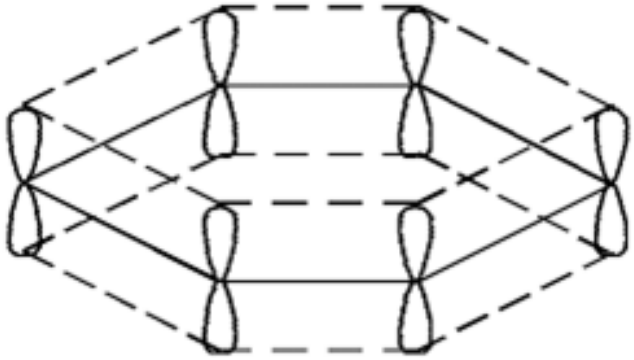


The above two forms are canonical forms of benzene. The energy of the actual molecule is obviously less than that of any one Lewis structure, since otherwise it would have one of those structures. The difference in energy between the actual molecule and the Lewis structure of lowest energy is called resonance energy.

The resonance picture is often used to describe the structure of molecules, but quantitative valence-bond calculations become much more difficult as the structures become more complicated. Therefore, molecular orbital method is used much more often for the solution of wave equations.

Molecular orbital method can be best explained by taking the benzene as an example. In benzene each carbon atom is connected to three other atoms. It uses sp^2 orbitals to form bonds so that all 12 atoms are in one plane. Now each carbon has a 'p' orbital with one electron and each of these can overlap equally with the two adjacent 'p' orbitals. This overlap

of six orbitals produces six new orbitals, three of which are bonding and three antibonding. As a result of the overlap π e⁻s of six orbitals, a torus shaped electron cloud called aromatic sextet is produced. The C – C bond order for benzene, calculated by this method is 1.667.



Overlap π e⁻ s of 'p' orbitals in Benzene

For planar unsaturated and aromatic molecules, molecular orbital calculations have been made by treating the and electrons separately. In these calculations orbitals can be treated as delocalised bonds. First such calculations were made by Huckel, and they are called Huckel. Molecular Orbital calculations. Because electron – electron repulsions are either neglected or averaged out in the Huckel Molecular Orbital (HMO) method, another approach, the self-consistent field (SCF) method was devised.

Although these methods give many useful results, they are often unsuccessful for other molecules. It could be better if both the and electrons to be included in the calculations. The development of modern computers has now made this possible.

Both the Valence bond and Molecular orbital methods show that there is delocalization in benzene. Since each method is useful for certain purposes, we shall use one or the other as appropriate.

11.3 CONJUGATION:

When double bonds are in conjugation, they are arranged in an alternating single and double bond pattern. This allows for delocalization of π-electrons over multiple atoms, leading to increased stability.

Key Features of Conjugated Double Bonds:

1) **Electron Delocalization:**
    - The π-electrons are spread over multiple atoms instead of being localized between two atoms.

- This reduces the overall energy of the system, making it more stable.

2) Planarity:

- Conjugated systems tend to adopt a planar structure to maximize orbital overlap.

3) UV-Vis Absorption (Color & Spectroscopy):

- Conjugated molecules absorb light at longer wavelengths (lower energy) than non-conjugated molecules.
- More conjugation → lower energy absorption → shifts color toward red (bathochromic shift).

4) Chemical Reactivity:

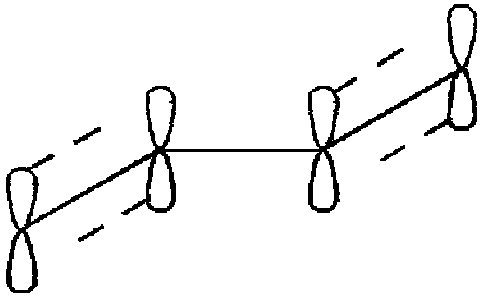
- Conjugated dienes (e.g., 1,3-butadiene) undergo reactions like Diels-Alder and electrophilic addition differently than isolated alkenes.

Examples of Conjugated Systems:

1) 1, 3-Butadiene (CH_2=CH-CH=CH_2)

Butadiene is the best example for this. In the molecular orbital π structure, the overlap of four orbitals gives two bonding and two antibonding orbitals.

H_2C=CH-CH=CH_2 ⟷ $H_2\overset{\oplus}{C}-CH=CH-\overset{\ominus}{C}H_2$ ⟷ $H_2\overset{\ominus}{C}-CH=CH-\overset{\oplus}{C}H_2$



Overlapping of '4p' orbitals of Butadiene

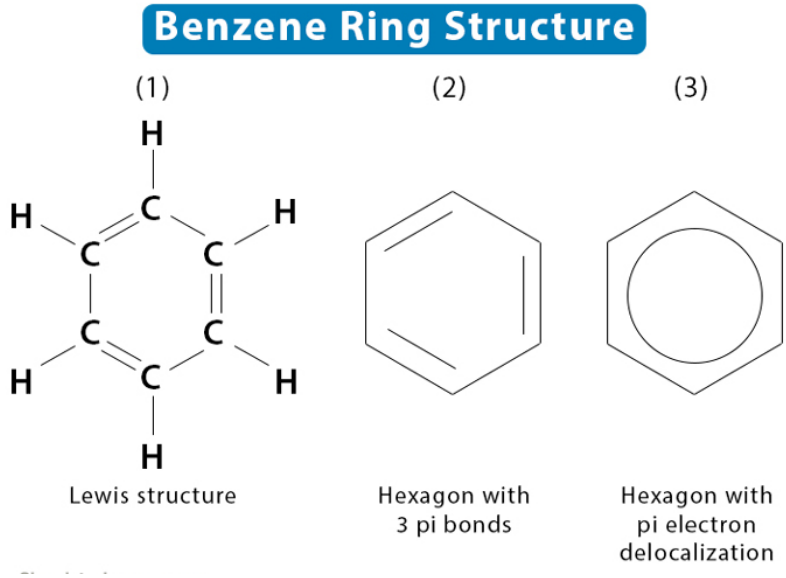
Bond lengths in Butadiene are 1.34Aº for double bonds and 1.48 Aº for single bond. But the ty π cal single bond distance of a bond adjacent to an unsaturated group is 1.53 Aº. This shortening can be explained by resonance.

2. Benzene (Aromatic System with Alternating Double Bonds)

Benzene (1) has six carbon atoms arranged in a ring. Single and double bonds alternately separate the carbon atoms. This kind of atomic arrangement is known as a conjugated structure. Each carbon atom is singly bonded with a hydrogen atom. This structure is also known as the Lewis dot structure of benzene.

Another way of benzene (2), a hexagon with each edge representing one carbon atom. The three double bonds are also shown. However, the hydrogen atoms are not shown.

Illustration (3) represents a hexagon with a circle inside. The circle represents the delocalized pi electrons. The structural formula of benzene is often represented by this structure.



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LESSON - 12

CROSS CONJUGATION

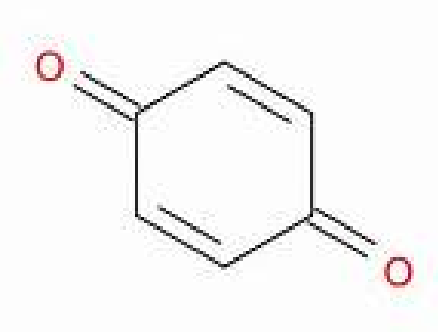
12.1 CROSS CONJUGATION:

In a cross conjugated compound, three groups are present two of which are not conjugated with each other, although each is conjugated with the third.

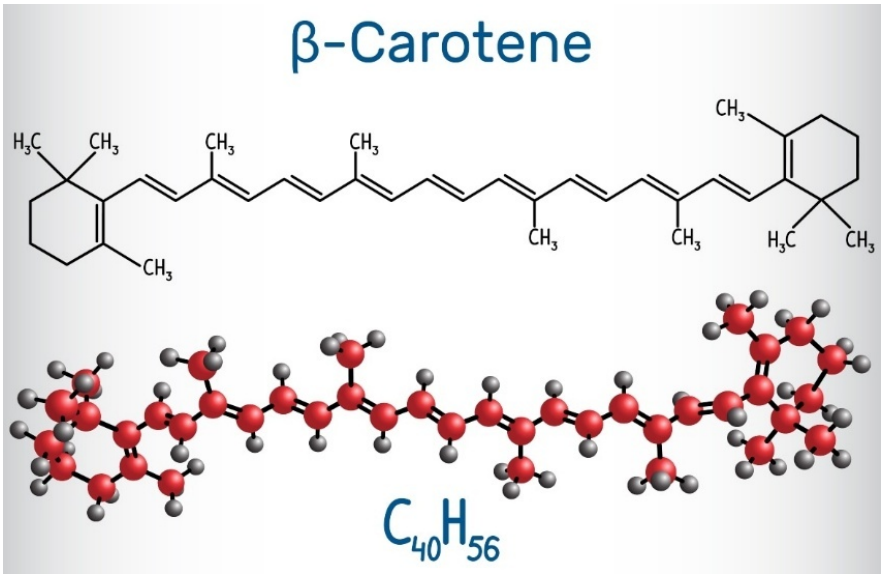
Cross conjugation is a special type of conjugation where a central atom or group participates in conjugation with two separate π-systems, but these two systems are not conjugated with each other.

Example of Cross Conjugation:

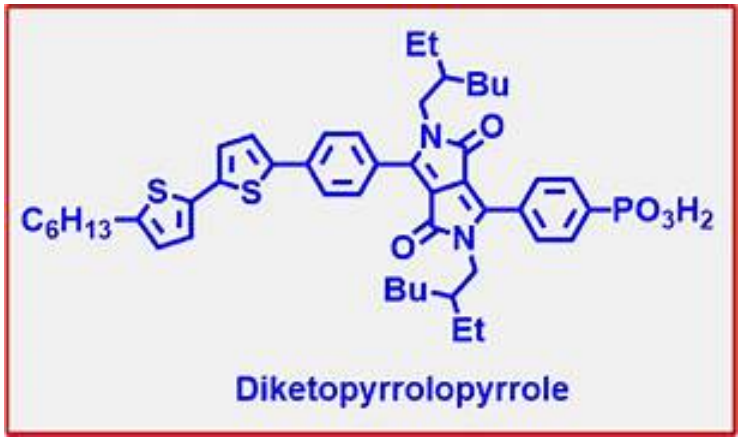
1) **Toluquinone (p-benzoquinone):** The central quinone system is conjugated with two separate alkene groups but not with each other.



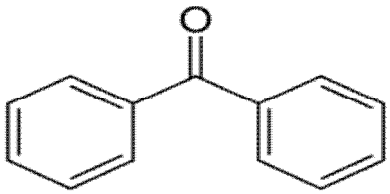
2) **β-Carotene Fragment:** The alternate pathway of electron delocalization leads to cross-conjugation.



3) **Molecules like DPP (Diketopyrrolopyrrole):** Used in organic semiconductors.



Ex:



CH_2= CH- C- CH= CH_2

||

CH_2

It can be best explained by taking the following example.

CH_2= CH- C- CH= CH_2

||

CH_2

In the above compound we find that overlap of six 'p' orbitals gives six molecular orbitals of which three are bonding and three are antibonding.

12.1.1 Effects of Cross Conjugation:

Different Electronic Properties: Compared to linearly conjugated systems, cross-conjugation results in unique UV-Vis absorption and electronic distribution.

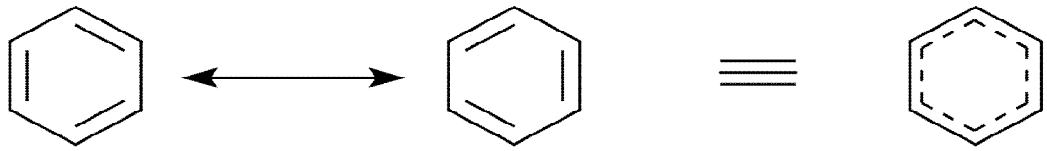
Lower Delocalization Efficiency: Cross-conjugated systems often have lower resonance stabilization compared to fully conjugated structures.

Application in Organic Electronics: Molecules with cross conjugation are used in optoelectronics, dyes, and molecular electronics.

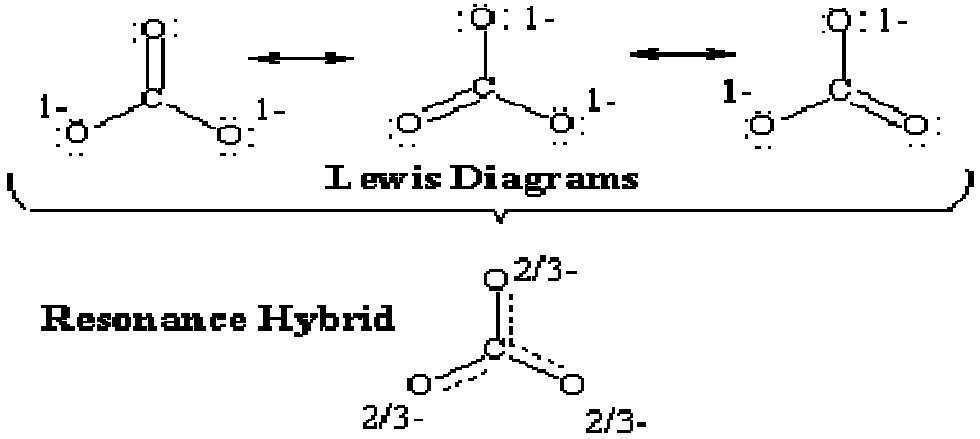
Resonance:

Resonance may be defined as the phenomenon is which two or more structures, involving identical position of atoms, can be written for a particular compound.

Ex.: Benzene



To deal with circumstances such as bonding in ozone, the notion of resonance between Lewis structures was developed. According to resonance concept, when more than one Lewis structure may be written for a molecule, a single structure is insufficient to describe it. Rather, the true structure has an electron distribution that is a hybrid of all possible Lewis structures that can be written for the molecule.



12.2 HYPER CONJUGATION:

Hyperconjugation is the delocalization of electrons involving the interaction of σ-bonds (usually C-H or C-C) with an adjacent empty or partially filled p-orbital, π-orbital, or antibonding orbital. It is often referred to as **"no-bond resonance"** or **"Baker-Nathan effect."**

Key Features of Hyperconjugation:

1) Involves σ and π orbital interactions – Unlike resonance, which involves π-electrons, hyperconjugation involves the delocalization of σ-electrons.

2) Occurs in systems with an adjacent empty p-orbital or π-system – For example, carbocations, alkenes, and radicals.

3) Stabilizing Effect – It stabilizes carbocations, alkenes, and free radicals.

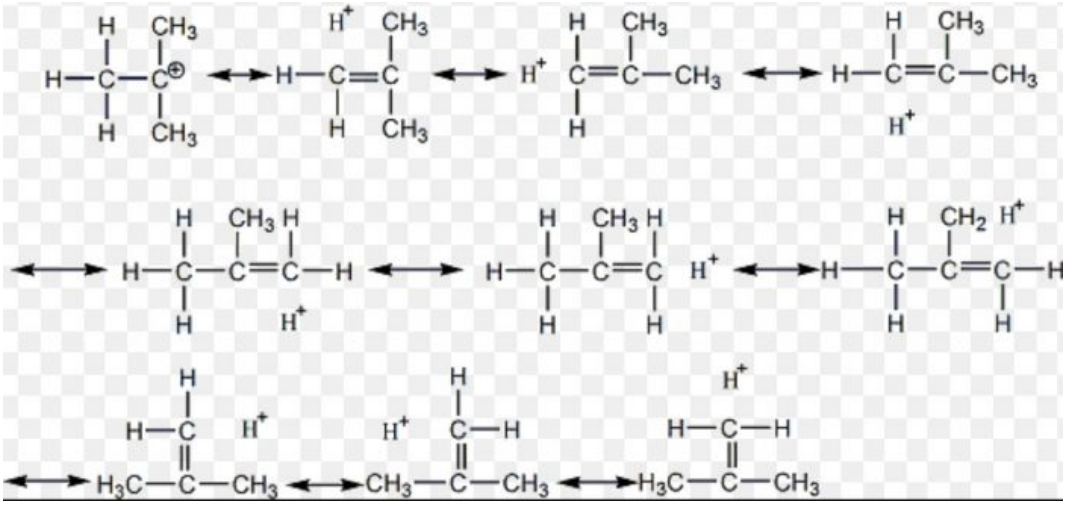
Examples of Hyperconjugation:

1) Carbocation Stability:

Hyperconjugation explains why **tertiary carbocations** are more stable than secondary and primary carbocations.

Example: $(CH_3)_3C^+$ (Tertiary Carbocation)

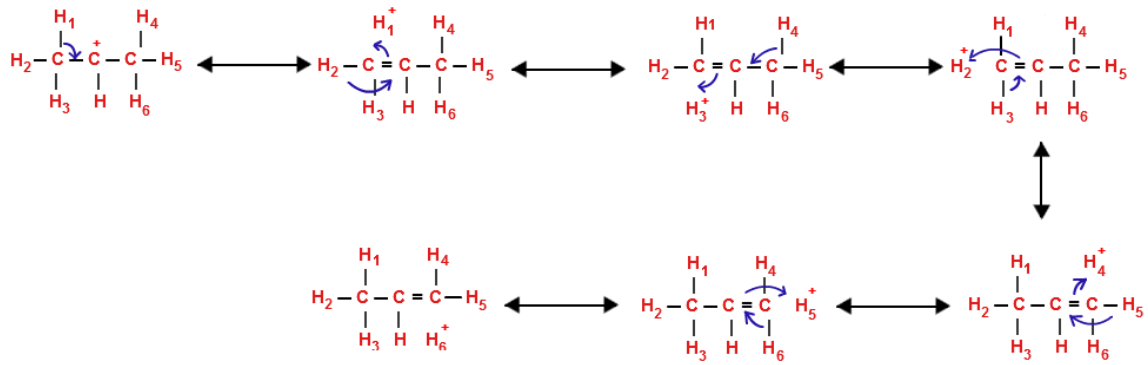
- The positively charged carbon has an empty p-orbital.
- The adjacent C-H bonds can donate electron density through hyperconjugation, reducing the positive charge.



Carbocation Stability Order:

3° > 2° > 1° > Methyl (CH_3^+, least stable)

$(CH_3)_2CH^+$ (Secondary Carbocation):

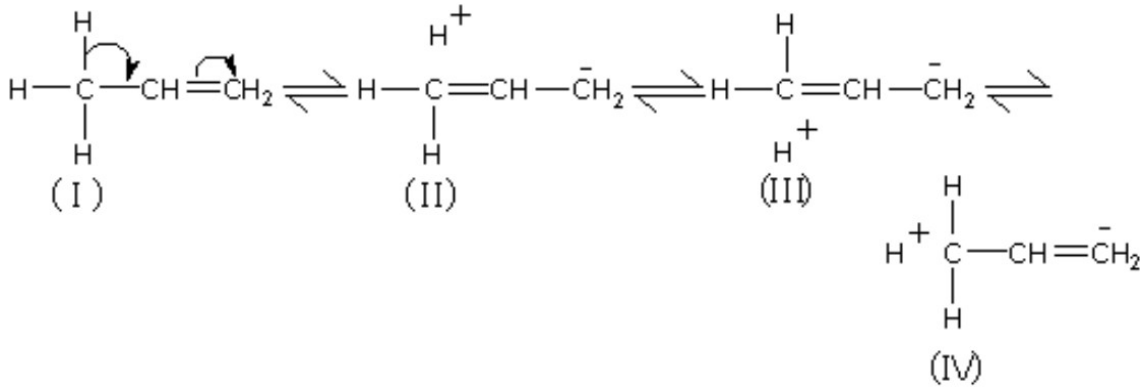


2) Alkene Stability:

Hyperconjugation stabilizes alkenes by delocalizing electrons from adjacent C-H bonds.

Example: CH_2=CH-CH_3 (Propene)

- The C-H bond of the -CH_3 group donates electron density to the π-bond of the alkene.
- More alkyl groups lead to greater hyperconjugation, increasing stability.

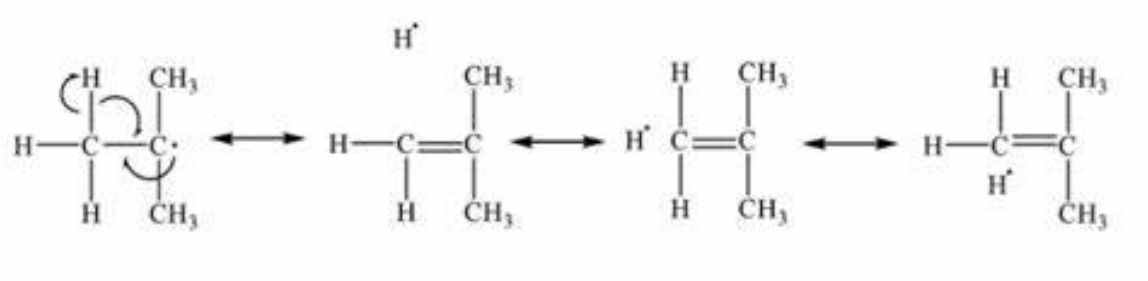


Alkene Stability Order:

Tetrasubstituted>Trisubstituted>Disubstituted>Monosubstituted>Ethene (Least stable)

3) Free Radical Stability:

- Similar to carbocations, hyperconjugation stabilizes free radicals by delocalizing the unpaired electron over adjacent C-H bonds.



Effects of Hyperconjugation:

1) **Bond Length Changes** – Due to electron delocalization, the C-C bond acquires partial double bond character.

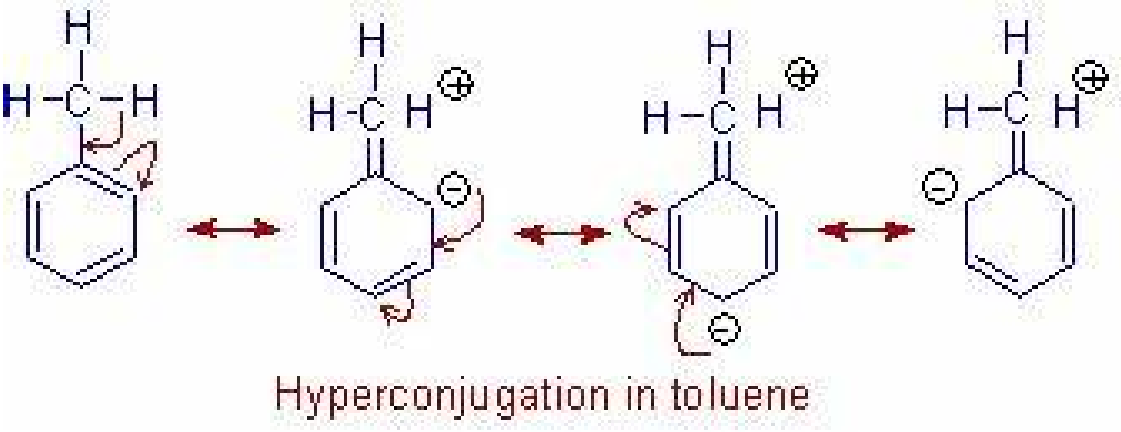
   H-CH=O → **1.20A°,** CH_3-CH=O → **4.21A°**

2) **Inductive Effect Compensation** – It can offset the destabilizing effect of an electron-withdrawing group.

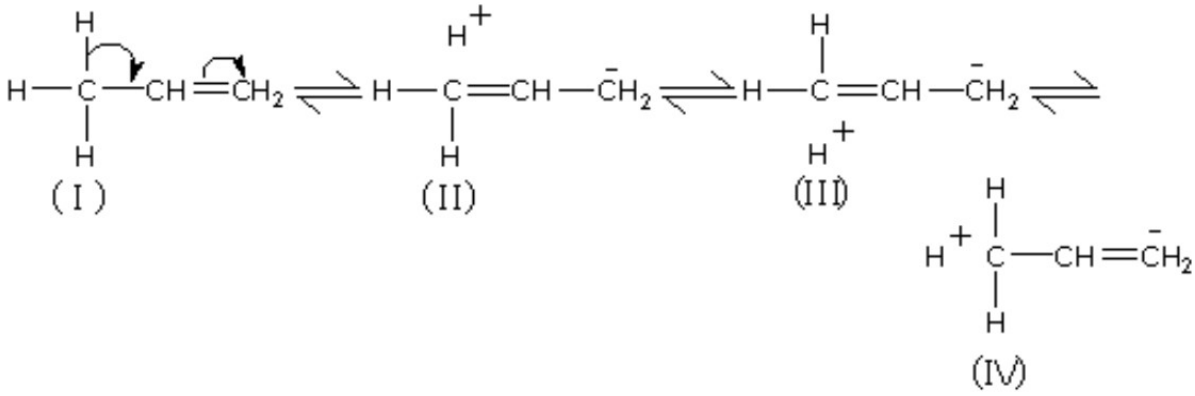
3) **Influences Dipole Moments** – Due to partial charge distribution.

$CH_2=CH_2$ **μ=0** CH_3-CH=CH_2 **μ=0.4 debye**

4) **Explains the Stability of Benzyl and Allyl Systems** – Delocalization extends to these systems, enhancing their stability.



Hyperconjugation in toluene



(I) (II) (III) (IV)

12.3 TAUTOMERISM:

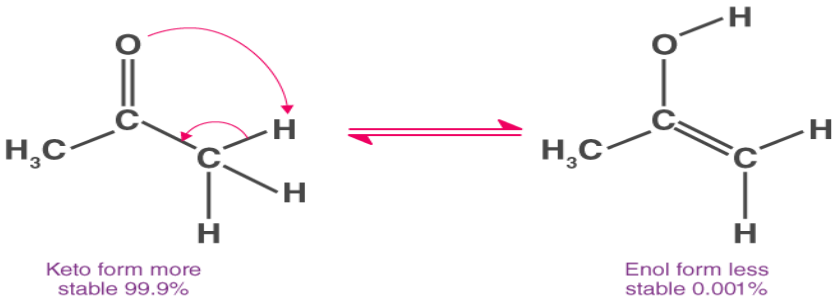
Tautomerism can be defined as "The phenomenon by which a single compound exists in two or more readily inter convertible structures that differ markedly in the relative positions of at least one atomic nucleus, generally hydrogen".

The tautomeric forms are quite chemically distinct entities and can be separated and characterised. In tautomers, the position of an ion differs by several angstrom units.

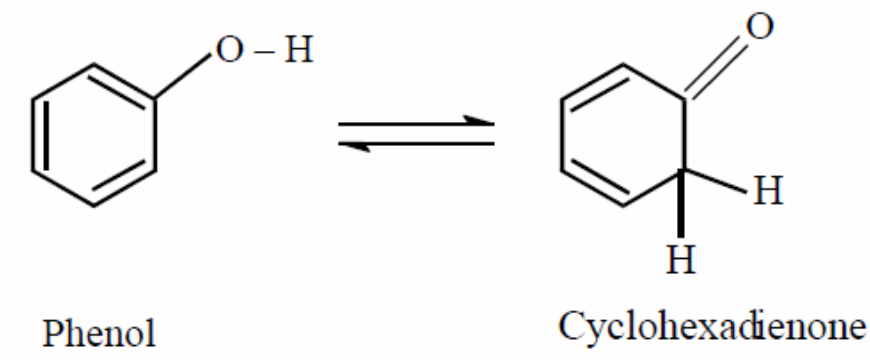
Types of Tautomerism:

1) Keto-Enol Tautomerism:

A very common form of tautomerism is that between a carbonyl compound containing an – hydrogen atom and its end form which is known as Keto – Enol Tautomerism. It can be shown as follows.

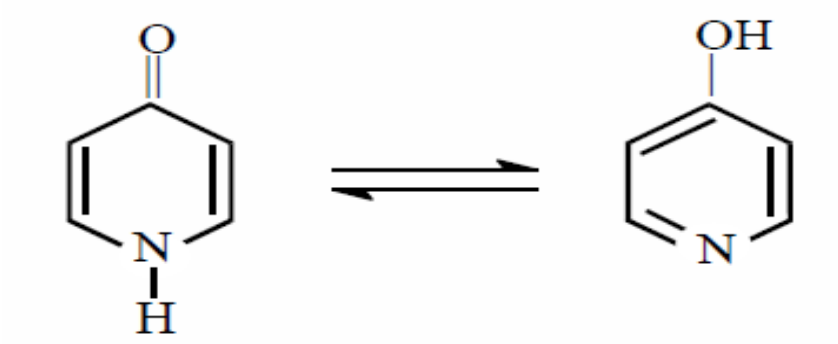


2) Phenol - Keto Tautomerism:

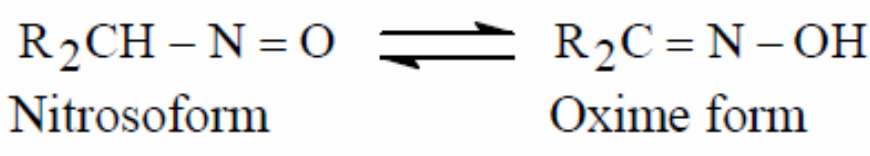


For phenol itself there is no evidence for the existence of keto form. However keto form becomes important and may predominate when certain groups like second –OH or N = O groups are present. It is also found in heterocyclic systems, fused aromatic rings.

Ex.:

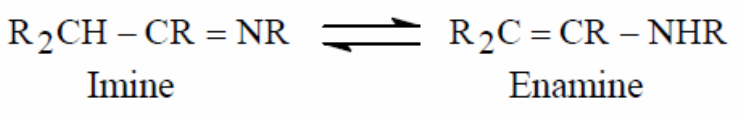


3) Nitroso – Oxime Tautomerism:



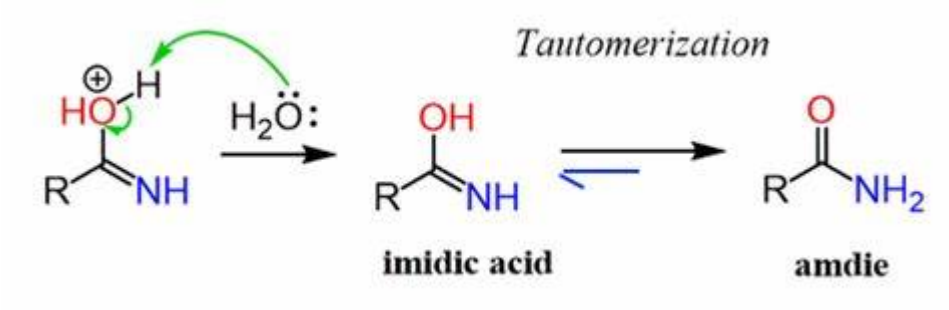
This equilibrium lies far to right, and as a rule nitroso compounds are stable only when there is no α –hydrogens.

4) Imine-Enamine Tautomerism:



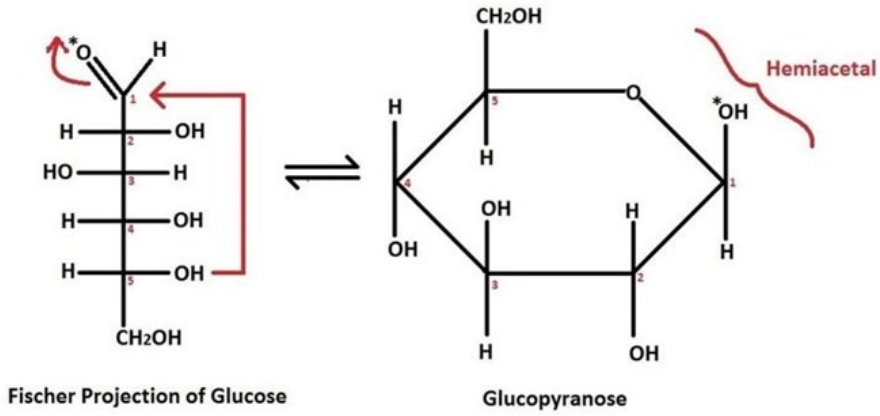
5) Amide-Imidic Acid Tautomerism:

Observed in **amides** when they tautomerize into imidic acid forms.



6) Ring-Chain Tautomerism:

- Seen in carbohydrates, where the open-chain form of glucose converts into its cyclic form.



Dr. K. Chandra Mohan

LESSON - 13

GROUP THEORY IN CHEMISTRY

13.1 INTRODUCTION:

Group theory is a mathematical method by which aspects of a molecules symmetry can be determined. The symmetry of a molecule reveals information about its properties (i.e., Structure, Spectra, polarity, chirality, etc., the systematic discussion or mathematical study of symmetry is called Group theory.

13.2 SYMMETRY ELEMENTS AND SYMMETRY OPERATIONS:

Symmetry plays a central role in the analysis of the structure, bonding, and spectroscopy of molecules. Let us discuss the basic symmetry elements and operations and their use in determining the symmetry classification (point group) of different molecules.

The symmetry properties of objects (and molecules) may be described in terms of the presence of certain symmetry elements and their associated symmetry operations. The various symmetry elements and operations are described in the table below.

13.2.1 Symmetry Elements:

Symmetry elements are defined as imaginary geometrical entities such as points, lines and planes that are present in a molecule, about which when symmetry operations are performed, the molecules present an indistinguishable configuration. The element of symmetry divided into five operations.

i) Identity symmetry (E)

ii) Axis of symmetry (Cn where n=360/angle of rotation in θ)

iii) Plane of symmetry (σ)

iv) Improper axis of symmetry (Sn and then $\perp$ Cn)

v) Point of symmetry (i)

13.2.2 Symmetry Operations:

These are simple geometric operations such as reflection, rotation or inversion which when performed on the molecule, give rise to an indistinguishable configuration of the same molecule.

S.No.	Symmetry Element	Symmetry Operation
1	Identity Element (E)	Doing nothing (3600 rotation)
2	Axis of symmetry (Cn)	Rotation through an angle of $\left(\frac{360^0}{n}\right)$ about an axis. (n = order)
3	Plane of symmetry (σ)	Reflection
4	Improper axis of symmetry (Sn)	Inversion
5	Centre of symmetry (i)	Rotation through an angle of $\left(\frac{360^0}{n}\right)$ about an axis followed by reflection about a plane perpendicular to the original axis.

1) Identity (E):

The operation, which brings back the molecule to the original orientation, is called identity operation. It is represented as E from the German word Einhert meaning unity. The identity operation in effect means doing nothing on the molecule. Each molecule has this type of symmetry. This situation can be visualized by two ways either;

i) We do not do anything on the molecule (or)

ii) We rotate the molecule by 3600

It is also called as 'Leave-it-alone' operation. Every molecule in the universe having identity symmetry operation.

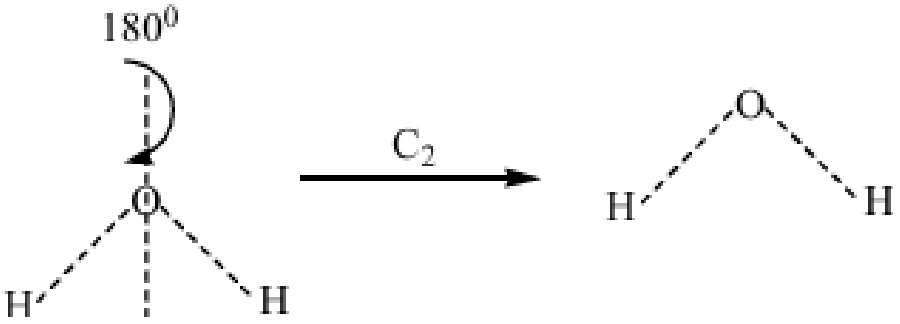
2) Axis of Symmetry (Cn):

When an imaginary axis passing through the molecule followed by rotation operation about some angle ($^{\theta}0$) to give one or more equivalent orientation of the molecule is called Axis of symmetry It is represented as Cn.

$$\theta = \frac{360^0}{n}$$

Where n is always an integer. This axis defined is an n-fold rotation axis, Cn.

In water there is a C2 axis so we can perform a 2-fold (180°) rotation to get the identical arrangement of atoms.



Rotations are considered positive in the counter-clockwise direction. Each possible rotation operation is assigned using a superscript integer m of the form C_{nm}. The rotation C_{nm} is equivalent to the identity operation (nothing is moved)

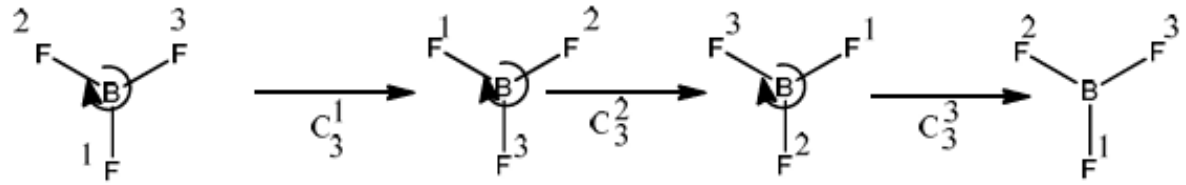
Classification of Axis of Symmetry:

Many molecules have more than one Cn axis. It can be divided into two different types:

(a) Principal axis of symmetry & (b) Secondary/ subsidiary axis of symmetry

(a) Principal Axis of Symmetry: The principal axis in an object is the highest order rotation axis i.e. having largest value of n. It is usually easy to identify the principal axis and this is typically assigned to the z axis if we are using Cartesian coordinates. If there are more than one axis of same order, then the axis passing through maximum number of atoms is called Principal axis.

Example: In BF3 molecule three-fold rotation axis (C3) and two-fold rotational axis (C2) is present. The three-fold axis is coincident with the perpendicular to the plane and the rotation angle is 1200. After two C3 operations molecule comes into identity operation. Three-fold axis have higher order than two-fold axis, therefore C3 is the principal axis of BF3 molecule.



C_3^1=120° , C_3^2= 240° , C_3^3=E=360°

(b) Subsidiary or Secondary Axes of Symmetry: Lower fold of rotation axis (lowest order of axis of symmetry) is the secondary or subsidiary axis of the molecule.

Example: In BF3 molecule C3 axis is principal axis and C2 axis is secondary axis. In ethane molecule C2 is the principal axis and C2 is subsidiary axis. In NH3 molecule three-fold of axis present that is principal axis, here subsidiary axis is absent.

3) Plane of Symmetry (σ):

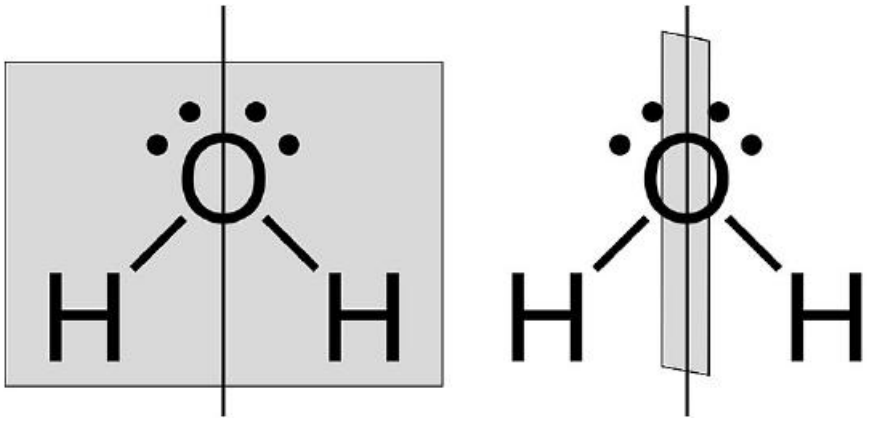
When an imaginary plane passing through the molecule or an object which bisects the molecule into two equal halves is called plane of symmetry (also known as a mirror plane). It is represented as (σ).

Classification of Planes: Planes are classified on the basis of principal axis. There exist three types of mirror planes.

σ_h – a horizontal mirror plane of a molecule is perpendicular to the primary axis of a molecule.

σ_v – a vertical mirror plane of a molecule includes the primary axis of a molecule and passes through the bonds (atoms).

σ_d – a dihedral (also known as a diagonal mirror plane) of a molecule includes the primary axis of a molecule while bisecting the angle between two C_2 axes that are perpendicular to it. Therefore, σd does not pass through the bonds (atoms).



Bent structure of H_2O. The water molecule has two σ_v along C_2 axis and no σ_h

4) Improper axis of symmetry (S_n):

Improper rotation operates with respect to an axis called rotation-reflection axis. In other words, it is a combination operation of a rotation about an axis by 360°/n (or 2π/n2π/n) followed by reflection in a plane perpendicular to the rotation axis. (Sn and then $\perp$ C_n)

$$S_n = C_n \perp \sigma_n$$

Example: In CH_4 has tetrahedral geometry. CH_4 having S_4 it doesn't mean that C_4 symmetry is present.

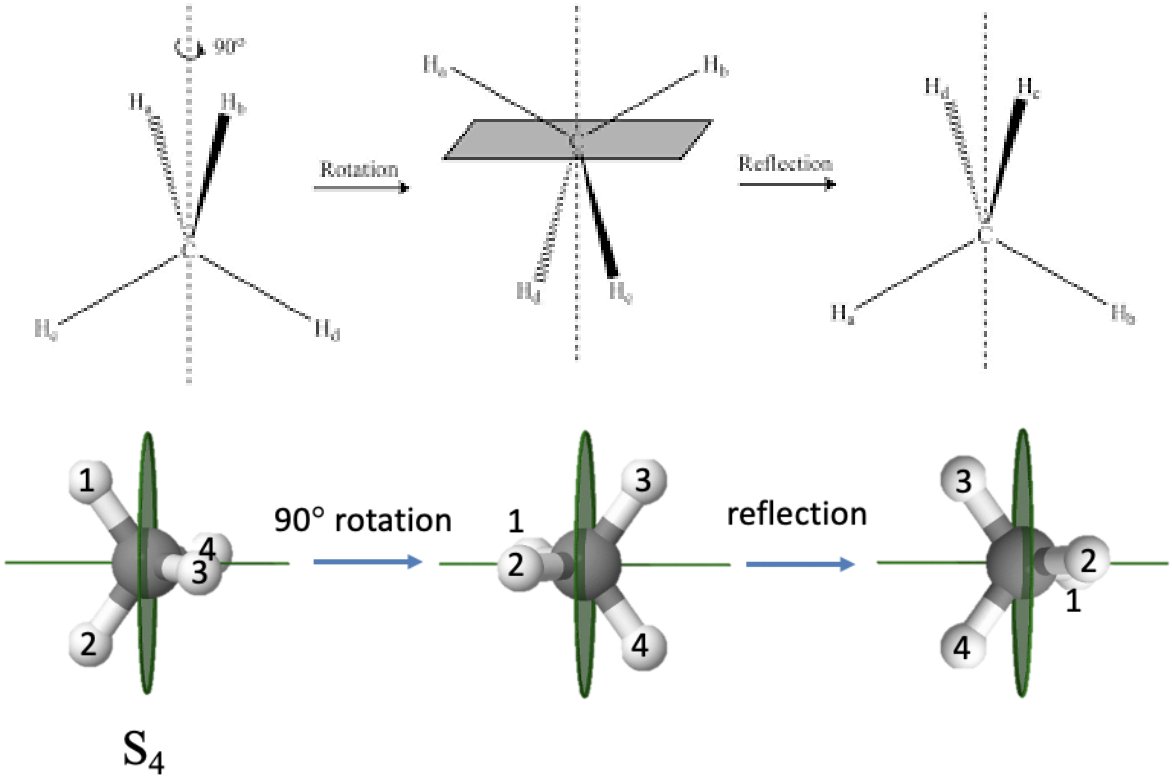
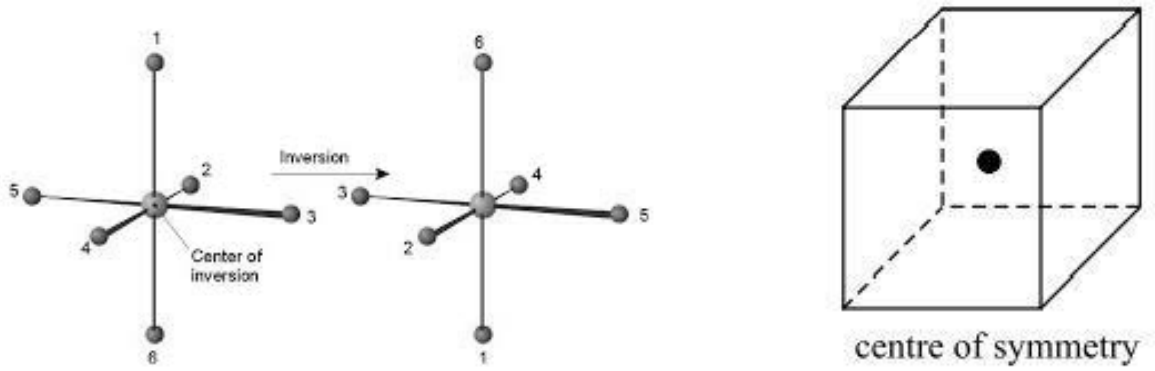


Fig. 3D Representation of CH_4

5) Centre of Symmetry (i):

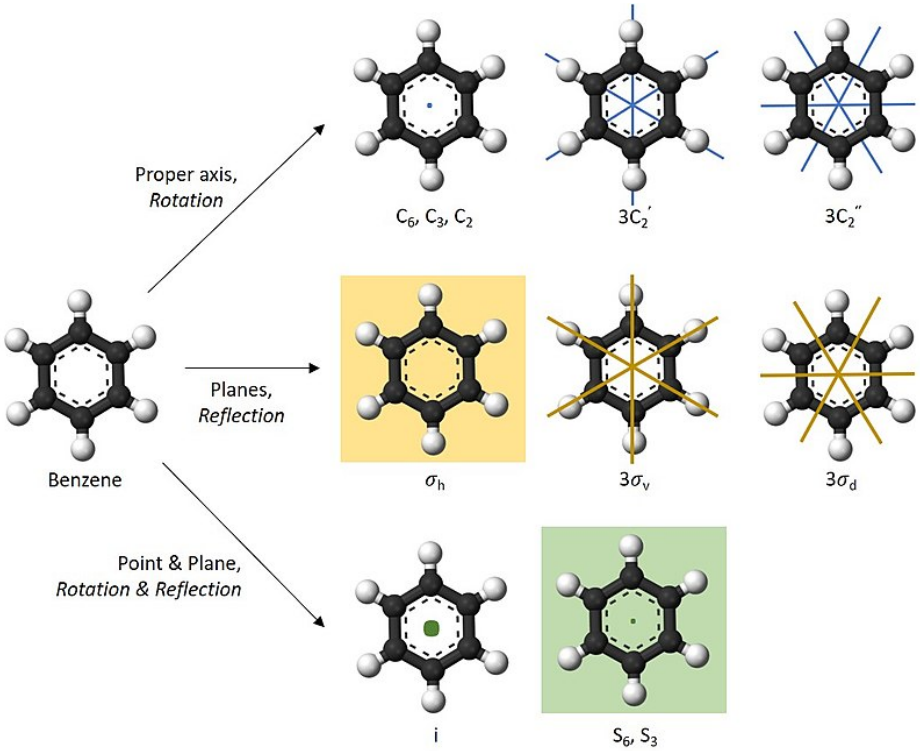
Inversion operates with respect to a point called a Centre of Symmetry (also known as an inversion centre). It gives the same result to rotating a molecule around C_2 axis then reflecting it with respect to a mirror plane that is perpendicular to C_2.

For example, SF_6



Inversion of SF6, all fluorine atoms inverts through one point **Cube**

Benzene is one of the molecules that possess various symmetry elements and symmetry operations



Dr. P. Bharath

LESSON - 14

A COMPLETE SET OF SYMMETRY OPERATIONS AS MATHEMATICAL GROUP

14.1 GROUP:

Each molecule has a set of symmetry operations that describes the molecule's overall symmetry. This set of operations define the group of the molecule. A group G is a finite or infinite set of elements together with a binary operation (called the group operation) that together satisfy the four fundamental properties of closure, associativity, the identity property, and the inverse property. The operation with respect to which a group is defined is often called the "group operation," and a set is said to be a group "under" this operation.

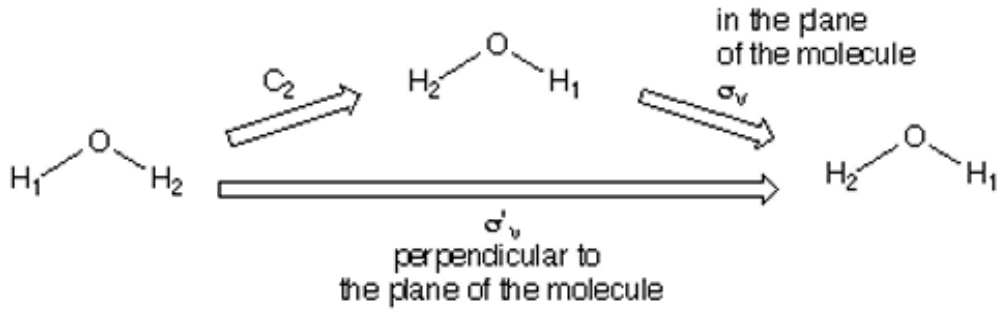
The study of groups is known as group theory.

14.1.1 A group is a set of operations which satisfies the following requirements:

Closure: If any two symmetry operations are in the same group, then their product, resulting in another operation, will also be in the same group:

$$\text{If } A \in G \text{ and } B \in G, \text{ then } (A \cap B) \in G$$

Consider H_2O which has E, C_2 and 2 σ_v' s.



i.e., $\hat{C}_2\hat{\sigma}_v \equiv \hat{\sigma}'_v$ **of course** $\hat{C}_2\hat{C}_2 \equiv \hat{E}$ **etc…**

The table is closed, i.e., the results of two operations is an operation in the group, the elements are commutable.

Identity: There exists an operation that commutes with other operations (identity, E) and leaves them unchanged:

$$\text{If } A \in G \text{ and } E \in G, \text{ then } AE = EA = A$$

Inverses: For every symmetry operation in the group, there exists an inverse operation that their product results identity:

If A ∈ G, then there exists A−1 ∈ G such that AA−1 = A−1A = E

Associativity: The law of associativity applies to all symmetry operations:

(AB) C = A (BC)

Example:

The point group for the water molecule is C_{2v}, with symmetry operations E, C_2, σ_v and σ_v'. Its order is thus 4. Each operation is its own inverse. As an example of closure, a C_2 rotation followed by a σ_v reflection is seen to be a σ_v' symmetry operation: $\sigma_v * C_2 = \sigma_{v'}$.

The group multiplication table obtained is therefore for water molecule:

	E	C_2	σ_v	σ'_v
E	E	C_2	σ_v	σ'_v
C_2	C_2	E	σ'_v	σ_v
σ_v	σ_v	σ'_v	E	C_2
σ'_v	σ'_v	σ_v	C_2	E

$\sigma_v . \sigma_v = E$

$C_2 . \sigma_v = \sigma'_v$

$C_2 . E = E\ C_2 = C_2$

$C_2 (\sigma_v . \sigma'_v) = (C_2 . \sigma_v) \sigma'_v$

Another example is the ammonia molecule, which is pyramidal and contains a three-fold rotation axis as well as three mirror planes at an angle of 120° to each other. Each mirror plane contains an N-H bond and bisects the H-N-H bond angle opposite to that bond. Thus, ammonia molecule belongs to the C_{3v} point group which has order 6: an identity element E, two rotation operations C_3 and C_3^2, and three mirror reflections σ_v, σ_v' and $\sigma_{v''}$.

14.1.2 Classification of Group:

i) **Abelian Group:** All elements are commutable. Example, Water

ii) **Non-Abelian Group:** All elements do not commute with one another.

Example: Phosphine symmetry operations are E, C_3, C_34, σ_v' and σ_v''.

$$C_3, \sigma v \neq \sigma v . C_3$$

i) Cyclic group: In cyclic group all the elements of a group can be generated from one element. It is denoted by An. A represents identity element & n represents total no of elements & is called as order of group. Each cyclic group is abelian but each abelian group is not cyclic.

Example: Trans 1,2 dichlorocyclopropane.

Classification of group on the basis of element-

a) Monoid - A group is a monoid each of whose elements is invertible.

b) Trivial Group- A group must contain at least one element, with the unique (up to isomorphism) single-element group known as the trivial group.

c) Finite group - If there are a finite number of elements, the group is called a finite group

14.2 SUBGROUPS:

Any subset of element which form a group is called as subgroup.

A subgroup is a subset of group elements of a group that satisfies the four group requirements. It must therefore contain the identity element. "H is a subgroup of G" is written $H \subseteq G$, or sometimes $H \leq G$. A subset of a group that is closed under the group operation and the inverse operation is called a subgroup.

The elements of a subgroup should obey the following conditions - If g is the order of the group & s is the order of the subgroup, then g/s is a natural number. Example- water molecule has symmetry elements- E, C_2, σ_v, σ_v^1

GROUP – E, C_2, σ_v, σ_v^1

SUBGROUPS – E

E, C_2

E, σ_v

E, σ_v^1

14.2.1 Classes:

This is the subdivision of a group.

Two elements A & B in a group form a class if they are conjugate to each other. Conjugate elements are related by the equation

$$X^{-1}.AX = B$$

Where X is similarity transformation element. It is used to find whether a set of elements form a class. Example- water molecule has symmetry elements- E, C_2, σ_v, σ_v^1

14.2.2 Order:

The order of a class of a group must be an integral factor of the order of a group and the number of elements is called the group order of the group. It is represented by ‘h’.

14.3 RELATION BETWEEN ORDERS OF A FINITE GROUP & ITS SUBGROUP:

If there are a finite number of elements, the group is called a finite group and the number of elements is called the group order of the group.

- A subset of a group that is closed under the group operation and the inverse operation is called a subgroup. Subgroups are also groups, and many commonly encountered groups are in fact special subgroups of some more general larger group.
- A finite group is a group having finite group order. Examples of finite groups are the modulo multiplication groups, point groups, cyclic groups, dihedral groups, symmetric groups, alternating groups, and so on.
- The finite (cyclic) group C_2 forms the "Finite Simple Group of Order 2"
- A basic example of a finite group is the symmetric group Sn, which is the group of permutations (or "under permutation") of n objects.

Dr. P. Bharath

LESSON - 15

POINT SYMMETRY GROUPS

15.1 INTRODUCTION:

Each molecule has a set of symmetry operations that describes the molecule's overall symmetry. This set of operations define the point group of the molecule. Since all the elements of symmetry present in the molecule intersect at a common point & this point remains fixed under all symmetry operations of the molecule and is known as point symmetry groups.

15.2 SCHONFLIES NOTATION:

The point groups are denoted by their component symmetries. There are a few standard notations used by crystallographers. A point group in the Schoenflies convention is completely adequate to describe the symmetry of a molecule; this is sufficient for spectroscopy.

Schönflies Notation:

In Schönflies notation, point groups are denoted by a letter symbol with a subscript. The symbols used in crystallography mean the following:

- The letter O (for octahedron) indicates that the group has the symmetry of an octahedron (or cube), with (O_h) or without (O) improper operations.
- The letter T (for tetrahedron) indicates that the group has the symmetry of a tetrahedron. Td includes improper operations, T excludes improper operations, and T_h is T with the addition of an inversion.
- The letter I (for icosahedron) indicates that the group has the symmetry of an icosahedron (or dodecahedron), either with (I_h) or without (I) improper operations.
- C_n (for cyclic) indicates that the group has an n-fold rotation axis. C_{nh} is C_n with the addition of a mirror (reflection) plane perpendicular to the axis of rotation. C_{nv} is C_n with the addition of a mirror plane parallel to the axis of rotation.
- S_n (for Spiegel, German for mirror) denotes a group that contains only an n-fold rotation-reflection axis.

- D_n (for dihedral, or two-sided) indicates that the group has an n-fold rotation axis plus a twofold axis perpendicular to that axis. D_{nh} has, in addition, a mirror plane perpendicular to the n-fold axis. D_{nv} has, in addition to the elements of D_n, mirror planes parallel to the n-fold axis.

15.3 POINT GROUPS:

A Point Group describes all the symmetry operations that can be performed on a molecule that result in a conformation indistinguishable from the original. Point groups are used in Group Theory, the mathematical analysis of groups, to determine properties such as a molecule's molecular orbitals.

In order to find out the point groups of molecules systematically, the molecules are classifying into three categories.

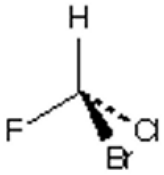
- Molecules of Low symmetry – MLS (C_1, C_i, C_s)
- Molecules of High symmetry – MHS (C_n, C_{nv}, C_{nh}, D_n, D_{nh}, D_{nd}, S_n)
- Molecules of Special Symmetry – MSS (T_d, O_h, I_h)

15.3.1 Molecules of Low Symmetry:

C_1 Point Group: Contains only the identity (a C1 rotation is a rotation by 360° and is the same as the identity operation E)

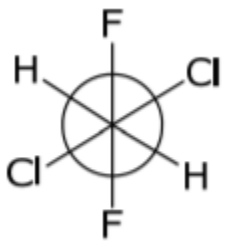
e.g. CHFBrCl

C_1: only E



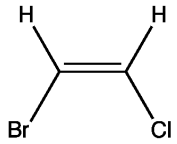
Ci **Point Group:** Contains the identity E and only a centre of inversion i (rare point group)

Here, Order of the Point group, h = 2 (E, i)



C_S Point Group: Contains the identity E and only a plane of reflection σ

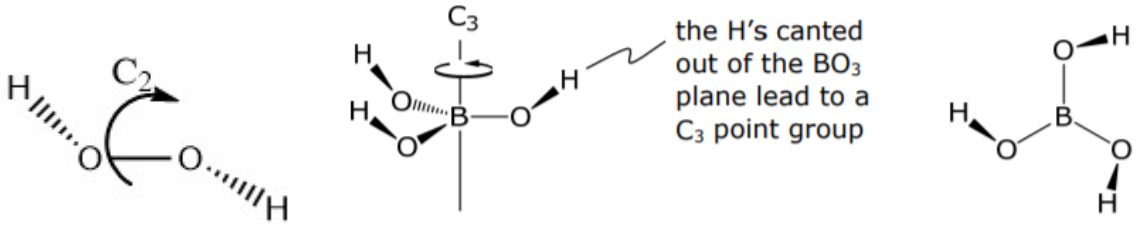
Here, Order of the Point group, h = 2 (E, σ)



15.3.2 Molecules of High Symmetry:

Cn Point Group: Contains the identity E and only an n-fold axis of rotation. Cn and all powers up to C_n n, E. Here, Order of the Point group (h = 2) ⟹ a cyclic point group

Example, H_2O_2, H_3BO_3

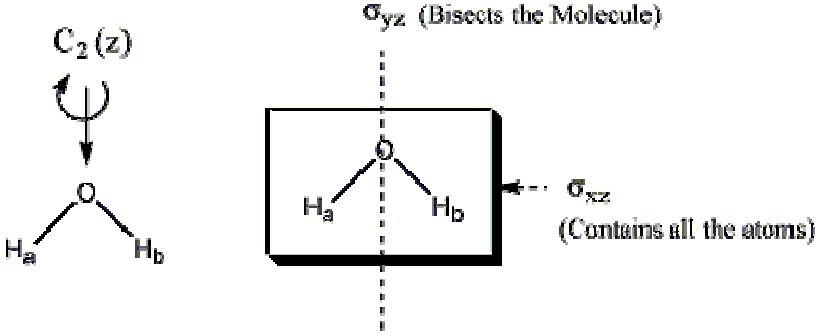


Cnv Point Group: Contains the identity E, an n-fold axis of rotation, and n vertical mirror planes σ_v.

Here, Order of the Point group, h = 2n

C_{2v}: E, C_2, 2 σ_v H_2O

C_{3v}: E, C_3, 3 σ_v NH_3

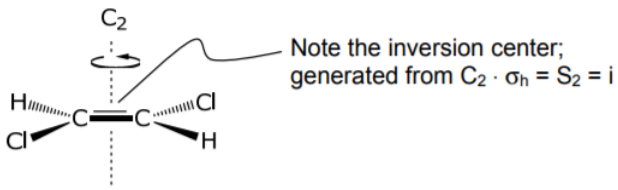


C_{nh} Point Group: Contains the identity, an n-fold axis of rotation, and a horizontal reflection plane σ_h (note that in C_{2h} this combination of symmetry elements automatically implies a centre of inversion).

C_n and σ_h (normal to C_n) are generators of S_n operations as well (h = 2n)

C_{2h}: E, C_2, σ_h, I

Example, Trans: 1,2- Dichloro ethylene



D_n Point Group: Contains the identity, an n-fold axis of rotation, and n 2-fold rotations about axes perpendicular to the principal axis.

D_n: E, C_n, n C_2 axes to C_n

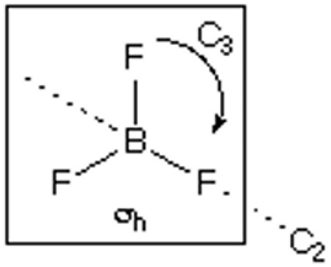
Example, Twistane and trans-trans-trans perhydro-triphenylene

D_2 D_3

D_{nh} Point Group: Contains the same symmetry elements as D_n with the addition of a horizontal mirror plane.

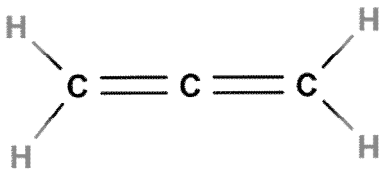
D_{nh}: E, C_n, n C_2 axes , σ_h

D_{3h}: E, C_3, 3 C_2, σ_h



D_{nd} Point Group: Contains the same symmetry elements as D_n with the addition of n dihedral mirror planes.

D_{nd}: E, C_n, n C_2 axes ⊥ to C_n

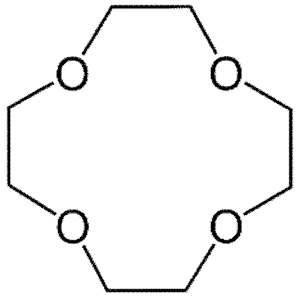


D2d

S_n Point Group: Contains the identity and one Sn axis. Note that molecules only belong to Sn if they have not already been classified in terms of one of the preceding point groups (e.g. S2 is the same as Ci, and a molecule with this symmetry would already have been classified).

S_{2n}: E, C_n, S_{2n} (no mirror planes)

S_4, S_6, S_8, etc. (Note: never S_3, S_5, etc.)



S_4: E, C_2, S_4

15.3.3 Molecules of Special Symmetry:

The following groups are the cubic groups, which contain more than one principal axis. They separate into the tetrahedral groups (T_d, T_h and T) and the octahedral groups (O and O_h). The icosahedral group also exists but is not included below. (T, T_h, O, and I are rare high symmetry groups)

T_d Point Group: Contains all the symmetry elements of a regular tetrahedron, including the identity, 4 C_3 axes, 3 C_2 axes, 6 dihedral mirror planes, and 3 S_4 axes e.g. CH_4.

T Point Group: As for Td but no planes of reflection.

T_h Point Group: As for T but contains a centre of inversion.

O_h Point Group: The group of the regular octahedron e.g. SF_6.

O **Point Group:** As for O_h but with no planes of reflection.

15.4 REPRESENTATION OF GROUPS BY MATRICES:

Group actions, and in particular representations, are very important in group theory, & also to physics and chemistry. Since a group can be thought of as an abstract mathematical object, the same group may arise in different contexts. It is therefore useful to think of a representation of the group as one particular incarnation of the group, which may also have other representations. Any symmetry operation about a symmetry element in a molecule involves the transformation of a set of coordinates x, y, z of an atom into a set of new coordinates x‘, y‘, z‘.

$$\begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

The two sets of coordinates can be related by a set of equation which is formulated in matrix notation. Thus, each symmetry operation can be represented by special matrix which helps to solve structural problems in chemistry.

Matrix Representation of Symmetry Operations:

The matrices for the different symmetry operations can be obtained by considering the effect of these operations on the components of a two-dimensional vector. The results can be extended to 3 dimensions.

Matrix for Rotations:

$$R_x(\theta) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\theta & -\sin\theta \\ 0 & \sin\theta & \cos\theta \end{pmatrix}$$

$$R_y(\theta) = \begin{pmatrix} \cos\theta & 0 & -\sin\theta \\ 0 & 1 & 0 \\ \sin\theta & 0 & \cos\theta \end{pmatrix}$$

$$R_z(\theta) = \begin{pmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Matrix for Reflection Operation:

σ_{xy}

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x \\ y \\ -z \end{bmatrix}$$

σ_{xz}

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x \\ -y \\ z \end{bmatrix}$$

Identity Matrix:

$$E = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Matrix for the Inversion i Operation:

$$i = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

Matrix for Rotatory Reflection Sn(z):

$$S_n(z) = \sigma_z C_n = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} \cos 2\pi/n & \sin 2\pi/n & 0 \\ -\sin 2\pi/n & \cos 2\pi/n & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} \cos 2\pi/n & \sin 2\pi/n & 0 \\ -\sin 2\pi/n & \cos 2\pi/n & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

15.5 CHARACTER OF A REPRESENTATION:

The set of matrices for the various symmetry operations of a point group forms a representation. The set of vectors of the coordinate system, with respect to which the matrices are defined is called the basis of the representation

Example: C_{2h} point group

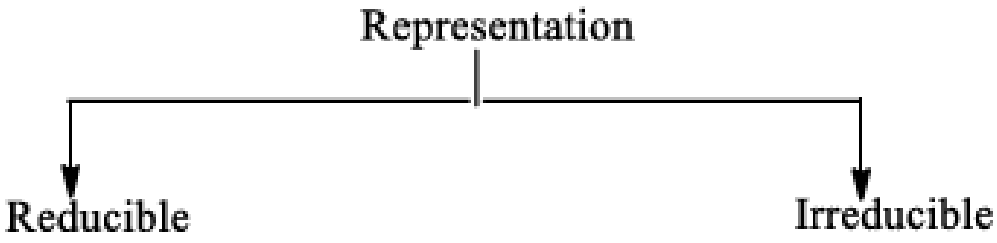
Four symmetry operation – E, C_2, σ_{xy}, i

Matrix representation -

$$\underbrace{\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}}_{C_2} \times \underbrace{\begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}}_{\sigma_v} = \underbrace{\begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}}_{\sigma_v'}$$

15.6 REPRESENTATION OF A GROUPS:

Representation is set of matrices for a group each corresponding to a single operation in the group, that can be combine among themselves in a manner parallel to the way in which the group elements



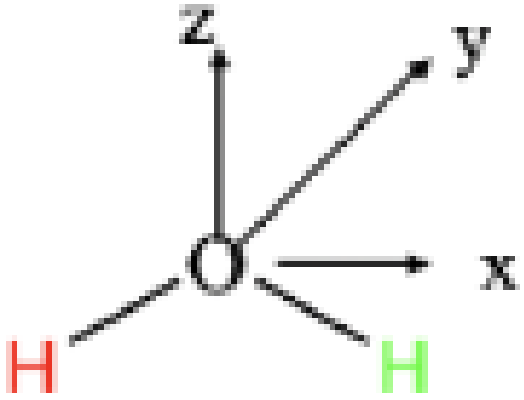
15.6.1 Reducible Representation:

Representation of higher dimension which can reduce to a lower dimension representation it known as reducible Representation.

To drive a reducible representation first of all we have to choose the basis set according to our need.

i) Basis Set: 3-Catesion coordinates (X, Y, Z):

C_{2v}	E	$C_2(Z)$	σ_{xz}	σ_{yz}
X	1	-1	1	-1
Y	1	-1	-1	1
Z	1	1	1	1
Reducible Representation	3	-1	1	1



Dimension E = 3 i.e. 3-dimension reducible representation

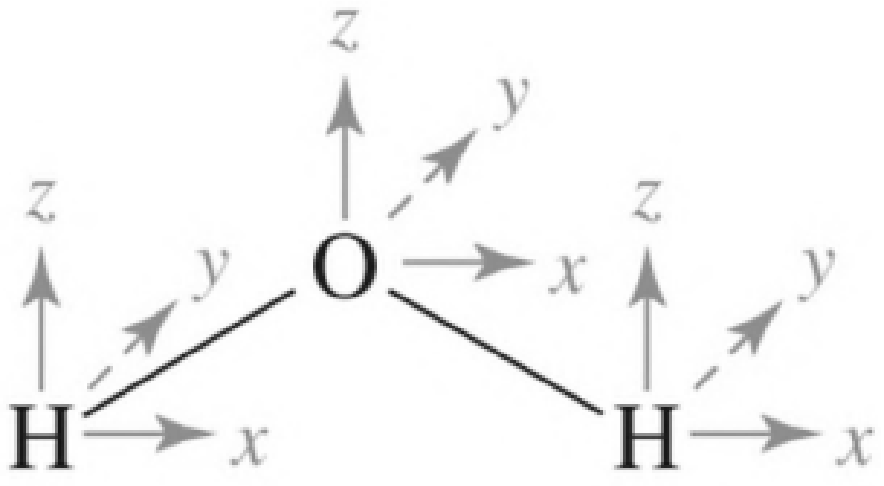
ii) 3N-Cartesian Coordinate:

C_{2V}	E	$C_2(Z)$	σ_{xz}	σ_{yz}
No. of unshifted atom	3	1	1	3
Contribution of atom	3	-1	1	1
Reducible representation	3 X 3	1 X -1	1 X 1	3 X 1
	9	-1	1	3

Dimension E = 9 i.e. 9-dimension reducible representation

iii) Bond Vector: Example, CH_4 i.e. T_d point group

	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
Nomber of unshifted atoms	4	1	0	0	2
Conlribution per atoms	1	1	1	1	1
R.R.	4	**1**	0	0	2



Dimension E = 4, i.e. 4-dimension reducible representation

15.6.2 Irreducible Representation:

A representation of lower dimension which cannot be further reduced is known as irreducible representation. The irreducible representation for a group can derive by using great orthogonality theorem (GOT).

Postulates of Great Orthogonality Theorem (GOT) and derivation of Irreducible representation:

1st Postulate: Number of irreducible representations is always equal to the number of classes.

No. of IR = No. of classes

Example: In H2O molecule there are E, C2(z), σv(xz), σv(yz) elements are present.

The number of order = 4

The number of classes = 4

C_{2v}	E	$C_{2(z)}$	$\sigma v_{(xz)}$	$\sigma v_{(yz)}$
I.R. 1	L_1	M_1	N_1	O_1
I.R. 2	L_2	M_2	N_2	O_2
I.R. 3	L_3	M_3	N_3	O_3
I.R. 4	L_4	M_4	N_4	O_4

Here four IR representations occur because C2v has four classes.

2nd Postulate: The sum of square of dimension of all the IR in the group will equal to the order of group

$$L_1^2+ L_2^2+L_3^2+L_4^2=4$$

$$1^2+1^2+1^2+1^2=4$$

3rd Postulate: The sum of square of the characters of IR will be equal to order of the group.

$$L_1^2+M_2^2+N_3^2+O_4^2 = 4$$

C_{2v}	E	$C_{2(z)}$	$\sigma v_{(xz)}$	$\sigma v_{(yz)}$
I.R. 1	1	1	1	1
I.R. 2	1	M_2	N_2	O_2
I.R. 3	1	M_3	N_3	O_3
I.R. 4	1	M_4	N_4	O_4

4th Postulate: The characters of any two IR in the same group will be always orthogonal to each other (on multiplying any two IR the result should be zero).

$IR_1 \times IR_2 = 0$

$IR_1 \times IR3 = 0$

$IR_1 \times IR_4 = 0$

$IR_3 \times IR_2 = 0$

$IR_4 \times IR_2 = 0$

$IR_1 \times IR_2 = 0$

$1\times1\times L_2+1\times1\times M_2+1\times1\times N_2+1\times1\times O_2 = 0$

$1\times1\times1+1\times1\times1+1\times1\times(-1)+1\times1\times(-1) = 0$

$IR_1 \times IR_3 = 0$

$1\times1\times L_3+1\times1\times M_3+1\times1\times N_3+1\times1\times O_3 = 0$

$1\times1\times1+1\times1\times(-1)+1\times1\times1+1\times1\times(-1) = 0$

$IR_1 \times IR_4 = 0$

$1\times1\times L_4+1\times1\times M_4+1\times1\times N_4+1\times1\times O_4 = 0$

$1\times1\times1+1\times1\times(-1)+1\times1\times(-1)+1\times1\times1 = 0$

C_{2v}	E	$C_{2(z)}$	$\sigma v_{(xz)}$	$\sigma v_{(yz)}$
I.R. 1	1	1	1	1
I.R. 2	1	1	-1	-1
I.R. 3	1	-1	1	-1
I.R. 4	1	-1	-1	1

LESSON - 16

GREAT ORTHOGONALITY THEOREM (GOT) AND APPLICATIONS OF GROUP THEORY

16.1 GREAT ORTHOGONALITY THEOREM (GOT):

This theorem is concerned with the elements of matrices constituting irreducible representation of a point group. The properties of irreducible representations can be obtained from this theorem.

The GTO states:

$$\sum_{G}[\Gamma i(G)mn]\,[\Gamma j(G)m'n']^{*}=(h/\sqrt{lilj})\,\delta ij\delta mm'\delta nn'$$

Where,

h: Order of the group: the number of elements of the group.

I & j are two irreducible representations of the group.

l_i & l_j are the dimensions of these two irreducible representations.

Γ_i: i_{th} irreducible representation.

G: Generic element of the group. It represents particular symmetry operation in the group

$\Gamma_i\,(G)_{mn}$: Matrix element at the intersection of the m_{th} row with nth column of the matrix representing G in the i–th irreducible representation.

$\Gamma_j\,(G)_{mn}$* - The element in the m_{th} & n_{th} column of the matrix in the j_{th} irreducible representation.

$\Gamma j(G)_{m'n'}$ - The complex conjugate of the element in the m_{th} row & n_{th} column of a matrix in the j_{th} irreducible representation.

$\delta_{ij}\delta_{mm'}\,\delta_{nn'}$- Denotes Kronecker Delta symbol. The Kronecker Delta symbol δ_{ij} has the meaning $\delta_{ij} = 0$ for $i \neq j$ & $\delta_{ij}=1$for i=j.

It Shows Three Cases:

$$\sum_{G}[\Gamma i(G)mn]\,[\Gamma i(G)m'n']^{*}=\sum_{G}|[\Gamma i(G)mn]|^{2}=h/li$$

$$\sum_{G}[\Gamma i(G)mn]\,[\Gamma j(G)m'n']^{*}=(h/\sqrt{lilj})\,\delta ij=0$$

$$\sum_{G}[\Gamma i(G)mn]\,[\Gamma j(G)m'n']^{*}=(h/\sqrt{li})\,\delta ij\delta mm'\,\delta nn'=0$$

It represents elements of different set of matrices of same irreducible representation are orthogonal.

16.2 IMPORTANCE OF ORTHOGONALITY THEOREM:

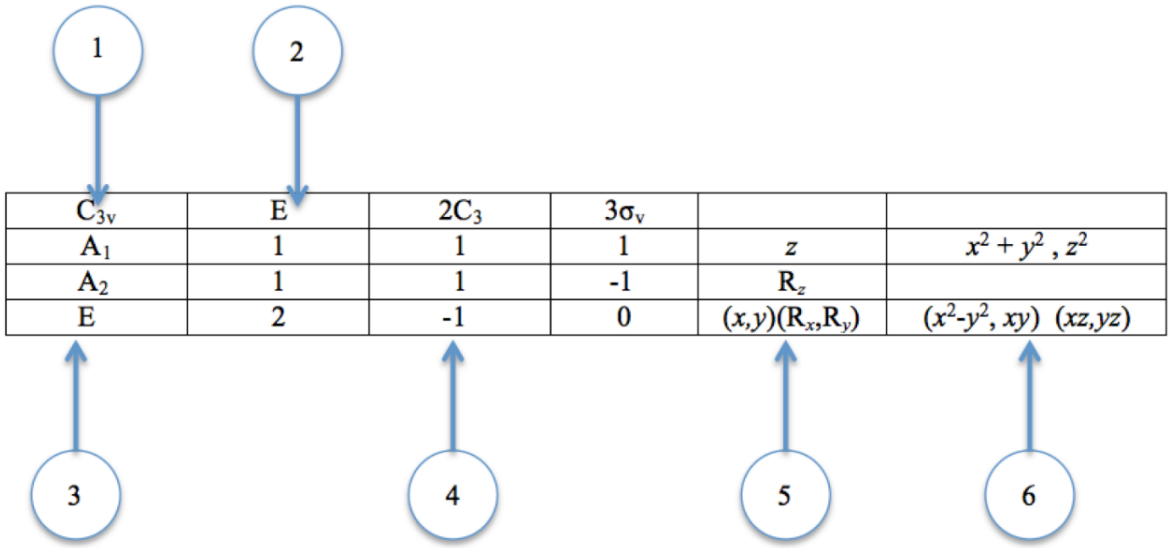
It defines the properties of irreducible representation. By considering the three classes, 5 corollaries can be derived & these gives the 5 rules about the irreducible representation of a group & their character.

16.3 CHARACTER TABLE:

A character table is a 2-dimensional chart associated with a point group that contains the irreducible representations of each point group along with their corresponding matrix characters. It also contains the Mulliken symbols used to describe the dimensions of the irreducible representations, and the functions for symmetry symbols for the Cartesian coordinates as well as rotations about the Cartesian coordinates

Components of a Character Table:

A character table can be separated into 6 different parts, namely:



C_{3v}	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	x^2+y^2 , z^2
A_2	1	1	-1	R_z	
E	2	-1	0	$(x,y)(R_x,R_y)$	(x^2-y^2, xy) (xz,yz)

An example of a character table with different parts labeled:

1) The Point Group
2) The Symmetry Operation
3) The Mulliken Symbols
4) The Characters for the Irreducible Representations
5) The Functions for Symmetry Symbols for Cartesian Coordinates and Rotations
6) The Function for Symmetry Symbols for Square and Binary Products

1. The Point Group:

The symbol for the point group is found on the uppermost left corner of the character table. It denotes a collection of symmetry operations that are present in a molecule. It is called a point group because all the symmetry elements will intersect at one point.

2. The Symmetry Operations/Elements:

A symmetry operation is "a geometrical operation that moves an object about some symmetry element in a way that brings the object into an arrangement that is indistinguishable from the original" (Pfennig, 199). The symmetry operations are at the first row at the top of the table. They are organized into classes, with each class having an order number in front of it. For example, 2S4 represents the operation S4 with order number 2. Operations can belong to the same class when one operation may be replaced by another in a new coordinate system that is accessible by a similar symmetry operation.

Common symmetry operations that are present in character tables are:

E	**C_n**	**C'_n**
σ_d	**σ_v**	**σ_d**
I	**S_n**	**C''_n**

3. The Mulliken Symbols:

These are symbols that occur under the first column of the character table. They are named after Robert S. Mulliken, who suggested using the symbols to describe the irreducible representations. The meanings of the symbols are as follows:

The dimensions/degeneracy of characters are denoted by the letters A, B, E, T, G and H with each letter representing degeneracy 1,1, 2, 3, 4 and 5 respectively i.e.

Mulliken Symbol	Number of Dimensions
A, B	1
E	2
T	3
G	4
H	5

For example, the Mulliken symbol A is singly degenerate and symmetric with respect to the rotation about the principal axis whereas the symbol B is anti-symmetric with respect to rotation about the principal axis even though it is also singly degenerate.

The subscripts featured with each Mulliken symbol also represent different aspects of symmetry i.e.

4. The Characters for Irreducible Representations:

These are the rows of numbers at the centre of the character table. They represent the irreducible representations of each Mulliken symbol under the point group. A representation is "a set of matrices, each corresponding to a single operation in the group, which can be combined amongst themselves similarly to how the group elements (symmetry operations) combine".

These characters correspond to the characters of individual symmetry operations that can be described matrices, themselves. Each character can adopt a +1 or -1 or multiple of this numerical value depending on the symmetric or anti-symmetric behavior of the object undergoing a specific symmetry operation. If the object is symmetric with respect to itself after undergoing the operation, then the character is +1. If the object is anti-symmetric, then the character is -1[5].

5. The Functions for Symmetry Symbols for Cartesian Coordinates and Rotations:

These are the symbols that correspond to the symmetry of the Cartesian coordinates (x, y, z) and the symmetry of the rotations about the Cartesian coordinates (R_x, R_y, R_z). They

form basis representations for the group and are related to the transformation properties of the group.

For example, for the C_{3v} point group, it can be said that z forms a basis for the A_1 representation, x forms a basis for the E representation, and R_z forms a basis for the A_2 representation.

6. The Functions for Symmetry Symbols for Square and Binary Products:

These are the symbols for the functions that correspond to the square (x^2+y^2, z^2, x^2-y^2) and binary products (xy, xy, yz) of the Cartesian Coordinates with respect to their transformation properties.

For example, for the C_{3v} point group, it can be said that z^2 forms a basis for the A_1 representation, (xz,yz) forms a basis for the E representation, and there is no function for the A_2 representation.

Example: The character table for water molecule (for bent XY_2 type molecule) h = 4

Table: Character Table for Water Molecule

C_{2v}	E	$C_{2(z)}$	$\sigma v_{(xz)}$	$\sigma v_{(yz)}$	Basis functions or Symmetry of functions	
A_1	1	1	1	1	Z	x^2, y^2, z^2
A_2	1	1	-1	-1	Rz	Xy
B_1	1	-1	1	-1	(x, Ry)	Yz
B_2	1	-1	-1	1	(y, Rx)	Zx

16.4 APPLICATION OF GROUP THEORY IN IR AND RAMAN SPECTROSCOPY:

Group theory is a powerful tool in IR and Raman spectroscopy, helping chemists predict which vibrational modes are active in each type of spectroscopy.

Objective:

To determine which vibrational modes in a molecule are IR active, Raman active, both, or inactive.

i) Vibrational Modes Overview:

- A molecule with N atoms has: 3N total degrees of freedom
- 3N – 6 vibrational modes (for non-linear molecules)
- 3N – 5 (for linear molecules)
- These vibrational modes can stretch, bend, rock, etc.

ii) Using Group Theory to Analyze Vibrations:

a) **Determine the Point Group:** Use the molecule's symmetry elements to classify it (e.g., C_{2v}, D_{3h}, etc.).

b) **Find the Character Table:** Each point group has a character table with Symmetry operations, Irreducible representations (irreps), and Basis functions like x, y, z (for IR) and x^2, xy, etc. (for Raman)

Example from C_{2v} point group:

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$	IR Active?	Raman Active?
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	–	R_z
B_1	1	-1	1	-1	x	xy
B_2	1	-1	-1	1	y	xz, yz

iii. IR Activity:

- A vibration is IR active if it involves a change in dipole moment.
- Look for irreps that correspond to x, y, or z.
- These are the directions along which dipole moment can change.
- If a vibrational mode transforms as x, y, or z, it is IR active.

iv. Raman Activity:

- A vibration is Raman active if it involves a change in polarizability.
- Look for irreps that correspond to quadratic functions like x^2, yz, etc.
- These relate to changes in the shape of the electron cloud.
- If a mode transforms as quadratic functions, it is Raman active.

v. Complementarity Rule:

- For centrosymmetric molecules (those with an inversion center):
- IR active modes are Raman inactive
- Raman active modes are IR inactive
- This is called mutual exclusion.

Example: CO_2 ($D_{\infty}h$)

Symmetric stretch: Raman active

Asymmetric stretch: IR active

Example: Water (H_2O, C_{2v})

3 atoms → 3N – 6 = 3 vibrational modes

From group theory, modes belong to:

$2 \times A_1$

$1 \times B_2$

From the character table:

A_1: IR and Raman active

B_2: IR and Raman active

So, all three modes in H_2O are both IR and Raman active.

LESSON - 17

ENVIRONMENTAL CHEMISTRY-I

17.1 ENVIRONMENTAL CHEMISTRY: A CONCISE OVERVIEW:

Environmental Chemistry is a branch of chemistry that studies the chemical processes occurring in the environment and the impact of human activities on these processes. It focuses on the composition, behavior, and transformation of chemical substances in air, water, soil, and living organisms. This interdisciplinary field combines elements of chemistry, biology, physics, and environmental science to analyze pollutants, understand natural chemical cycles, and promote sustainability.

The Environment is made up of Four Major Segments:

- **Atmosphere (Air):** Involves reactions like smog formation and acid rain due to pollutants such as NO_x and SO_2.
- **Hydrosphere (Water):** Includes oceans, rivers, and lakes, where pollutants like heavy metals and nutrients can affect aquatic ecosystems.
- **Lithosphere (Soil):** Contamination from industrial waste and pesticides alters soil chemistry and can impact plant and microbial life.
- **Biosphere (Living Organisms):** Reflects how pollutants bioaccumulate and interact with life forms, often entering the food chain.

Environmental chemistry examines both **natural processes** (e.g., carbon and nitrogen cycles) and **human-induced changes** like pollution from industrial, agricultural, and urban sources. Understanding the fate and transport of chemical species is essential for controlling pollution and mitigating its effects on ecosystems and human health.

Air Pollution, caused by emissions from industries and vehicles, includes substances like CO, SO_2, NO_x, ozone, and particulate matter. These degrade air quality, harm health, and contribute to phenomena like smog and climate change.

Water Pollution, results from sources like sewage, agricultural runoff, and chemical spills. Contaminants such as heavy metals and nutrients can lead to eutrophication, bioaccumulation, and disruption of aquatic life.

Soil Pollution, involves harmful substances like pesticides, heavy metals, and industrial chemicals. These can reduce soil fertility and contaminate crops, with implications for food safety and ecosystem health.

Acid Rain, formed when sulfur and nitrogen oxides react with atmospheric moisture, damages vegetation, aquatic systems, and infrastructure. Environmental chemistry helps trace its formation and impact while supporting emission control strategies.

Global Warming is linked to greenhouse gases like CO_2, CH_4, and N_2O. These trap heat in the atmosphere, driving climate change, sea level rise, and extreme weather. Environmental chemists study the sources, behavior, and mitigation of these gases.

In addition to addressing pollution, environmental chemistry is crucial for understanding **natural chemical cycles** (carbon, nitrogen, water) and their disruption due to human actions. It also supports **green chemistry**, which aims to design processes that minimize environmental harm by using safer materials and reducing waste.

Environmental Monitoring relies on tools like mass spectrometry and chromatography to detect pollutants at trace levels. This data informs regulations, assesses ecosystem health, and guides remediation efforts.

Ultimately, environmental chemistry plays a key role in **public health, sustainability, and policy development**. It provides the scientific foundation for pollution control, environmental protection, and the development of clean technologies. By understanding chemical interactions in the environment, we can create more sustainable solutions for a healthier planet.

17.2 CLASSIFICATION OF ENVIRONMENTAL SEGMENTS:

Environmental chemistry classifies the environment into four major segments based on the physical components that make up the Earth's system. Each segment plays a crucial role in supporting life and is interconnected through various chemical and biological processes.

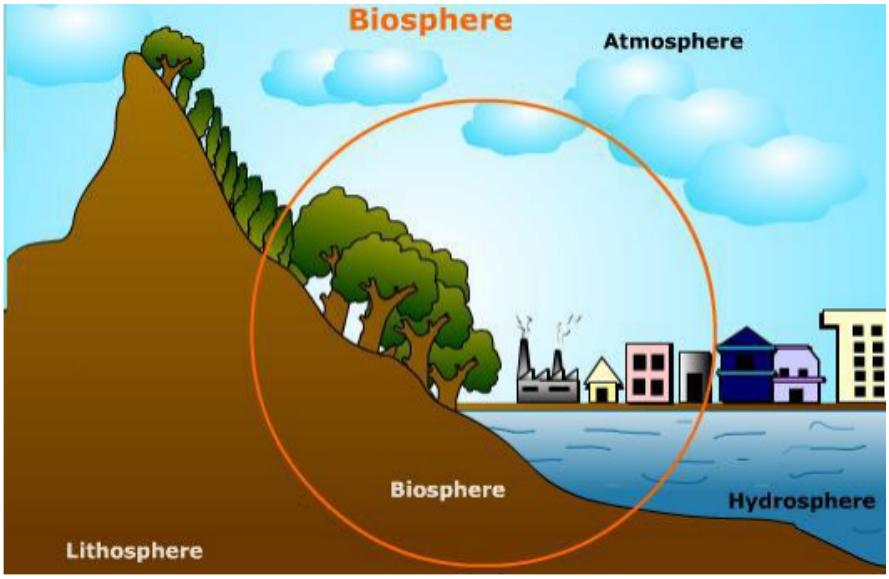


Figure 17.1 Environmental Segments

17.2.1 Atmosphere:

The atmosphere is the layer of gases that surrounds the Earth, held in place by gravity. It is composed primarily of nitrogen (about 78%) and oxygen (around 21%), with trace amounts of carbon dioxide, argon, water vapor, and other gases. This layer is essential for life, providing oxygen for respiration and protecting living organisms from the Sun's harmful ultraviolet (UV) radiation through the ozone layer. Environmental chemistry studies the physical and chemical processes within the atmosphere, such as the formation of air pollutants, greenhouse gases, and acid rain. For example, nitrogen oxides (NO_x) and sulfur dioxide (SO_2) released from vehicles and industrial sources react with water vapor to form nitric and sulfuric acids, leading to acid rain. Photochemical smog is another atmospheric phenomenon caused by sunlight-driven reactions involving volatile organic compounds (VOCs) and nitrogen oxides. These processes have direct implications for air quality, human health, and climate regulation.

The atmosphere is also the site of key chemical phenomena. Photochemical reactions, such as the formation of ground-level ozone, are triggered by sunlight interacting with pollutants. Acid rain results from the conversion of SO_2 and NO_x into sulfuric and nitric acids. Ozone depletion, particularly in the stratosphere, occurs due to the breakdown of ozone molecules by chlorofluorocarbons (CFCs). Additionally, greenhouse gases like carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O) trap infrared radiation, contributing to global warming and climate change. These chemical processes influence weather patterns, environmental conditions, and the overall health of ecosystems.

The Earth's atmosphere is divided into five distinct layers, each with unique characteristics. The troposphere, the lowest layer extending up to 15 kilometers above the surface, contains most of the atmospheric mass and is where weather phenomena such as clouds and storms occur. It is also where most human activity takes place, and the temperature decreases with altitude in this layer. Above it lies the stratosphere, extending to about 50 kilometers. Unlike the troposphere, the temperature here increases with altitude due to the presence of the ozone layer, which absorbs UV radiation. This layer is important for protecting life on Earth and is also used for high-altitude air travel.

The mesosphere extends from 50 to 85 kilometers above the Earth and is characterized by extremely low temperatures, often reaching -90°C. It is the layer where meteors burn up upon entry into the atmosphere, producing visible shooting stars. The thermosphere, reaching up to 600 kilometers, experiences high temperatures due to the

absorption of solar radiation. Despite the high temperatures, it feels cold due to the low density of particles. This layer supports satellite operations, radio communications, and houses the International Space Station (ISS). Finally, the exosphere is the outermost layer, gradually transitioning into outer space. It consists mainly of hydrogen and helium and has very low pressure and density. Gases in this layer can escape into space, and it plays a role in long-term climate monitoring and space research.

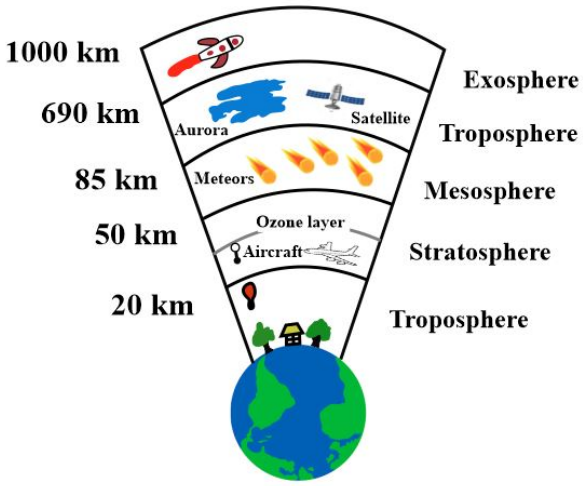


Figure 17.2 Layers of Atmosphere

Below is a table summarizing the different layers of Earth's atmosphere, their temperature ranges, altitude ranges, and key features:

Layer of Atmosphere	Temperature with Altitude	Key Features	Temperature Range	Altitude Range
Troposphere	Decreases with altitude	Weather, breathable air, UV protection	-55°C to 20°C	0 to 15 kilometres
Stratosphere	Increases with altitude	Ozone layer, UV protection	-55°C to 20°C	15 to 50 kilometers
Mesosphere	Decreases with altitude	Meteor protection	-90°C to -55°C	50 to 85 kilometers
Thermosphere	High, but thin atmosphere	Satellite orbits, radio signals	-55°C to 500°C	85 to 600 kilometers
Exosphere	Virtually no atmosphere	Transition to space, spacecraft passage	500°C to 2000°C	600 to 10,000 kilometers

17.2.2 Hydrosphere:

The hydrosphere includes all the water present on, beneath, and above the Earth's surface-oceans, rivers, lakes, glaciers, groundwater, and atmospheric vapor. Covering about 71% of the planet, water is essential for all life forms and plays a vital role in shaping natural and human environments. Despite the abundance of water, over 97% is saline and found in oceans, while only about 1% is accessible freshwater used for drinking, agriculture, and industry.

In environmental chemistry, the hydrosphere is studied to understand water distribution, movement, and quality. Pollutants like heavy metals, nitrates, and organic compounds can significantly impact ecosystems and human health. Excess nutrients, for example, can cause eutrophication, which depletes oxygen in water bodies and harms aquatic life.

Water is also central to Earth's biogeochemical cycles and energy flow. It acts as a carrier of minerals, nutrients, and heat. In the anthrosphere, water supports technological systems like municipal supply, industrial processes, and power generation. It also helps regulate climate through heat redistribution and atmospheric circulation.

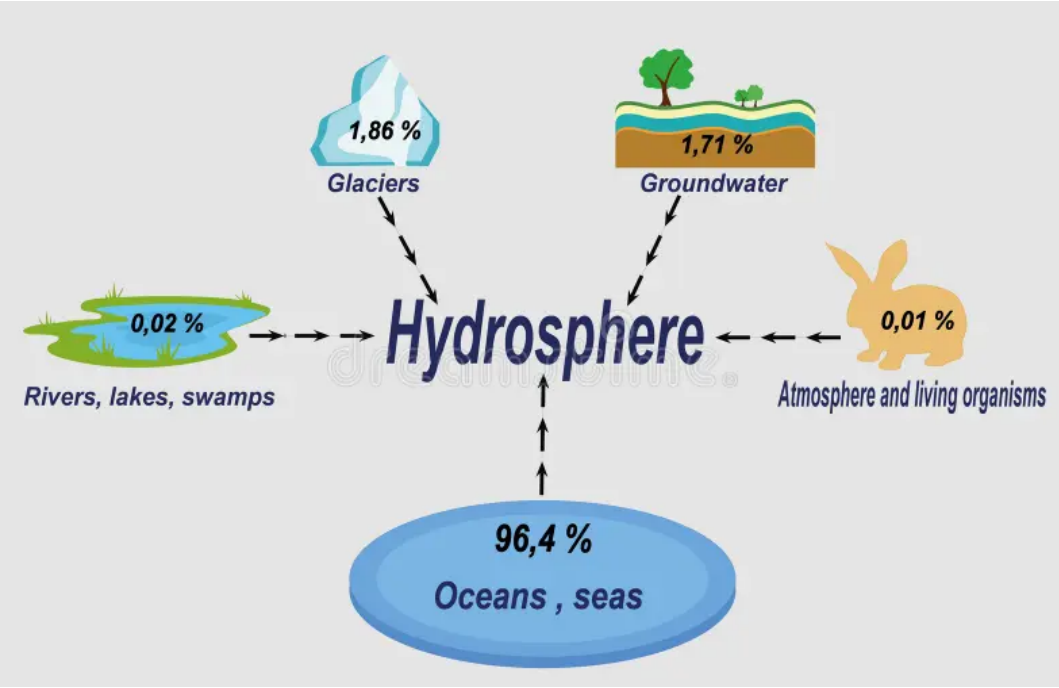


Figure 17.3 Distribution of Earth's Water Supply

Water is fundamental to environmental chemistry (covered in more depth in Chapters 3 through 8) and serves as a crucial agent in the transport of energy and matter throughout

Earth's systems. In the anthrosphere - the human-influenced segment of the environment - water is integral to various technological systems, including municipal water supply networks, industrial boilers, and energy production.

Across all environmental spheres, water is a powerful carrier:

- It leaches soluble minerals from geological formations and transports them either to the oceans or to new locations, where they may precipitate as mineral deposits.
- It delivers essential nutrients from the soil into plants via their root systems, enabling the growth of vegetation that sustains ecosystems.
- Through the process of evaporation, water absorbs solar energy, which is then transported as latent heat and released inland during condensation. This heat transfer is a major driver of global energy movement.
- Water movement contributes to climate regulation by redistributing thermal energy from the equator toward the poles and is a major force behind atmospheric circulation and storm formation.
- Thus, water not only sustains life but also acts as a dynamic force in shaping Earth's physical, chemical, and biological environments. It links the atmosphere (air), lithosphere (earth), biosphere (life), and anthrosphere (human activity) into an interconnected system.

17.2.3. Lithosphere:

The lithosphere is the rigid, outermost shell of the Earth, composed of the crust and the uppermost portion of the mantle that behaves elastically over long geological timescales. It serves as the solid foundation of the planet and is defined by its chemical composition and mineralogical characteristics. This layer interacts with other Earth systems - such as the atmosphere, hydrosphere, and biosphere - primarily through the uppermost zone known as the *pedosphere,* where soil formation occurs.

The composition of the lithosphere is not uniform; the Earth's crust comprises various rock types arranged in layers. Sedimentary rocks typically form the surface, followed by granitic and metamorphic rocks in the middle, and denser basaltic rocks at the base. Additionally, the crust is segmented into large, dynamic tectonic plates that float atop the semi-fluid asthenosphere. These plates are in constant motion, drifting at an average rate of about 10 cm per year. This movement has played a significant role in shaping the Earth's surface; for instance, around 180 million years ago, North America and Europe were part of a single landmass before the Atlantic Ocean formed due to the divergence of the Eurasian and North American plates.

There are two primary types of lithosphere: the *oceanic lithosphere*, which is associated with dense, basaltic oceanic crust and found beneath the ocean basins; and the *continental lithosphere*, which is thicker, less dense, and associated with granitic continental crust. These structural differences influence geological activity, such as the formation of mountains, earthquakes, and volcanic eruptions.

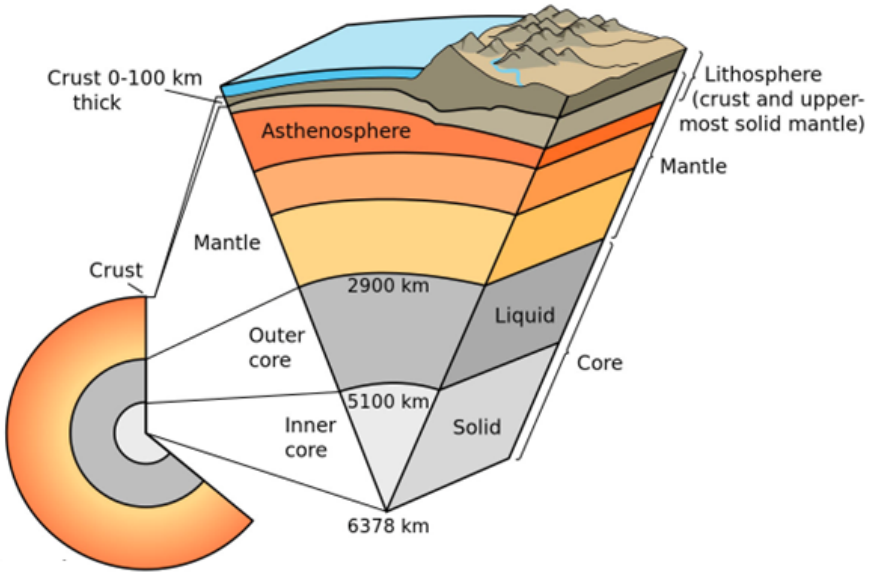


Figure 17.4: Lithosphere

The above diagram illustrates the Earth's internal structure, showing its major layers: the crust, mantle, and core. The lithosphere, comprising the crust and the uppermost solid mantle, lies above the asthenosphere, a semi-fluid layer that allows tectonic plates to move. Beneath the mantle is the core, divided into a liquid outer core and a solid inner core. Depth measurements (in km) mark the boundaries: the mantle begins below the crust, the core starts around 2900 km, and the inner core at 5100 km, ending at Earth’s center (6378 km). The image also contrasts the internal layers to scale and not to scale.

17.2.4. Biosphere:

The biosphere refers to the global sum of all living organisms and their interactions with the atmosphere, hydrosphere, and lithosphere. It is an intricate and vast system divided into smaller units called ecosystems, where plants, animals, and microorganisms coexist with physical components like soil, water, and air. These ecosystems are interconnected through natural cycles such as the hydrologic, oxygen, nitrogen, phosphorus, and sulfur cycles. These cycles ensure a balanced circulation of essential elements, sustaining and stabilizing life on Earth.

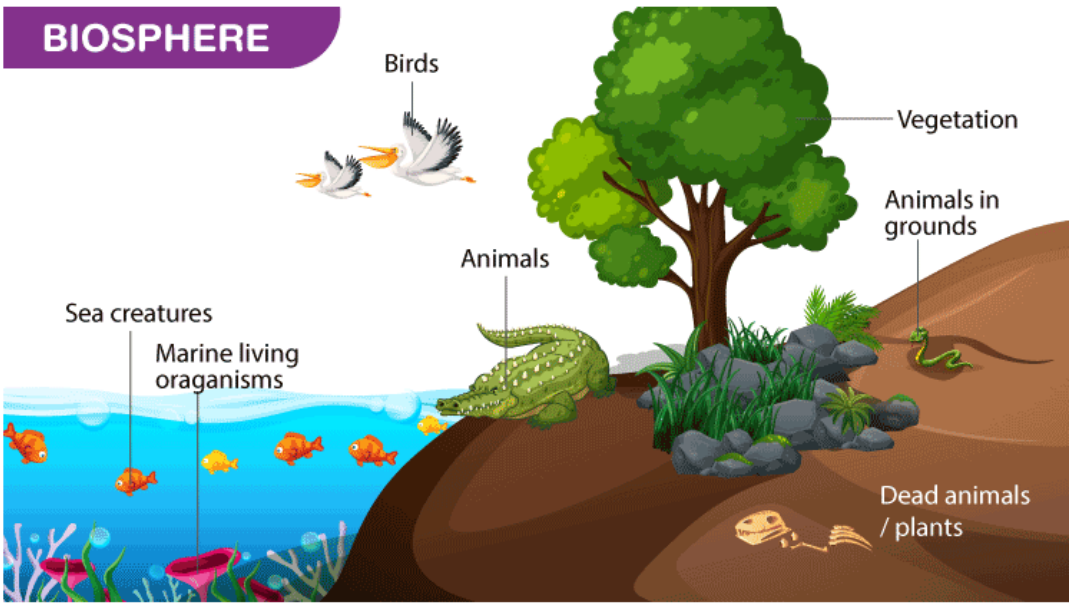


Figure 17.5 Biosphere

Importance of the Biosphere: The biosphere is essential for survival as it provides ecosystems that support biodiversity, food sources, and climate adaptation. It functions as Earth's life support system by regulating atmospheric composition, soil health, and water cycles. Biosphere reserves are designated safe zones for conserving biodiversity and protecting traditional ways of life, especially for indigenous communities. As the highest level of ecological organization, the biosphere encompasses all biomes and living systems on Earth.

Examples of the Biosphere: The biosphere includes all regions where life exists - ranging from deep within Earth's crust to the lower atmosphere. It combines parts of the lithosphere, atmosphere, and hydrosphere where conditions support life. Each biome within the biosphere has unique climates, organisms, and adaptations. Photosynthesis drives energy flow in ecosystems, and biospheric processes are closely linked with atmospheric and geospheric cycles, especially in regulating CO_2 levels through the balance between respiration and photosynthesis.

Prof. M. Subba Rao

LESSON - 18

ENVIRONMENTAL CHEMISTRY - II

18.1 TYPES OF POLLUTION:

There are various types of pollution chiefly arising as a result of anthropogenic causes. Also contributing to pollution is globalisation, where humanity's constant need for natural resources has slowly started to change the face of the earth.

Though the quality of living has drastically improved, other new issues have risen that gradually impact human health and the environment. In this article, we shall explore the meaning, causes and types of pollution. Also, we shall analyse the repercussions of pollution on human health and the environment.

As stated before, there are different types of pollution, which are either caused by natural events (like forest fires) or by man-made activities (like cars, factories, nuclear wastes, etc.) These are further classified into the following types of pollution:

- Air Pollution
- Water Pollution
- Soil Pollution
- Noise Pollution

Besides these 4 types of pollution, other types exist such as light pollution, thermal pollution and radioactive pollution. The latter is much rarer than other types, but it is the deadliest.

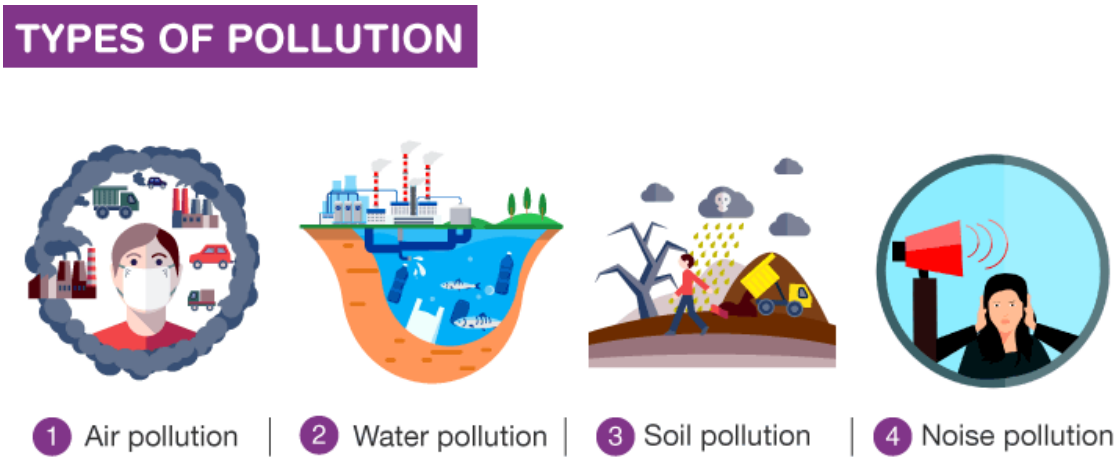


Figure 18.1: Types of Pollution

18.1.1 Air pollution, involves the emission of harmful substances like toxic gases, particulates, and chemicals into the atmosphere, often from sources such as burning fossil fuels, mining, and industrial emissions. Its effects include respiratory and cardiovascular issues, skin diseases, global warming, and damage to ecosystems. In extreme scenarios, it could even contribute to a runaway greenhouse effect similar to what is theorized to have occurred on Venus.

18.1.2 Water pollution, occurs when contaminants like industrial waste, sewage, and agricultural runoff enter water bodies. This not only threatens marine life but also poses serious health risks to humans through the accumulation of toxins in the food chain. Historical events, such as mercury poisoning in Japan's Minamata Bay, illustrate the severe consequences of water pollution on communities.

18.1.3 Soil pollution, or land contamination, results from the introduction of harmful substances into the soil through activities like industrial waste dumping, excessive use of pesticides, and acid rain. These pollutants can be absorbed by plants and passed up the food chain, affecting entire ecosystems. Long-term exposure can lead to uninhabitable land, as seen in the Chernobyl disaster.

18.1.4 Noise pollution, is characterized by excessive or disruptive sounds from urbanization, transportation, industry, and social activities. Sounds above 85 decibels can harm hearing and lead to other health issues such as stress, sleep disturbances, and high blood pressure. Unlike other forms of pollution, noise is more immediately perceptible but equally harmful.

18.2 ACID RAIN:

Acid rain refers to the precipitation of rainwater that has been rendered acidic due to the presence of certain pollutants in the atmosphere. It forms primarily when sulfur dioxide (SO_2) and nitrogen oxides (NO_x), released into the atmosphere from burning fossil fuels, react with water vapor to form sulfuric and nitric acids. These acids then mix with rainwater and fall to the earth as acid rain.

The chemical reactions leading to acid rain include:

1. **Formation of sulfuric acid:**

- **$SO_2 + O_2 \rightarrow SO_3$**
- **$SO_3 + H_2O \rightarrow H_2SO_4$ (sulfuric acid)**

2. **Formation of nitric acid:**

- **$2NO + O_2 \rightarrow 2NO_2$**
- **$4NO_2 + 2H_2O + O_2 \rightarrow 4HNO_3$ (nitric acid)**

These acids lower the pH of rainwater (normal rain has a pH of around 5.6 due to dissolved CO_2 forming weak carbonic acid), often making it fall below pH 4.0.

Figure 18.2

18.2.1 Effects of Acid Rain:

Acid rain has numerous harmful effects on the environment. It leaches vital nutrients like calcium and magnesium from the soil, affecting plant growth. It also damages aquatic ecosystems by lowering the pH of lakes and rivers, which can be fatal to fish and other aquatic organisms. Furthermore, acid rain accelerates the decay of buildings, monuments, and cultural heritage, especially those made of limestone or marble, through reactions like:

$CaCO_3$ (limestone) + $H_2SO_4 \rightarrow CaSO_4 + CO_2 + H_2O$

Human health can also be indirectly affected through the contamination of drinking water and the food chain.

To mitigate acid rain, reducing emissions of SO_2 and NO_x is essential. This can be achieved through cleaner energy sources, using scrubbers in industrial chimneys, and promoting public awareness and environmental regulations.

The effects of acid rain are severe. It leaches essential nutrients from soil, affecting plant growth and agriculture. When it enters aquatic ecosystems, it lowers water pH, disrupting marine life and causing water pollution. Acid rain also damages infrastructure; it corrodes metal and deteriorates stone structures. For instance, the Taj Mahal in Agra has suffered significant marble corrosion due to sulfuric acid reacting with calcium carbonate:

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

Similarly, the Statue of Liberty, made of copper, has undergone color changes and corrosion due to prolonged exposure to acid rain and oxidation. Acid rain, therefore, is a critical environmental issue, demanding stricter pollution control and cleaner energy practices.

Before and After effects of acid rain on the Taj Mahal

Figure 18.3

18.2.2 Prevention of Acid Rain:

The only precaution that we can take against acid rain is having a check at the emission of oxides of nitrogen and sulphur.

- Acid rain is harmful to animals, plants and the monuments.
- Being responsible citizens, one should be aware of the harmful effects they cause and of the industries which give out nitrogen and sulphur compound wastes unethically.

18.3 GLOBAL WARMING:

"*Global warming is a gradual increase in the earth's temperature generally due to the greenhouse effect caused by increased levels of carbon dioxide, CFCs, and other pollutants".*

18.3.1 Global Warming: Causes, Effects, and Impact:

Global warming refers to the long-term rise in Earth's average surface temperature due to increased concentrations of greenhouse gases in the atmosphere. This phenomenon is

primarily driven by human activities such as burning fossil fuels (coal, oil, and natural gas), deforestation, and large-scale industrialization. These activities release excessive amounts of **carbon dioxide (CO_2)**, **methane (CH_4)**, **nitrous oxide (N_2O)**, and **chlorofluorocarbons (CFCs)**, which trap heat in the Earth's atmosphere—a process known as the **greenhouse effect**. Under natural conditions, this effect is crucial for maintaining life-supporting temperatures, but the excess accumulation of gases enhances the effect unnaturally, leading to global warming.

The consequences of global warming are profound and far-reaching. One of the most visible effects is the **melting of polar ice caps and glaciers**, which contributes to **rising sea levels**, threatening coastal communities and ecosystems. Global warming also leads to **more frequent and severe weather events**, such as hurricanes, droughts, floods, and heatwaves. **Agriculture** is impacted through altered rainfall patterns and reduced crop yields, posing a threat to global food security.

Furthermore, rising temperatures affect **biodiversity** by altering habitats and causing species extinction. Ocean warming and acidification, caused by increased CO_2 absorption, damage marine ecosystems, including coral reefs. Human health is also at risk due to heat-related illnesses, the spread of vector-borne diseases, and respiratory issues from air pollution.

To mitigate global warming, global cooperation is essential. This includes reducing greenhouse gas emissions through clean energy sources like **solar**, **wind**, and **hydropower**, enhancing **energy efficiency**, protecting forests, and adopting sustainable lifestyles. Agreements like the **Paris Climate Accord** aim to limit temperature rise to below 2°C above pre-industrial levels.

In essence, global warming is a pressing environmental issue that requires immediate and collective action to protect the planet for future generations.

18.3.2 The Greenhouse Effect and Its Role in Global Warming:

To understand the connection between the greenhouse effect, climate change, and global warming, it's essential to first grasp what the greenhouse effect actually is. A useful everyday example is stepping into a parked car on a hot day - it feels significantly warmer inside than outside. This happens because sunlight (composed of ultraviolet radiation, visible light, and infrared radiation) enters through the car's glass windows but is not completely

able to escape. The glass traps the heat, as does the build-up of gases inside, leading to a rise in internal temperature. This same principle applies to greenhouses used in agriculture, which are made primarily of glass to trap heat and create a warmer environment ideal for plant growth.

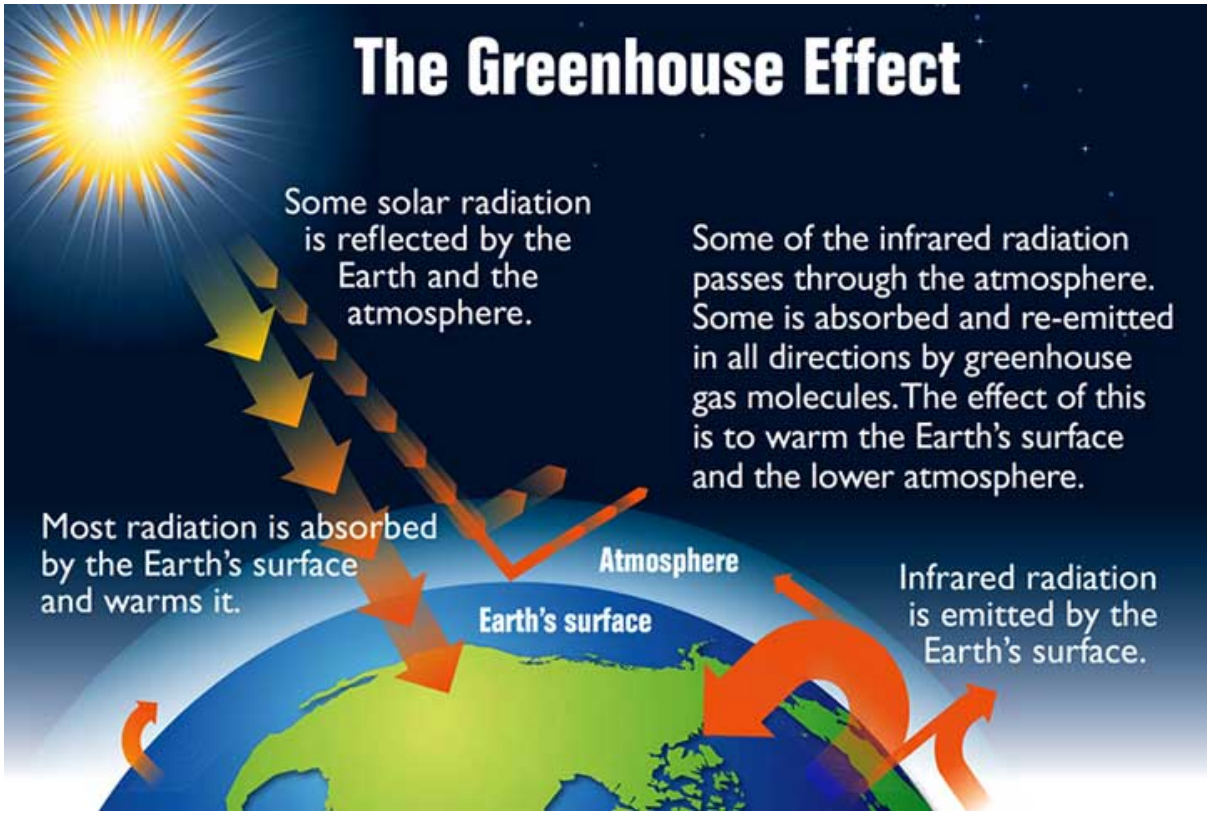


Figure 18.4

On a global scale, a similar phenomenon occurs due to the Earth's atmosphere. Certain gases - namely carbon dioxide (CO_2), methane (CH_4), water vapour, and nitrous oxide (N_2O) - act like the glass of a greenhouse, allowing sunlight to enter while trapping some of the outgoing heat. These **greenhouse gases** (GHGs), which occur naturally, are crucial in maintaining Earth's habitable temperature. Without them, the planet would be about 33°C (60°F) colder, rendering life as we know it impossible.

However, since the 18th century and the onset of industrialisation, the atmospheric concentration of these gases - particularly CO_2 - has increased dramatically, rising by nearly 40%. Human activities such as burning fossil fuels, deforestation, and large-scale agriculture have intensified the greenhouse effect unnaturally. This enhanced greenhouse effect is the primary driver of **global warming**, a sustained rise in Earth's average surface temperature.

18.3.3 Climate Change as a Consequence of Global Warming:

There is a strong scientific consensus that the Earth's climate has warmed significantly over the past century. This warming trend is causing glaciers and polar ice caps to melt, leading to rising sea levels and threatening coastal regions. Freshwater sources are diminishing, and ocean acidification is altering marine ecosystems. Moreover, the increase in temperature is contributing to the frequency and intensity of extreme weather events, including hurricanes, droughts, and floods.

According to organizations like NASA, unchecked global warming may lead to irreversible environmental damage. Some scientists, such as Josef Werne of the University of Pittsburgh, suggest that we may have already passed a critical threshold. While complete prevention may no longer be possible, it is still feasible to **mitigate** the severity of climate change through robust policy measures, technological innovation, and international cooperation. Others remain more optimistic, believing that through stringent global agreements and collective action, we can slow or even reverse some of the damage.

18.3.4 Greenhouse Gases and Their Impact:

Greenhouse gases are chemical compounds in the atmosphere that absorb and emit infrared radiation. While they allow shortwave solar radiation to pass through, they trap the longer-wavelength infrared radiation (heat) emitted by the Earth's surface. This retained heat warms the planet and is known as the **greenhouse effect**. Although naturally occurring and vital to sustaining life, excessive greenhouse gases can upset Earth's energy balance.

The major greenhouse gases include:

- **Carbon dioxide (CO_2):** Released through burning fossil fuels, deforestation, and various industrial processes.
- **Methane (CH_4):** Emitted by agricultural practices, landfills, and fossil fuel production.
- **Nitrous oxide (N_2O):** Arising from agricultural activities and industrial emissions.
- **Industrial Gases:** Such as hydrofluorocarbons (HFCs), perfluorocarbons (PFCs), and sulphur hexafluoride (SF_6), which are synthetic and have high global warming potential.

The increasing concentration of these gases, as depicted in atmospheric data charts, underscores the urgent need for climate action. Without deliberate intervention, the greenhouse effect will continue to intensify, driving global temperatures higher and further destabilising ecosystems worldwide.

LESSON - 19

CHEMISTRY OF BIOMOLECULES-I

19.1 CHEMISTRY OF BIOMOLECULES: DEFINITION

The chemistry of biomolecules is a branch of chemistry that deals with the study of chemical processes and compounds that occur within living organisms. Biomolecules are organic molecules that are essential for life and are involved in various biological functions such as growth, development, metabolism, and reproduction.

These molecules include carbohydrates, proteins, lipids, nucleic acids, enzymes, and vitamins. Each of these biomolecules plays a critical role in maintaining the structure and function of cells and organisms. The chemistry of biomolecules involves understanding their structure, function, interactions, and biosynthesis, as well as how they are broken down and utilized in biological systems.

A **biomolecule**, also known as a **biological molecule**, refers to any chemical compound that is produced by or found within living organisms and is essential for various biological functions such as cell division, development (morphogenesis), and overall functioning. Biomolecules include both **macromolecules** like **proteins, carbohydrates, lipids, and nucleic acids**, as well as smaller **primary and secondary metabolites**. Collectively, these substances are often termed **biological materials**.

Biomolecules are crucial components of life. Some are synthesized internally by organisms (**endogenous biomolecules**), while others must be acquired externally through diet or the environment (**exogenous biomolecules**), such as essential nutrients.

The field of **biochemistry** focuses on the chemical processes within living organisms, particularly the roles and interactions of biomolecules. Over the past century, research in biochemistry has led to the discovery that, at the molecular level, all living organisms exhibit remarkable **uniformity** in their biomolecular makeup.

19.1.1 Properties of Biomolecules:

- **Organic Nature:** Biomolecules are primarily organic compounds. Unlike general organic molecules, biomolecules exhibit consistent chemical behavior and follow the same physical principles across different life forms.

- **Elemental Composition: Carbon** is the central element, forming versatile structures such as linear chains, branched frameworks, rings, and aromatic compounds. Other essential elements include **hydrogen (H), oxygen (O), nitrogen (N), phosphorus (P), and sulfur (S)**. Trace elements like **iodine** and metals also play key biological roles.
- **Functional Groups:** Biomolecules contain common functional groups such as **hydroxyl (-OH)**, **amino (-NH2)**, **carbonyl (C=O)**, and **carboxyl (-COOH)**. Many are **polyfunctional**, meaning they contain multiple functional groups influencing each other's reactivity.
- **Structural Categories:**
  - **Micromolecules**: Small biomolecules with low molecular weights (18–800 Da) and high solubility. These include **minerals, amino acids, and nucleotides**. They can be organic or inorganic.
  - **Macromolecules**: Large biomolecules (typically >800 Da) with low solubility, including **carbohydrates, proteins, nucleic acids, and lipids** (though lipids don't polymerize like the others).

Most biomolecules have **complex 3D structures**, stabilized by **non-covalent interactions**, essential for their function.

19.1.2 Types of Biomolecules:

1. Amino Acids and Proteins:

- **Amino acids** are organic molecules containing both amino and carboxyl groups, usually attached to the same carbon (the α-carbon).
- They serve as the building blocks of **proteins**, provide energy, and act as precursors to other biomolecules (e.g., hormones).
- **Proteins** are long chains (polymers) of amino acids that fold into specific 3D structures. They function as **enzymes, structural components, transport molecules, antibodies**, and more.

2. Carbohydrates (Sugars and Starch):

- Carbohydrates are **polyhydroxy aldehydes or ketones** and their derivatives.
- They are a primary energy source and also serve **structural functions**.
- **Monosaccharides** (1 unit), **oligosaccharides** (2-10 units), and **polysaccharides** (>10 units) are the structural classifications based on sugar units.

3. Lipids (Fats and Oils):

- Lipids are **water-insoluble** biomolecules, mainly **esters of fatty acids and alcohols**.
- They serve as **energy stores**, **membrane components**, and **precursors of hormones and vitamins**.
- Though they do not form polymers, lipids can assemble into large structures (e.g., membranes) via **non-covalent interactions**.

4. Nucleotides and Nucleic Acids:

- **Nucleotides** are composed of a nitrogenous base, a sugar, and a phosphate group.
- They participate in **energy transfer (e.g., ATP)** and **enzyme activity**.
- **Nucleic acids** (DNA and RNA) are polymers of nucleotides that store, transmit, and express **genetic information**, typically structured as a **double helix**.

5. Small Organic Molecules:

Cells also rely on numerous **small organic molecules** that don't fit neatly into the major classes. These include **vitamin-related cofactors, intermediates in metabolism**, and **signaling molecules**.

6. Inorganic Ions:

- Though not organic, **inorganic ions** like **Ca^{2+}, Na^{+}, $Fe^{2+/3+}$, Mg^{2+}, K^{+}**, and **Cl^{-}** are vital to life.
- They support **structural integrity (e.g., calcium in bones)**, **osmotic balance**, **electrical conductivity**, and are **cofactors in enzyme functions**.

19.1.3 Combinations of Biomolecules:

Certain biomolecules are hybrids of two major classes:

- **Lipoproteins**: Combinations of **lipids and proteins**, important in lipid transport.
- **Glycoproteins**: Combinations of **carbohydrates and proteins**, involved in **cell recognition and immune function**.

19.2 FUNCTIONAL USES AND EXAMPLES FOR CARBOHYDRATES:

19.2.1 Carbohydrates:

Carbohydrates are the most abundant organic molecules in nature, primarily composed of carbon, hydrogen, and oxygen. The term "carbohydrate" literally means

"hydrates of carbon," and many of them follow the empirical formula $(CH_2O)_n$, where n is typically equal to or greater than 3. This suggests that carbohydrates are carbon hydrates; however, some compounds like acetic acid ($C_2H_4O_2$) and lactic acid ($C_3H_6O_3$) also resemble carbon hydrates but are not classified as carbohydrates. Conversely, certain authentic carbohydrates such as rhamnohexose ($C_6H_{12}O_5$) and deoxyribose ($C_5H_{10}O_4$) do not strictly follow the general formula, indicating that carbohydrates cannot always be defined as simple hydrates of carbon. Instead, carbohydrates are best defined as polyhydroxy aldehydes or ketones, or substances that yield such compounds upon hydrolysis. Carbohydrates that are water-soluble and sweet to taste are commonly referred to as sugars.

Carbohydrates are primarily produced by plants and represent a large group of naturally occurring organic compounds. Common examples include cane sugar, glucose, and starch. Most carbohydrates have a general formula of $Cx(H_2O)y$, which originally led to the belief that they were hydrates of carbon—hence the name *carbohydrates*. For instance, glucose has the molecular formula $C_6H_{12}O_6$, which fits the general formula as $C_6(H_2O)_6$.

However, not all compounds that fit this formula are classified as carbohydrates. For example, acetic acid (CH_3COOH) fits $C_2(H_2O)_2$ but is not a carbohydrate. Conversely, rhamnose ($C_6H_{12}O_5$) is a carbohydrate but does not strictly fit this formula. This shows that structural characteristics, not just molecular formulae, define carbohydrates.

19.2.1.1 Chemical Nature of Carbohydrates:

Structurally, carbohydrates are organic compounds organized as aldehydes or ketones with multiple hydroxyl groups attached to a carbon backbone. The basic building blocks of all carbohydrates are monosaccharides—simple sugars that can be either polyhydroxy aldehydes (aldoses) or polyhydroxy ketones (ketoses). These molecules can be represented in three structural forms: open-chain, hemiacetal, and Haworth structures. The open-chain form is a linear arrangement of carbon atoms; the hemiacetal structure arises when the first carbon of glucose reacts with the hydroxyl group on the fifth carbon to form a ring; and the Haworth structure depicts a cyclic pyranose ring.

Carbohydrates exhibit several distinctive physical properties. Stereoisomerism occurs when compounds have the same structural formula but differ in spatial arrangement; for example, D-glucose and L-glucose are isomers differing at the penultimate carbon. Optical activity is another key trait, as carbohydrates can rotate plane-polarized light - glucose exists in both dextrorotatory (+) and levorotatory (–) forms. Diastereomers, such as mannose and

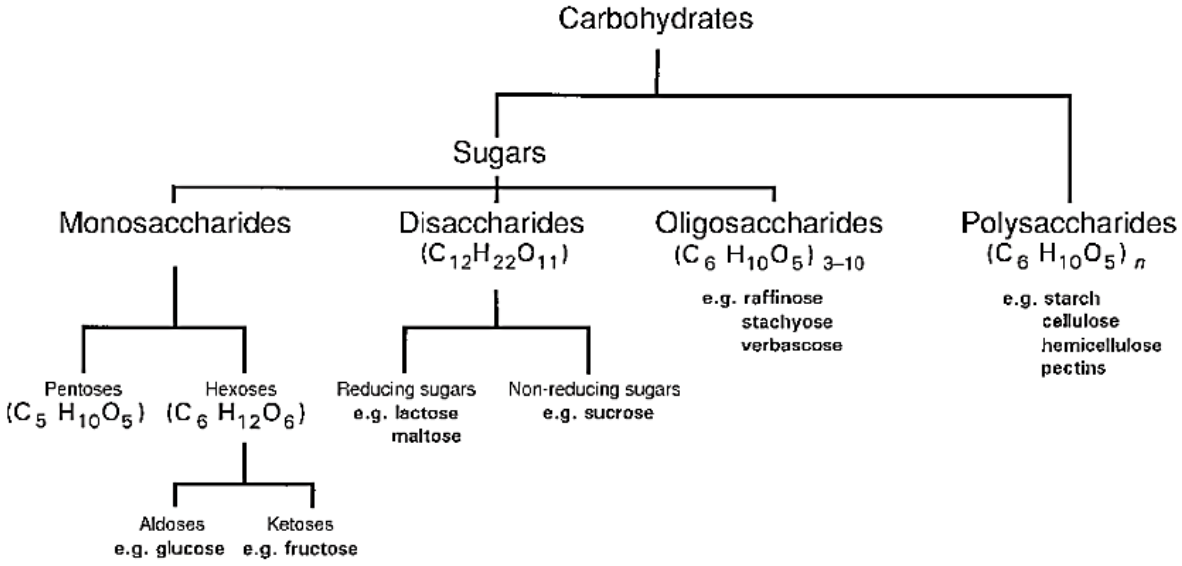
galactose, differ in configuration at carbons C2, C3, or C4, while anomerism refers to variation in spatial configuration at the first carbon in aldoses or the second in ketoses.

Chemically, carbohydrates participate in various reactions. Osazone formation occurs when sugars react with excess phenylhydrazine, producing crystalline derivatives like glucosazone. Reducing sugars undergo Benedict's test, where heating with an alkali converts them to enediols, which then reduce copper ions in Benedict's reagent, causing a color change to brick red. Oxidation reactions convert the carbonyl group of monosaccharides into carboxylic acids, as seen when D-glucose is oxidized to D-gluconic acid. On the other hand, reduction reactions using agents like sodium borohydride ($NaBH_4$) or catalytic hydrogenation convert carbonyl groups into alcohols, forming sugar alcohols known as alditols.

Monosaccharides, the simplest form of carbohydrates, possess several unique properties. They are generally sweet-tasting, with fructose being the sweetest - approximately 73% sweeter than sucrose. These compounds are solid at room temperature and highly soluble in water due to the abundance of hydroxyl groups. For instance, glucose is so water-soluble that 1 gram can dissolve in just 1 mL of water to form a syrup. Carbohydrates, therefore, can be broadly classified based on their structure and behavior into various types, including monosaccharides, disaccharides, oligosaccharides, and polysaccharides.

19.2.2 Classification of Carbohydrates:

Carbohydrates are classified based on their behavior upon hydrolysis into three main categories:



Simple carbohydrates include single sugar molecules known as monosaccharides, as well as their polymeric forms - oligosaccharides and polysaccharides. **Monosaccharides** are the simplest form of carbohydrates and are often referred to as simple sugars because they cannot be hydrolyzed into smaller units. They are typically colorless, crystalline solids that are soluble in water but insoluble in nonpolar solvents. Monosaccharides possess either a free aldehyde or ketone group and follow the general formula $C_n(H_2O)_n$ or $C_nH_{2n}O_n$. These sugars are classified based on the number of carbon atoms they contain and the nature of their functional group. Depending on their carbon count, they are referred to as trioses (3C), tetroses (4C), pentoses (5C), hexoses (6C), heptoses (7C), and so on. Additionally, they are categorized as aldoses or ketoses depending on whether they contain an aldehyde or ketone group, respectively. Common examples of monosaccharides include glucose, fructose, erythrose, and ribulose.

Oligosaccharides are carbohydrates composed of 2 to 10 monosaccharide units linked together through glycosidic bonds. Upon hydrolysis, these compounds yield a corresponding number of monosaccharide molecules. Based on the number of constituent monosaccharides, oligosaccharides are further classified into disaccharides (2 units), trisaccharides (3 units), tetrasaccharides (4 units), and so on. For example, disaccharides such as sucrose, lactose, and maltose consist of two monosaccharide units. Trisaccharides like raffinose and rabinose consist of three units. The general formula of a disaccharide is $C_n(H_2O)_{n-1}$, while that of a trisaccharide is $C_n(H_2O)_{n-2}$, indicating the loss of a water molecule with each glycosidic bond formed.

Polysaccharides, also known as glycans, are complex carbohydrates that contain more than ten monosaccharide units and often consist of hundreds or even thousands of sugar residues. These macromolecules release more than ten monosaccharide molecules upon hydrolysis. Polysaccharides vary widely in terms of the type of recurring monosaccharide units, chain length, types of glycosidic bonds, and the degree of branching. Functionally, they play vital roles in structural support (e.g., cellulose in plant cell walls) and energy storage (e.g., starch in plants and glycogen in animals). Based on the uniformity of their monomeric units, polysaccharides are classified into **homopolysaccharides** (composed of a single type of monosaccharide) and **heteropolysaccharides** (composed of different types). Examples of homopolysaccharides include starch, glycogen, cellulose, and pectin, while hyaluronic acid and chondroitin serve as typical examples of heteropolysaccharides.

19.3 FUNCTIONS USES OF CARBOHYDRATES:

Carbohydrates are widely distributed in both plant and animal tissues, playing numerous essential roles in structural support, energy storage, and metabolism. In plants and arthropods, carbohydrates contribute to the formation of skeletal structures, while also serving as food reserves. As a primary source of energy, carbohydrates are crucial for sustaining various metabolic activities, with energy being released through their oxidation. They are the most abundant dietary source of energy, providing approximately 4 kcal per gram, and are thus vital for all living organisms.

In many animals, carbohydrates offer a rapid and readily accessible energy supply. Glucose, in particular, is a key molecule that undergoes glycolysis and the Krebs cycle to produce ATP, the primary energy currency of cells. Carbohydrates function as energy stores in the form of glycogen in animals and starch in plants, ensuring that the body has a reserve supply of fuel during times of energy demand. These stored forms of carbohydrates serve as an alternative energy source to proteins, thereby sparing muscle tissue from degradation.

Beyond their role in energy metabolism, carbohydrates are integral structural and protective components. They are found in the cell walls of plants (as cellulose), in microorganisms (as peptidoglycan or murein), and in arthropods and fungi (as chitin). Additionally, carbohydrates serve as biosynthetic intermediates in the formation of fats and proteins. They play a crucial role in regulating nerve tissue function and act as the primary energy source for the brain.

Carbohydrates also contribute to the formation of biological macromolecules by combining with proteins and lipids to form glycoproteins and glycolipids, which are involved in cell signaling, surface antigen formation, receptor function, and interactions within the cellular environment. Importantly, carbohydrates are foundational to the structural framework of nucleic acids—ribonucleic acid (RNA) and deoxyribonucleic acid (DNA). In animals, carbohydrates are vital components of connective tissues and play a role in maintaining tissue integrity.

Dietary carbohydrates, particularly those rich in fiber, help promote digestive health by preventing constipation. Furthermore, certain carbohydrates are involved in modulating the immune system, enhancing the body’s defense mechanisms. Overall, carbohydrates perform a diverse array of functions that are essential for life, from structural integrity and energy provision to cellular communication and immune response.

Carbohydrates serve a wide range of functional uses in both biological systems and industrial applications. Biologically, they are the primary source of energy for most organisms. For example, glucose, a monosaccharide, is central to cellular respiration, where it is broken down to produce ATP, the energy currency of the cell. In storage form, carbohydrates like glycogen in animals and starch in plants act as energy reserves that can be mobilized when needed. Structurally, carbohydrates contribute to the rigidity and protection of cells; cellulose forms the cell wall in plants, chitin provides strength to the exoskeletons of arthropods, and peptidoglycan is essential to bacterial cell walls. Carbohydrates also play a crucial role in cell signaling and recognition; for instance, glycoproteins and glycolipids on cell membranes function as receptors or antigens involved in immune responses. In nucleic acids, the sugars ribose and deoxyribose form the backbone of RNA and DNA, respectively. From a dietary perspective, fiber-rich carbohydrates such as whole grains and vegetables promote healthy digestion and prevent constipation. Industrially, carbohydrates like starch are used in the production of paper, textiles, and biodegradable plastics, while sugar derivatives are employed in pharmaceuticals and food processing. Thus, carbohydrates are not only indispensable in biological systems but also have broad practical uses across multiple sectors.

19.4 LIPIDS (FATS AND OILS):

Lipids (from the Greek *lipos*, meaning "fat") are a highly significant class of biomolecules, serving primarily as the body's most concentrated form of energy storage. In addition to this energy-related role, lipids are crucial components of cellular structures and participate in numerous biochemical functions. Unlike polysaccharides, proteins, and nucleic acids, lipids are not polymers and typically consist of small, diverse molecules. They are a **heterogeneous group of organic compounds** that are **insoluble in water but soluble in organic solvents** like alcohol and ether. Lipids are either derived from or structurally related to fatty acids and are extensively utilized by living cells.

Lipids, commonly known as fats and oils, are a diverse group of hydrophobic organic compounds that play vital roles in biological systems. Unlike carbohydrates, lipids are not polymers but are composed of smaller units like fatty acids and glycerol. Fats are typically solid at room temperature and are mostly derived from animals, while oils are liquid and generally obtained from plant sources. Lipids serve as a rich source of energy, providing about 9 kcal per gram—more than double the energy yield of carbohydrates or proteins. They function as long-term energy storage molecules and act as thermal insulators, protecting organisms from extreme temperatures. Structurally, lipids are essential components of cell

membranes in the form of phospholipids, which help maintain membrane fluidity and integrity. In addition, lipids play a crucial role in signaling pathways; steroid hormones like testosterone and estrogen are lipid-derived molecules that regulate various physiological processes.

A **fat molecule**, or triglyceride, consists of glycerol and three fatty acids. Glycerol is a three-carbon molecule with hydroxyl groups, while fatty acids are long hydrocarbon chains ending in a carboxyl group. These fatty acids can be saturated (with no double bonds and fully saturated with hydrogen) or unsaturated (containing one or more double bonds). Saturated fats, often solid at room temperature, are found in animal products like butter and meat, whereas unsaturated fats - liquid oils such as olive, canola, and corn oil - are usually plant-derived. Unsaturated fats, particularly polyunsaturated fats like omega-3 and omega-6 fatty acids, are considered beneficial for cardiovascular health. Omega-3 fatty acids, found in fishlike salmon and tuna, are essential fats that the human body cannot synthesize, and are vital for brain function and reducing the risk of heart disease and cancer.

In industrial food production, oils may be artificially hydrogenated to produce semi-solid forms for improved shelf life. This process often creates **trans fats**, which have been linked to increased levels of LDL (bad cholesterol) and a higher risk of heart disease. Because of these health concerns, many manufacturers and restaurants have reduced or eliminated the use of trans fats.

Phospholipids, another key class of lipids, are fundamental components of cellular membranes. They consist of two fatty acid tails and a phosphate group attached to a glycerol backbone. Phospholipids exhibit both hydrophobic (fatty acid tails) and hydrophilic (phosphate head) properties, allowing them to form the lipid bilayers of plasma membranes, where they align with tails inward and heads facing the aqueous environments inside and outside the cell. This unique arrangement is critical for cellular integrity and selective permeability.

Through an Indigenous lens, lipids have held cultural and nutritional significance. Among the First Peoples of the Pacific Northwest, the ooligan fish - rich in fat, with 20% body fat content - was a vital dietary staple and trade item. Its early spring arrival was so essential that its return was announced in Tsimshianic languages with the phrase “Hlaa aat’ixshi halimootxw!” meaning “Our Saviour has just arrived!” The ooligan’s fat composition - about 30% saturated and 55% monounsaturated - makes it a stable, healthful

grease that can be stored and used over time. It is rich in omega-3 fatty acids and fat-soluble vitamins A, E, and K, offering both sustenance and medicinal value. The fat is traditionally extracted by boiling the fish and skimming the floating fat, a method made possible by the hydrophobic nature of lipids. With a composition comparable or superior to olive oil in health benefits, ooligan grease is a powerful example of how cultural practices intersect with biological principles in meaningful and sustainable ways.

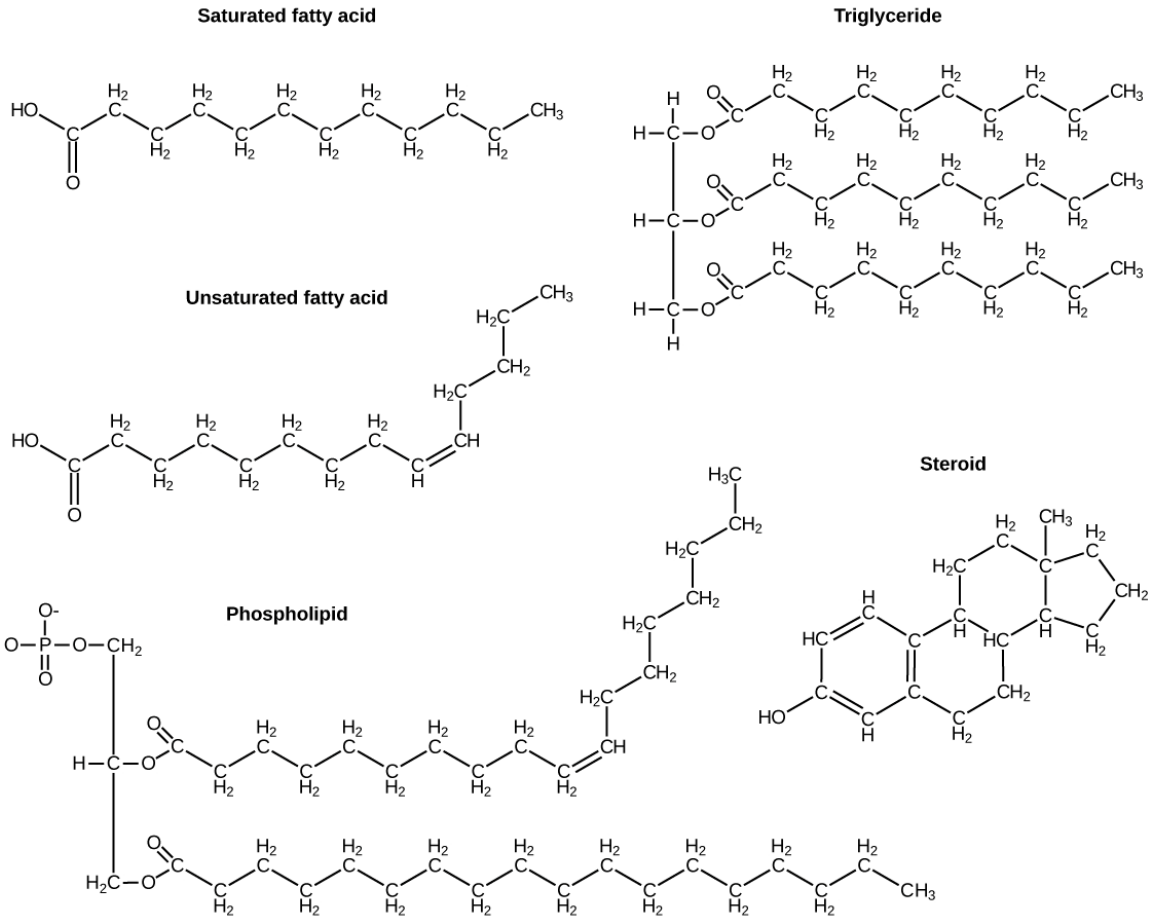


Figure 19.1: Lipids include fats, such as triglycerides, which are made up of fatty acids and glycerol, phospholipids, and steroids.

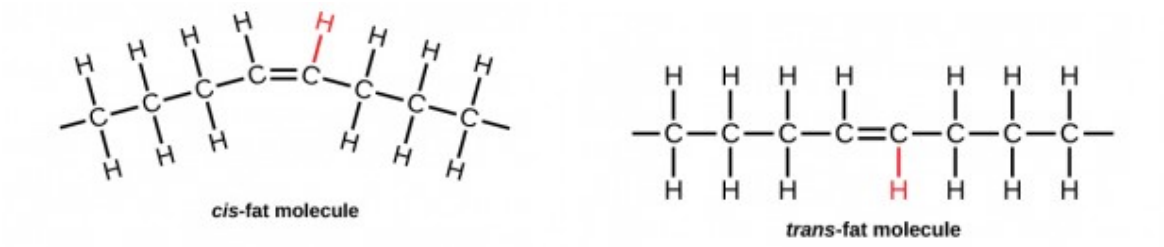


Figure 19.2: During the hydrogenation process, the orientation around the double bonds is changed, making a trans-fat from a cis-fat. This changes the chemical properties of the molecule.

19.4.1 Structure of Lipids:

Lipids are composed mainly of **carbon (C), hydrogen (H), and oxygen (O)**, though they contain a significantly **lower proportion of oxygen** compared to carbohydrates. This makes them more hydrophobic and energy-dense. A typical lipid molecule is formed from **two basic components: glycerol and fatty acids**.

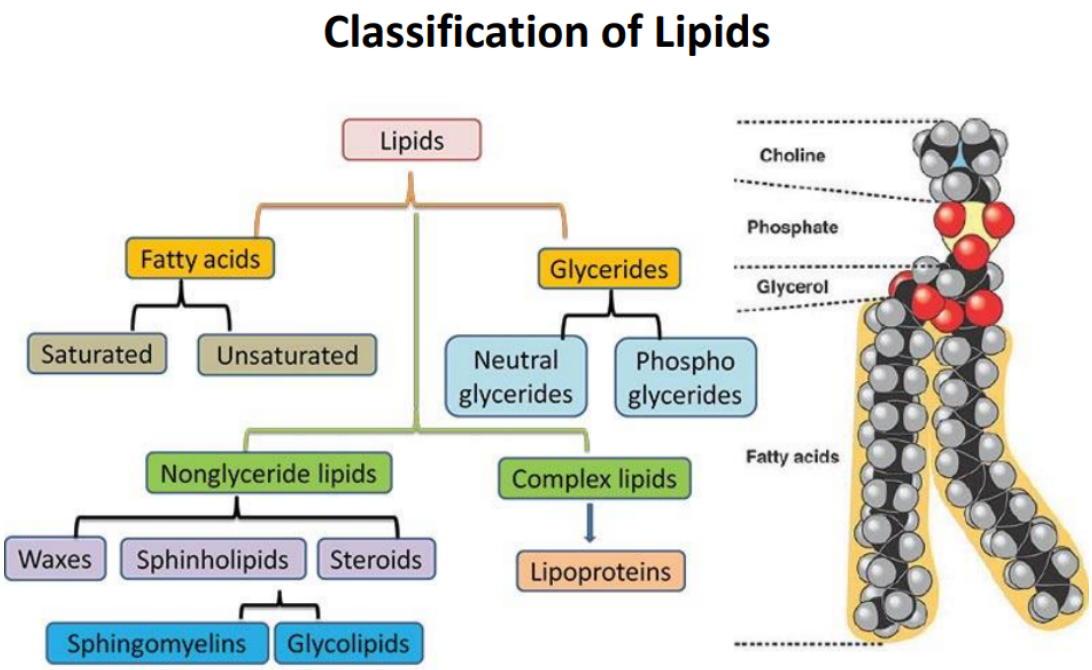
- **Glycerol** is a three-carbon alcohol, with each carbon bearing a hydroxyl (-OH) group.
- **Fatty acids** are long hydrocarbon chains with a terminal **carboxyl group (-COOH)**. They vary in length (usually between 12–18 carbon atoms) and in the presence or absence of **carbon-carbon double bonds (C=C)**.
    - A **saturated fatty acid** has no C=C bonds; all carbon atoms are fully "saturated" with hydrogen atoms.
    - An **unsaturated fatty acid** has one or more C=C bonds, introducing kinks into the hydrocarbon chain. If there is one double bond, it is **monounsaturated**; more than one makes it **polyunsaturated**.

Structure of Triglycerides:

A **triglyceride**, the most common type of fat found in the body and in food, consists of **one glycerol molecule bonded to three fatty acid chains**. These bonds are called **ester bonds**, formed through a **condensation reaction** (dehydration synthesis) that releases water molecules during the bonding process. Because the charges in a triglyceride are symmetrically distributed, these molecules do **not form hydrogen bonds with water**, rendering them **insoluble in water**. This insolubility is a key feature that allows lipids to serve as effective energy storage molecules without disrupting the aqueous environment of the cell.

19.4.2 Classification (Types) of Lipids:

Lipids are broadly classified (as modified from Bloor’s classification) into four main categories: simple lipids, complex lipids, derived lipids, and miscellaneous lipids. Each group includes various subclasses, as detailed below:



1) Simple Lipids:

These are esters of fatty acids with various types of alcohols and include two primary forms:

A. Fats and Oils (Triacylglycerols): These are esters formed from glycerol and three fatty acid molecules. The distinction between fats and oils is based on physical state - **fats are solid**, while **oils are liquid** at room temperature.

B. Waxes: Comprising esters of long-chain fatty acids with alcohols other than glycerol (which may be aliphatic or alicyclic), waxes commonly contain **cetyl alcohol**. They are used in **candles, lubricants, cosmetics, ointments**, and **polishes**.

2) Complex (Compound) Lipids:

These lipids are esters of fatty acids with alcohols and contain additional groups such as **phosphate, nitrogenous bases, carbohydrates, or proteins**. They are subdivided as follows:

A. Phospholipids: Contain fatty acids, an alcohol (glycerol or sphingosine), **phosphoric acid**, and often a **nitrogenous base**.

i) **Glycerophospholipids:** Contain glycerol as the backbone (e.g., **lecithin**, **cephalin**).

ii) **Sphingophospholipids:** Contain **sphingosine** as the alcohol (e.g., **sphingomyelin**).

B. Glycolipids: These consist of **fatty acids, a carbohydrate**, and a **nitrogenous base**, with **sphingosine** as the alcohol. They lack glycerol and phosphate. Examples include **cerebrosides** and **gangliosides**.

C. Lipoproteins: Macromolecular complexes formed by the combination of **lipids and proteins**, essential for lipid transport in blood.

D. Other Complex Lipids: These include **sulfolipids**, **aminolipids**, and **lipopolysaccharides**, which occur in various specialized biological roles.

3. Derived Lipids:

These are substances **obtained by hydrolysis** of simple and complex lipids and retain lipid-like characteristics. Examples include **fatty acids**, **glycerol**, **mono- and diacylglycerols**, **lipid-soluble vitamins (A, D, E, K)**, **steroid hormones**, **ketone bodies**, and various **hydrocarbons**.

4. Miscellaneous Lipids:

This category includes compounds that possess **some characteristics of lipids** but do not fit neatly into the other groups. Examples are **carotenoids**, **squalene**, **terpenes**, and **pentacosane** (found in beeswax).

Neutral lipids are lipids that carry no electrical charge. These include:

- **Monoacylglycerols**
- **Diacylglycerols**
- **Triacylglycerols**
- **Cholesterol**
- **Cholesteryl esters**

19.4.3 Functions of Lipids:

Lipids serve a wide range of essential functions in biological systems:

- **Energy Storage:** Triacylglycerols act as the **primary energy reserve**, providing more than twice the energy per gram compared to carbohydrates or proteins.
- **Structural Components:** Lipids such as **phospholipids and cholesterol** are key components of **cell membranes**, contributing to **membrane structure and permeability**.
- **Source of Fat-Soluble Vitamins:** Lipids are carriers of essential **fat-soluble vitamins A, D, E, and K**.
- **Regulatory Roles:** Certain lipids, including **steroid hormones** and **prostaglandins**, function as **metabolic regulators** involved in signaling pathways.

- **Protection and Insulation:** Lipids cushion and **protect internal organs**, serve as **thermal insulators**, and contribute to **body contour and smoothness**.
- **Compartmentalization:** Lipids provide the **hydrophobic barriers** necessary for the **partitioning of aqueous environments** within cells and organelles.
- **Enzyme Activation:** Some lipids act as **cofactors or activators** of enzymes. For example, **phosphatidylcholine micelles** are essential for the activity of enzymes like:
    - Glucose-6-phosphatase
    - Stearyl CoA desaturase
    - β-hydroxybutyric dehydrogenase (a mitochondrial enzyme)
    - ω-monooxygenase
- **Biological Importance in Plants and Seeds:** Lipids are also a **major energy source in animals** and **lipid-rich seeds**, supporting early growth and development.

19.5 CHEMISTRY OF BIOMOLECULES: ENZYMES

Enzymes are **biological catalysts -** primarily proteins - that speed up the rate of biochemical reactions without undergoing permanent change themselves. They are vital to life, enabling complex metabolic pathways to occur under mild conditions of temperature and pH.

Enzymes are biological catalysts that significantly increase the speed of biochemical reactions without undergoing any permanent change themselves. While all enzymes are proteins, not all proteins are enzymes. They exhibit a high degree of specificity, meaning each enzyme typically acts on a particular substrate. A notable exception to protein-based enzymes is ribozymes - RNA molecules with catalytic properties. Structurally, enzymes are composed of a three-dimensional (tertiary) configuration, with specific pockets called active sites where substrates bind. The interaction between an enzyme and its substrate follows the lock-and-key or induced fit model, where the substrate fits into the active site, forming an enzyme-substrate complex. This complex undergoes a transition state, leading to the formation of products and the release of the unchanged enzyme, ready to catalyze another reaction. Enzymes drastically lower the activation energy required for reactions, thereby accelerating their rates. For instance, carbonic anhydrase increases the rate of bicarbonate formation by over 10 million times compared to the uncatalyzed reaction.

Types of Chemical Changes:

1) **Physical Change**: Alters shape or state without breaking chemical bonds (e.g., melting ice).
2) **Chemical Change (Reaction)**: Breaks and forms chemical bonds; may be organic or inorganic.

Inorganic: $Ba(OH)_2 + H_2SO_4 \rightarrow BaSO_4 + 2H_2O$

Organic: Starch + $H_2O \xrightarrow{Hydrolysis} H_2CO_3$

Rate of Reaction:

$$\text{Rate} = \frac{\Delta \text{Product}}{\Delta t}$$

- **Velocity** is used when the direction of the process is specified.
- Reaction rates are influenced by temperature; typically, they double or halve with every 10°C change.
- Rate of enzyme catalysed reactions is very high. E.g. Carbonic anhydrase is the fastest enzyme. It accelerates the following reaction 10 million times.

$$CO_2 + H_2O \leftrightarrow H_2CO_3$$

In the absence of enzyme, only 200 molecules of H_2CO_3 are formed in an hour. In the presence of carbonic anhydrase about 600,000 molecules are formed per second. In a metabolic pathway, each step is catalysed by different enzymes.

Enzymes in Metabolic Pathways:

A different enzyme catalyzes each step in a metabolic pathway.

E.g. In glycolysis [Glucose ($C_6H_{12}O_6$) → 2 Pyruvic acid ($C_3H_4O_3$)], ten different enzymes take part.

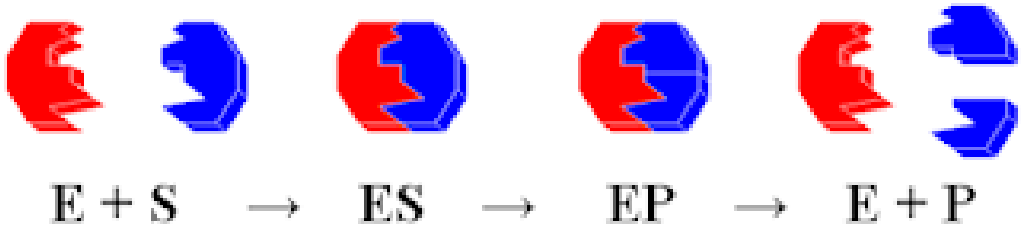
Mechanism of Enzyme Action (Catalytic Cycle):

Often explained using the **Lock-and-Key Model** or **Induced Fit Model**:

➢ The substrate binds to the active site of enzyme (E+S).

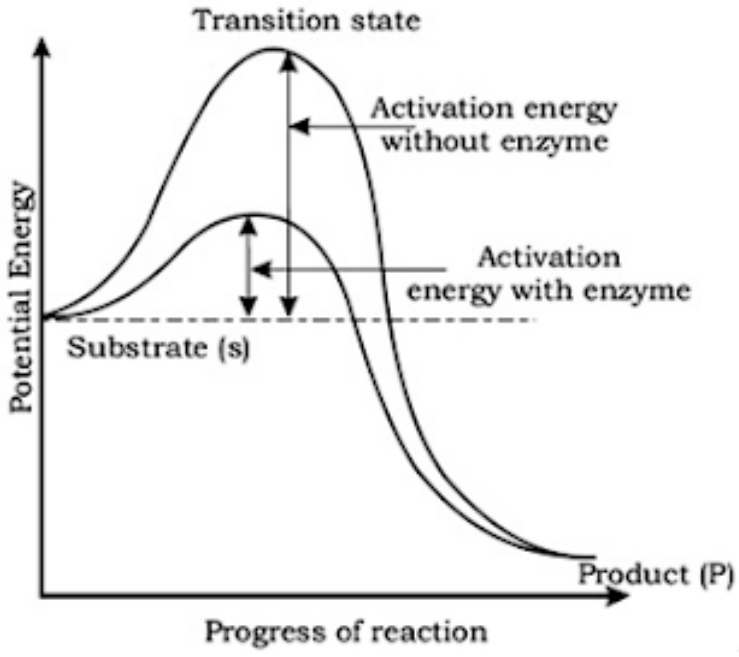
- This induces some changes in enzyme so that the substrate is tightly bound with active site of enzyme to form enzyme- substrate complex (ES).
- The active site breaks chemical bonds of substrate to form enzyme- product complex (EP).
- The enzyme releases the products and the free enzyme is ready to bind to other molecules of the substrate (E+P).

The reaction pathway involves transition states - temporary, unstable structures.



This pathway goes through some unstable transition state structures.

How do Enzymes Speed up a chemical Reaction? (Concept of activation energy)



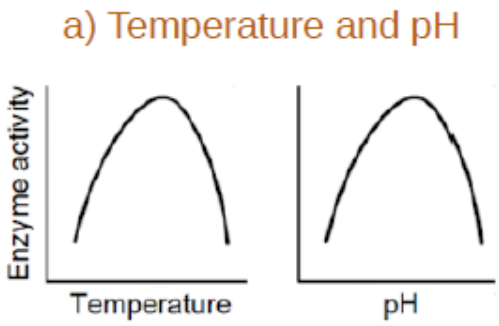
- Activation energy is the additional energy required to start a chemical reaction.
- In an exothermic or endothermic reaction, the substrate must go through a much higher energy state. It is called transition state energy. Therefore, activation energy is the difference between average energy of substrate and transition state energy.

- If the product (P) is at a lower energy level than the substrate (S), the reaction is an exothermic reaction (spontaneous reaction). It requires no energy (by heating) to form the product.
- In a biochemical reaction, enzymes lower the activation energy. As a result, speed of the reaction increases.

19.5.1 Factors Affecting Enzyme Activity:

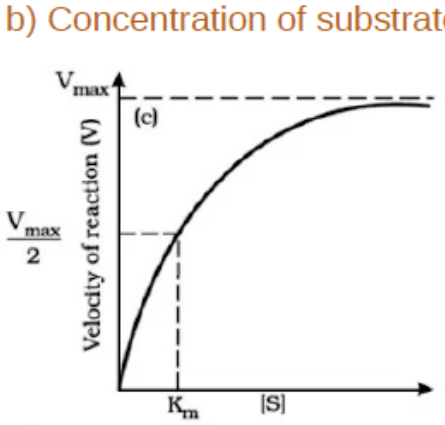
a) Temperature and pH

- Each enzyme has an **optimum temperature and pH**.
- **Low temperature**: Enzyme becomes temporarily inactive.
- **High temperature (>40°C)**: Enzyme denatures and loses activity.
- **Thermophilic organisms** possess heat-stable enzymes (optima at 80–90°C).



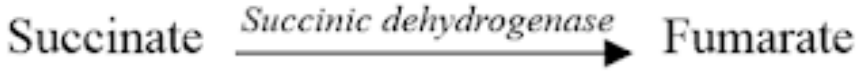
b) Substrate Concentration:

- Enzyme activity increases with substrate concentration until it reaches a **maximum velocity (Vmax)**.
- Beyond this point, enzyme sites are saturated; no further increase in rate occurs.



c) Presence of Inhibitors:

- **Inhibitors** reduce enzyme activity.
- **Competitive Inhibition**: Inhibitor resembles the substrate and competes for the active site.
  - E.g. *Malonate* inhibits *succinic dehydrogenase* by mimicking *succinate.*
- Competitive inhibitors are used in medicine to inhibit pathogens.



19.5.2 Classification of Enzymes (IUBMB System):

1) **Oxidoreductases**: Catalyze oxidation-reduction reactions

$$S_{reduced} + S'_{Oxidised} \rightarrow S_{Oxidised} + S_{reduced}$$

2) **Transferases**: Transfer functional groups (excluding hydrogen)

   S−G+S′→S+S′−GS-G + S'

3) **Hydrolases**: Catalyze hydrolysis of various bonds (e.g., ester, peptide, glycosidic)
4) **Lyases**: Remove groups to form double bonds: X-C-C-Y → X-Y + C=C
5) **Isomerases**: Interconvert isomers (optical, positional)
6) **Ligases**: Join two molecules using ATP: (e.g., forming C-O, C-S, C-N, or P-O bonds)

Cofactors and Enzyme Activation:

Apoenzyme: Protein portion of the enzyme

Cofactor: Non-protein part required for catalytic activity

Holoenzyme: Apoenzyme + Cofactor

Cofactors are classified as:

1) **Prosthetic Groups:**
   - Organic, tightly bound
   - E.g., *Haem* in peroxidase and catalase
   - Function: Breaks down hydrogen peroxide (H_2O_2)

2) **Coenzymes:**

- Organic, loosely bound (transient)
- Often derived from vitamins
- E.g., *NAD* and *NADP* (contain niacin)

3) **Metal Ions:**

- Form coordinate bonds with enzyme and substrate
- E.g., Zn^{2+} in carboxypeptidase

Prof. M. Subba Rao

LESSON - 20

CHEMISTRY OF BIOMOLECULES-II

20.1 CHEMISTRY OF PURINES AND PYRIMIDINES:

Purines and Pyrimidines are nitrogen-containing heterocyclic compounds that serve as the building blocks of nucleic acids - DNA and RNA. They play a fundamental role in the storage and transmission of genetic information and in various metabolic processes.

Purines are larger, double-ring structures composed of a fused imidazole and pyrimidine ring. The two main purines found in nucleic acids are **adenine (A)** and **guanine (G)**. These bases pair with specific pyrimidines via hydrogen bonds in the structure of DNA and RNA: adenine pairs with thymine (T) in DNA and with uracil (U) in RNA, while guanine always pairs with cytosine (C).

Pyrimidines, in contrast, are smaller, single-ring structures. The common pyrimidines are **cytosine (C)**, **thymine (T)** (found only in DNA), and **uracil (U)** (found only in RNA). These bases form complementary pairs with purines, maintaining the structure and function of nucleic acids.

The arrangement and pairing of purines and pyrimidines are crucial for the **double-helix structure** of DNA, where a purine always pairs with a pyrimidine, ensuring a uniform width of the helix. Additionally, purines and pyrimidines are involved in the formation of important biological molecules such as ATP (adenosine triphosphate), GTP, NAD^+, FAD, and coenzyme A, which are essential for energy transfer and enzymatic functions in cells.

The balance between purine and pyrimidine synthesis and degradation is tightly regulated in the cell. Disruptions in their metabolism can lead to diseases such as **gout** (caused by accumulation of uric acid, a purine degradation product) or **orotic aciduria** (related to defects in pyrimidine synthesis).

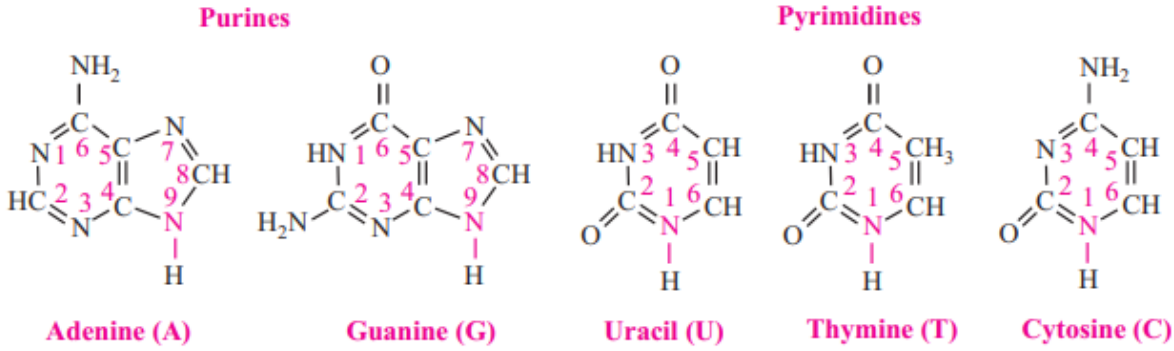
Purines and pyrimidines are the components of nitrogenous bases. The purine bases contain the purine ring (double ringsystem) while the pyrimidine base contain pyrimidine ring (single ring structure). The purine bases include Adenine and Guanine. The unusual forms of purines are hypoxathine, 1 methylguanine, 1 methylhypoxanthine etc. While the pyrimidine includes cytosine, thymine anduracil and its unusual forms are 5-methylcytosine, Thiouracil etc.

The **chemistry of purines and pyrimidines** involves their structure, synthesis, properties, and role in biological systems. These nitrogen-containing heterocyclic compounds are essential components of nucleic acids - DNA and RNA - and are involved in various cellular processes.

20.1.1 Structure Purines and Pyrimidines:

Purines are composed of a **fused double-ring system**: a six-membered pyrimidine ring joined to a five-membered imidazole ring. The two primary purines are **adenine (6-aminopurine)** and **guanine (2-amino-6-oxypurine)**.

Pyrimidines consist of a **single six-membered ring** containing two nitrogen atoms at positions 1 and 3. The main biological pyrimidines are **cytosine (2-oxy-4-aminopyrimidine)**, **thymine (5-methyl-2,4-dioxypyrimidine)** found in DNA, and **uracil (2,4-dioxypyrimidine)** found in RNA.



In nucleosides, nitrogenous bases are joined to pentose sugar through the hemiacetal hydroxyl group on the C-1 (first carbon atom of the sugar). The purines are attached to the sugar through the N-9 nitrogen atom while pyrimidine are attached through the N-1 nitrogen atom.

20.1.2 Chemical Properties:

1) **Aromaticity**: Both purines and pyrimidines are aromatic, which contributes to the stability and stacking interactions in nucleic acids.
2) **Hydrogen Bonding**: Their ability to form hydrogen bonds makes them suitable for base-pairing (A-T/U and G-C) in nucleic acid structures.
3) **Tautomerism**: Both purines and pyrimidines exhibit keto-enol or amino-imino tautomerism, which can influence base-pairing properties and lead to mutations during replication.

4) **Solubility**: They are weakly basic and only sparingly soluble in water, but more soluble in acidic or basic conditions due to ionization.

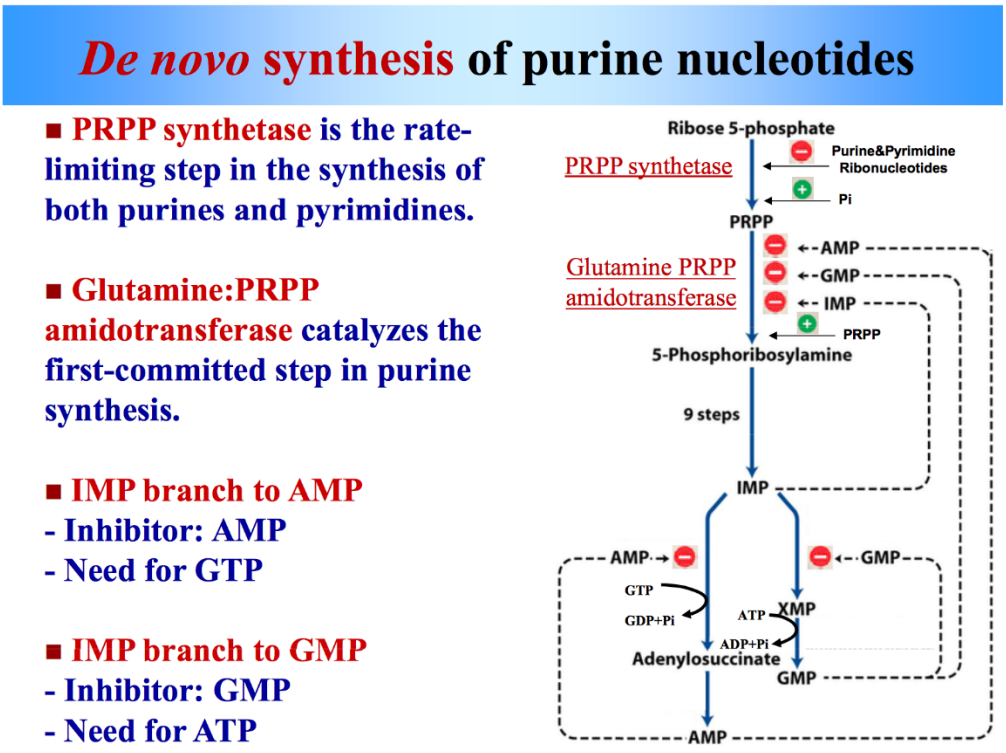
20.1.3 Biosynthesis:

Purine synthesis involves a **de novo pathway**, starting from simple molecules like **amino acids (glycine, glutamine, aspartate)**, **formyl groups from tetrahydrofolate**, and **CO_2**. The purine ring is **built gradually onto ribose phosphate (PRPP)** to form **inosine monophosphate (IMP)**, a precursor of both AMP and GMP.

De Novo Synthesis of Purine Ribonucleotides:

Nearly all organisms are capable of synthesizing purine and pyrimidine nucleotides via *de novo* biosynthetic pathways. The term *de novo*, meaning "anew" or "from scratch," refers to metabolic sequences that produce complex end products from simple precursors. In addition to these pathways, many organisms utilize more energy-efficient *salvage pathways*, which recycle preformed bases or nucleosides derived from dietary sources or nucleic acid degradation.

The fundamental distinction between these two pathways lies in their starting materials: *de novo* synthesis builds nucleotides from small molecules, whereas salvage pathways reuse existing nucleobases or nucleosides. This difference is illustrated in the following figure.



The *de novo* pathway for purine nucleotide synthesis is complex, branched, and energetically demanding. The key branch-point intermediate is **inosine monophosphate (IMP)**, which serves as a precursor to both **adenosine monophosphate (AMP)** and **guanosine monophosphate (GMP)**. The synthesis of IMP occurs through an eleven-step process in which the purine ring is constructed step-by-step directly onto a ribose sugar, derived from **ribose-5-phosphate**.

The primary site of purine synthesis is the **cytosol of liver cells**, although it occurs to a lesser extent in the brain. Overall, the synthesis of AMP requires the expenditure of approximately **8 ATP equivalents**, while the synthesis of GMP requires **9 ATP equivalents**, making the pathway highly regulated.

Overview of the Pathway:

- **Location:** All tissues can synthesize purines, but the liver is the major site, with limited activity in the brain.
- **Substrates:** Ribose-5-phosphate, glycine, glutamine, water (H_2O), ATP, carbon dioxide (CO_2), and aspartate.
- **Products:** GMP, AMP, glutamate, fumarate, and water.

The pathway begins with the conversion of **ribose-5-phosphate** (from the pentose phosphate pathway) into **phosphoribosyl pyrophosphate (PRPP)**, catalyzed by **PRPP synthetase**, a reaction requiring one ATP molecule. The **committed step** involves the transfer of an amino group from **glutamine** to PRPP, forming **5-phosphoribosylamine** via the enzyme **glutamine-PRPP amidotransferase**.

Subsequently, a series of **nine enzymatic reactions** lead to the synthesis of **IMP**, which can then follow two divergent paths:

- **IMP → GMP**, catalyzed by **IMP dehydrogenase**.
- **IMP → AMP**, catalyzed by **adenylosuccinate synthetase**.

Enzymes and Regulation:

- **PRPP synthetase:** Inhibited by AMP, IMP, and GMP (end-product inhibition).
- **Glutamine-PRPP amidotransferase:** Inhibited by AMP, IMP, and GMP.
- **IMP dehydrogenase:** Specifically inhibited by GMP.
- **Adenylosuccinate synthetase:** Specifically inhibited by AMP.

These feedback inhibition mechanisms ensure tight regulation of purine nucleotide levels in the cell, conserving energy and maintaining metabolic balance.

Significance of Purine Synthesis:

Purines are essential components of **DNA and RNA**, serving as building blocks of genetic material. Additionally, **ATP** plays a central role in **cellular energy metabolism** and acts as an **allosteric regulator** in various biochemical pathways. ATP is also involved in the **covalent modification of enzymes**, influencing their activity. Purine derivatives such as **cGMP** act as **secondary messengers** in signal transduction pathways.

Salvage pathways complement de novo synthesis by recovering bases and nucleosides released during nucleic acid degradation. These pathways are **more energy-efficient** and are particularly crucial in **brain and bone marrow tissues**, where de novo synthesis is limited.

Pyrimidine synthesis, unlike purines, starts with the formation of the **pyrimidine ring first**, from **carbamoyl phosphate** and **aspartate**, which forms **orotate**. Orotate is then combined with PRPP to form **OMP**, which is decarboxylated to **UMP**, the precursor of other pyrimidines like CMP, TMP, and UTP.

De Novo Biosynthesis of Pyrimidines:

Pyrimidine nucleotide biosynthesis begins with simple starting materials: **bicarbonate**, an **amine group from glutamine**, and a **phosphate group from ATP**, which together form **carbamoyl phosphate**. This reaction is similar to the one seen in the urea cycle. The carbamoyl phosphate then combines with **aspartic acid** to produce **carbamoyl aspartate**, a reaction catalyzed by the key regulatory enzyme **aspartate transcarbamoylase (ATCase)**, also known as **aspartate carbamoyltransferase**.

ATCase is finely regulated by three molecules. **Aspartate**, which also acts as a substrate, binds to the enzyme's catalytic site and promotes its active *R state*, thereby enhancing its activity. In contrast, **CTP** (cytidine triphosphate) serves as an inhibitor by binding to regulatory subunits, while **ATP** functions as an activator, ensuring a balance between purine and pyrimidine nucleotide synthesis.

The product **carbamoyl aspartate** is then converted through a series of reactions into **orotic acid**. Orotic acid subsequently reacts with **phosphoribosyl pyrophosphate (PRPP)** to

form **orotidyl monophosphate (OMP)**. OMP undergoes **decarboxylation** to yield **uridine monophosphate (UMP)** - the first true pyrimidine nucleotide in the pathway.

UMP is phosphorylated to **UDP (uridine diphosphate)** by nucleoside monophosphate kinases (NMPs), and then further phosphorylated to **UTP (uridine triphosphate)** by nucleoside diphosphate kinase (NDPK). UDP also acts as a branch point for the synthesis of **deoxyribonucleotides**, a reaction catalyzed by **ribonucleotide reductases**, which convert ribonucleoside diphosphates to their deoxy forms.

Finally, **UTP is converted into CTP (cytidine triphosphate)** by the enzyme **CTP synthase**, which uses an amino group donated by **glutamine**. This enzyme plays a crucial role in maintaining the proper balance between UTP and CTP levels in the cell, as its activity is **negatively regulated by excess CTP**, completing a feedback control loop that ensures nucleotide homeostasis.

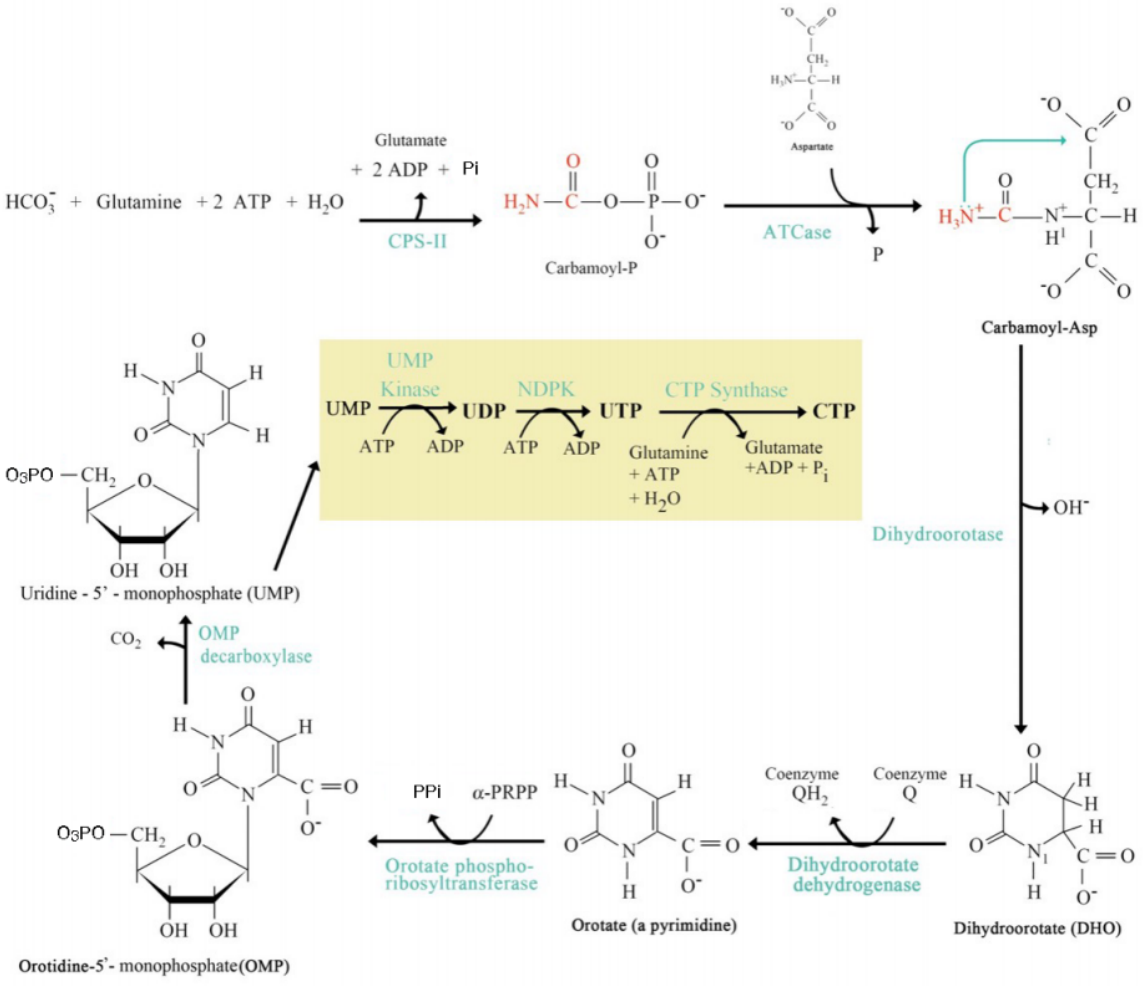


Figure 20.1: De Novo Synthesis of Pyrimidine Nucleotides

Degradation:

- **Purines** are degraded into **uric acid** in humans, which is excreted in urine. Excessive accumulation leads to **gout**.
- **Pyrimidines** degrade into highly soluble compounds such as **β-alanine and β-aminoisobutyric acid**, which are further broken down or excreted.

Biological Importance:

1) **Genetic Material**: Purines and pyrimidines are key components of nucleotides—the building blocks of DNA and RNA.
2) **Energy Metabolism**: Molecules like **ATP and GTP** (purine nucleotides) are critical for energy transfer.
3) **Enzyme Co-factors**: NAD^+, FAD, and CoA are derived from nucleotides and are vital for metabolism.
4) **Cell Signaling**: Cyclic AMP (cAMP) and cyclic GMP (cGMP) act as second messengers.

Understanding the **chemistry of purines and pyrimidines** is crucial for insights into molecular biology, genetics, and the development of drugs targeting nucleic acid metabolism, such as anticancer or antiviral agents.

20.2 NUCLEIC ACIDS - STRUCTURE AND FUNCTIONS OF DNA & RNA:

Nucleic acids, along with proteins, lipids, and polysaccharides, are one of the four major classes of biological macromolecules essential to life. The two primary forms of nucleic acids are **Deoxyribonucleic acid (DNA)** and **Ribonucleic acid (RNA)**, both of which serve as carriers of genetic information required for the development, functioning, growth, and reproduction of all known living organisms and viruses. Structurally, nucleic acids are polymers composed of repeating units of nucleotides, each containing a nitrogenous base, a five-carbon sugar, and a phosphate group. These nucleotides form a sugar-phosphate backbone, with nitrogenous bases attached to the sugar units.

The sugar component differs between the two: **DNA contains deoxyribose**, while **RNA contains ribose**. DNA includes four nitrogenous bases—adenine (A) and guanine (G), which are purines, and cytosine (C) and thymine (T), which are pyrimidines. In contrast, RNA contains **uracil (U)** instead of thymine. DNA typically exists as a **double-stranded**

helix with two antiparallel strands held together by hydrogen bonding between complementary base pairs. RNA, on the other hand, is **single-stranded**, but it can fold into complex **secondary and tertiary structures** resembling proteins, allowing it to perform various functional roles in the cell. These structural features underscore the versatility and fundamental importance of nucleic acids in molecular biology.

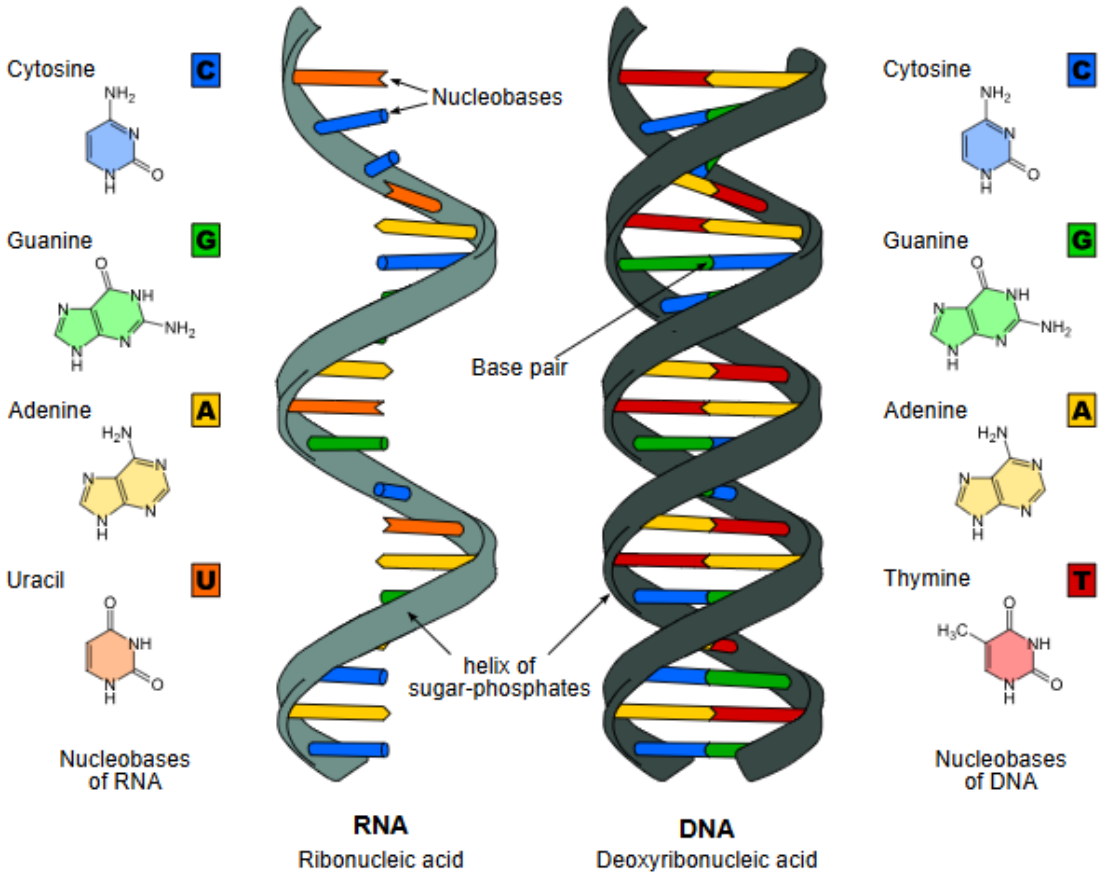


Figure 20.2: Comparison of the Structure of DNA and RNA.

20.2.1 Structure and Properties of Nucleic Acids:

Nucleic acids are long-chain polymers composed of repeating nucleotide units linked together by phosphodiester bonds. The two primary types of nucleic acids found in cells are Deoxyribonucleic acid (DNA) and Ribonucleic acid (RNA). DNA serves as the genetic material in most organisms, carrying hereditary information from one generation to the next. RNA, on the other hand, exists in several forms, each performing distinct functions - messenger RNA (mRNA) carries genetic information from DNA to ribosomes, ribosomal RNA (rRNA) is a structural and functional component of ribosomes, and transfer RNA (tRNA) decodes the mRNA sequence by delivering the correct amino acids during protein synthesis.

Each nucleotide in DNA and RNA consists of three components: a nitrogenous base, a pentose sugar, and a phosphate group. The pentose sugar is either 2-deoxy-D-ribose in DNA or D-ribose in RNA. Both sugars exist in a closed five-membered ring structure known as the β-furanose form.

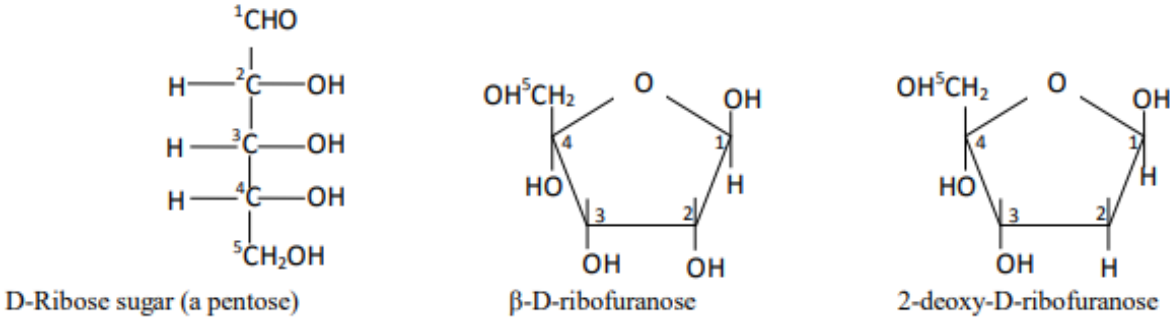


Figure 20.3: Structure of Pentose Sugars Present in Nucleic Acids

Nitrogenous bases are categorized into two types: purines and pyrimidines. The purines, adenine (A) and guanine (G), are common to both DNA and RNA. Among the pyrimidines, cytosine (C) is present in both DNA and RNA, while thymine (T) is found only in DNA and uracil (U) only in RNA. These nitrogenous bases are planar, aromatic compounds with conjugated double bonds, allowing them to absorb ultraviolet light, particularly around 260 nm, a property often used in quantifying nucleic acids.

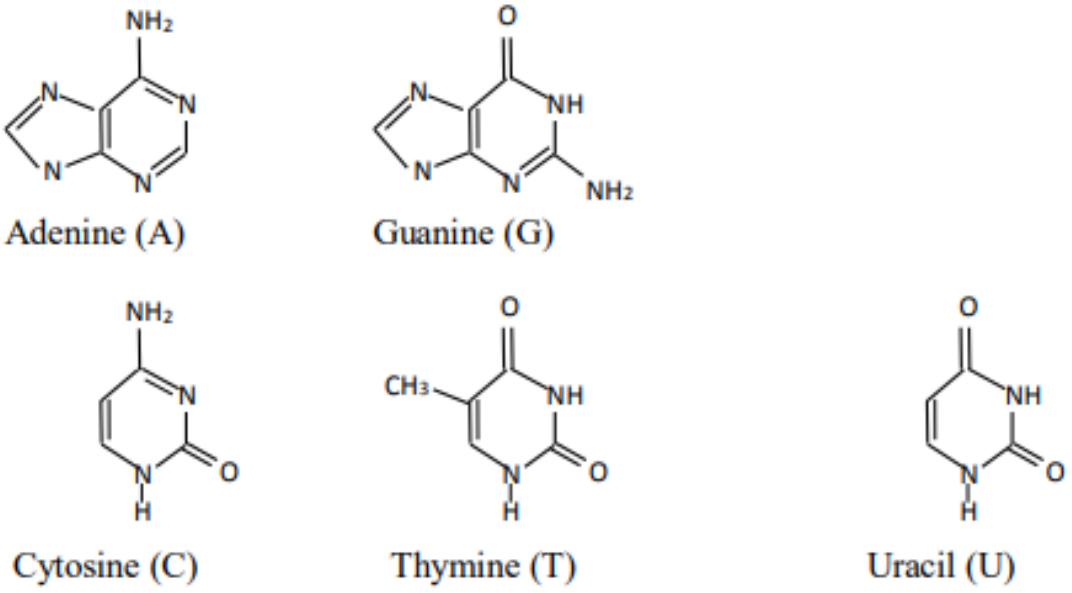


Figure 20.4 Structure of Nitrogenous Bases Present in Nucleic Acids

Formation of Nucleotides:

Nucleotides are the basic structural units of nucleic acids and are formed by the linkage of a nitrogenous base, a pentose sugar, and a phosphate group. In **purine bases** (adenine and guanine), the **N-9 nitrogen atom** forms an **N-β-glycosidic bond** with the **C-1 carbon** of the pentose sugar. In **pyrimidine bases** (cytosine, thymine, and uracil), the **N-1 nitrogen atom** forms the N-β-glycosidic bond with the **C-1 carbon** of the sugar.

A **phosphate group** is esterified to the **5′ carbon** of the sugar, resulting in the complete nucleotide structure. In DNA, the pentose sugar is **2-deoxy-D-ribose**, and the corresponding nucleotides are known as **deoxyribonucleotides** or **deoxyribonucleoside-5′-monophosphates**.

There are four types of deoxyribonucleotides, each corresponding to one of the nitrogenous bases in DNA:

- **Deoxyadenylate** (deoxyadenosine-5′-monophosphate)
- **Deoxyguanylate** (deoxyguanosine-5′-monophosphate)
- **Deoxycytidylate** (deoxycytidine-5′-monophosphate)
- **Deoxythymidylate** (deoxythymidine-5′-monophosphate)

These nucleotides are the monomeric units that link together to form the DNA polymer through phosphodiester bonds. (Refer to the following Figure for structural representation)

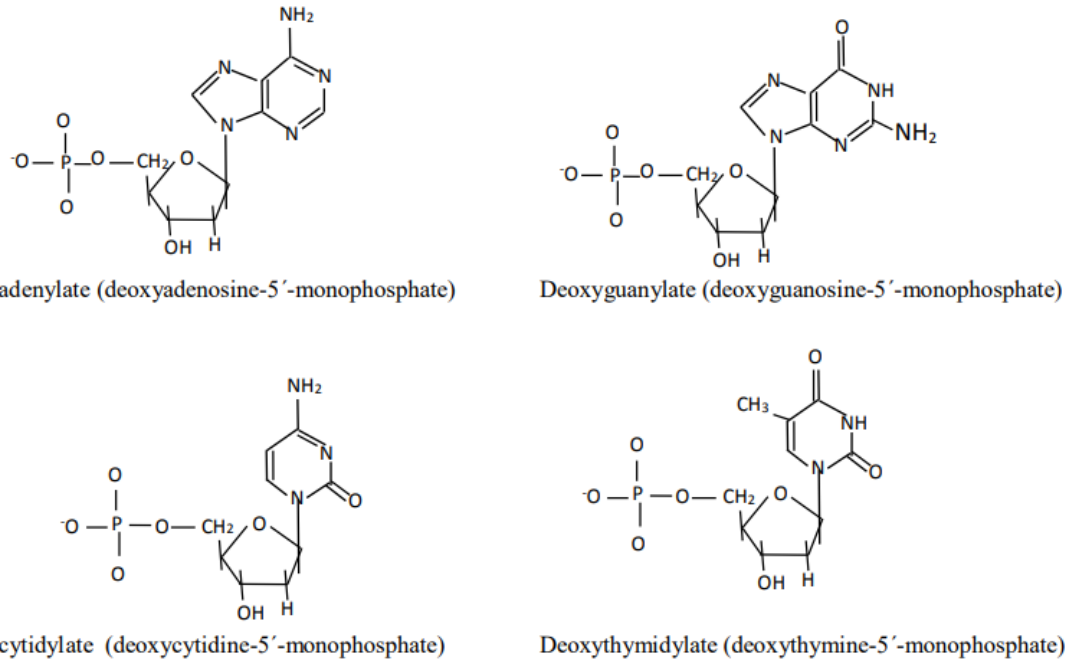


Figure 20.5 The Nucleotides Present in DNA

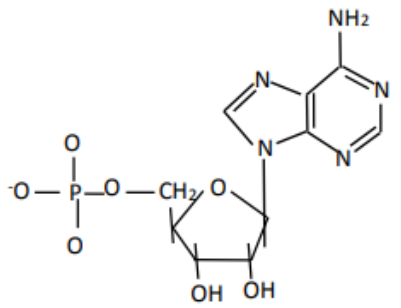
Ribonucleotides in RNA:

The nucleotides that make up RNA are called **ribonucleotides** or **ribonucleoside-5′-monophosphates**, and they serve as the fundamental structural units of RNA. Unlike DNA, the sugar in RNA is **D-ribose**, which contains a hydroxyl group at the 2′ carbon position.

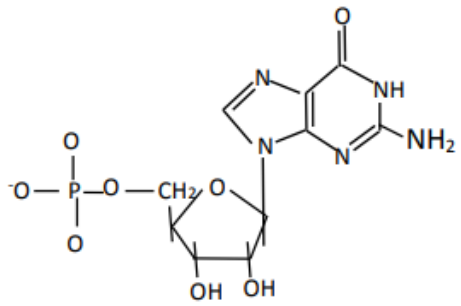
There are four primary types of ribonucleotides in RNA, each corresponding to one of the nitrogenous bases found in RNA:

- **Adenylate** (adenosine-5′-monophosphate)
- **Guanylate** (guanosine-5′-monophosphate)
- **Cytidylate** (cytidine-5′-monophosphate)
- **Uridylate** (uridine-5′-monophosphate)

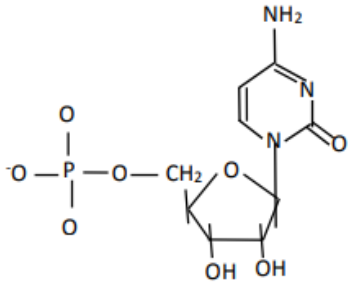
These ribonucleotides polymerize through **phosphodiester bonds** to form single-stranded RNA chains, which can fold into complex secondary and tertiary structures to perform diverse biological functions.



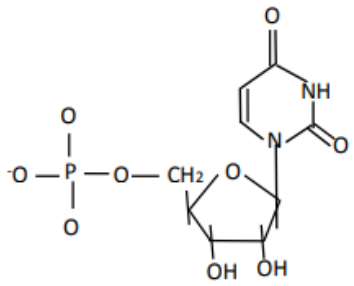
Adenylate (adenosine-5′-monophosphate)



Guanylate (guanine-5′-monophosphate)



Cytidylate (cytidine-5′-monophosphate)



Uridylate (uridine-5′-monophosphate)

Figure 20.6: The Nucleotides present in RNA

20.3 PRIMARY STRUCTURE OF NUCLEIC ACIDS:

The primary structure of nucleic acids (both DNA and RNA) refers to the **linear sequence of nucleotides** joined together by **phosphodiester bonds**. Each nucleotide is connected to the next via a covalent bond between the **5′ phosphate group** of one nucleotide and the **3′ hydroxyl group** of the next. This linkage forms a repeating **sugar-phosphate backbone**, with the nitrogenous bases projecting as side groups at regular intervals (see Figure 4).

The **alternating pentose and phosphate groups** create a stable and **hydrophilic backbone**, due to the –OH groups on the sugar residues, which can form hydrogen bonds with water. As a result, both DNA and RNA are polar molecules, with **distinct 5′ and 3′ ends**:

- The **5′ end** of a polynucleotide chain carries a free phosphate group attached to the 5′ carbon of the sugar.
- The **3′ end** carries a free hydroxyl (-OH) group on the 3′ carbon of the sugar.

This directionality is essential for biological functions like replication and transcription.

RNA is **less chemically stable** than DNA, particularly under alkaline conditions. This instability arises from the **2′-hydroxyl group** present in RNA's ribose sugar, which can act as a nucleophile and attack the adjacent phosphate group, leading to **cleavage of the phosphodiester bond**. DNA lacks the 2′-OH group, making its backbone **more resistant to hydrolysis** and chemically more stable.

The polynucleotide of upto 50 nucleotides is referred as an oligonucleotide. A larger nucleic acid is called as polynucleotide.

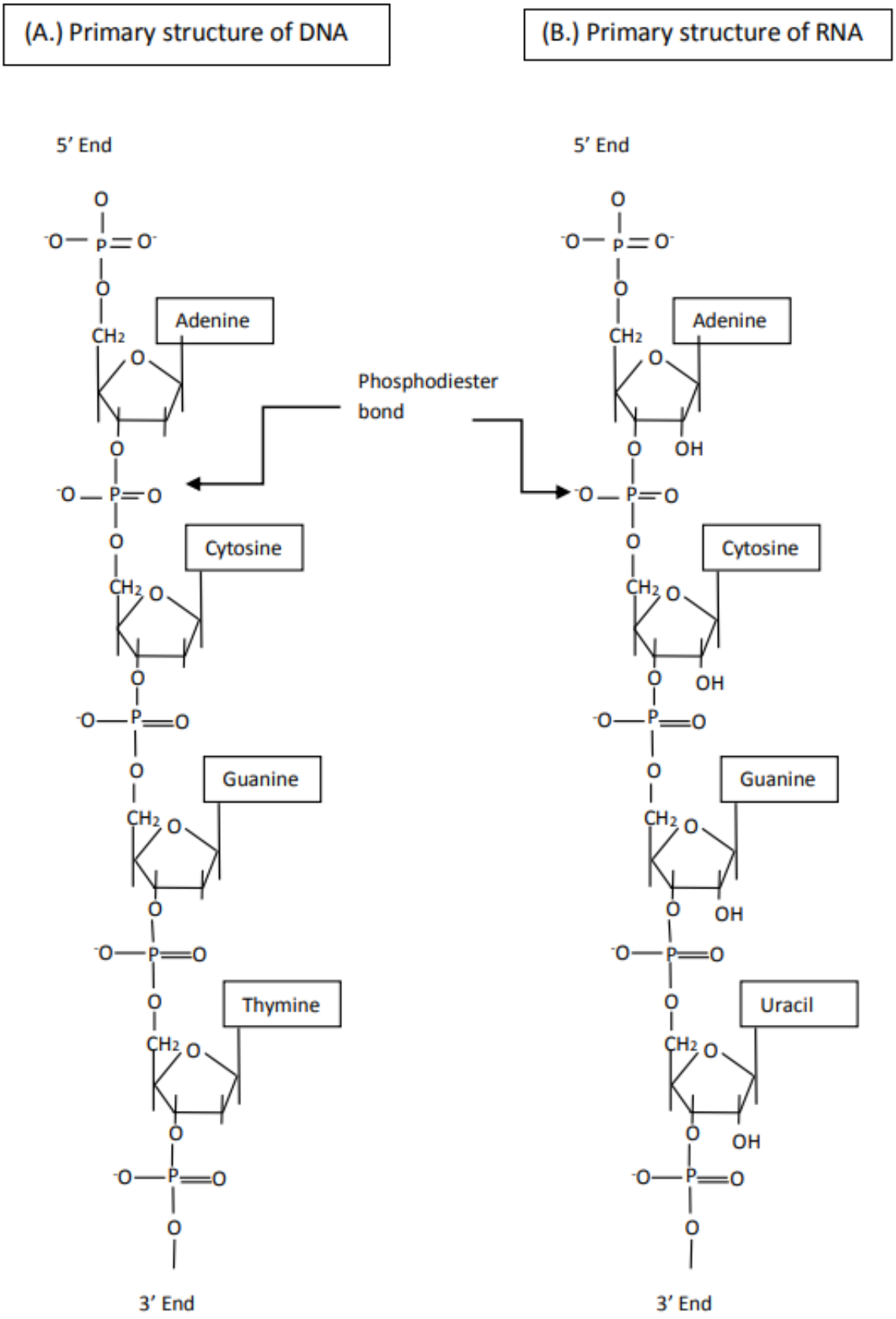


Figure 20.4: Primary Structure of DNA (A) and RNA (B)

Secondary Structure of DNA:

In 1953, James Watson and Francis Crick described the three-dimensional structure of DNA. DNA consists of two polynucleotide chains wound around the same axis to form a right-handed double helix. These strands are antiparallel - meaning their 5′ and 3′ ends run in opposite directions. The sugar-phosphate backbone forms the exterior of the helix, exposed to the aqueous environment, while the nitrogenous bases are stacked inside, forming a hydrophobic core. The base rings are planar and oriented perpendicular to the helix axis. The surface of the double helix contains two grooves: the major and minor grooves.

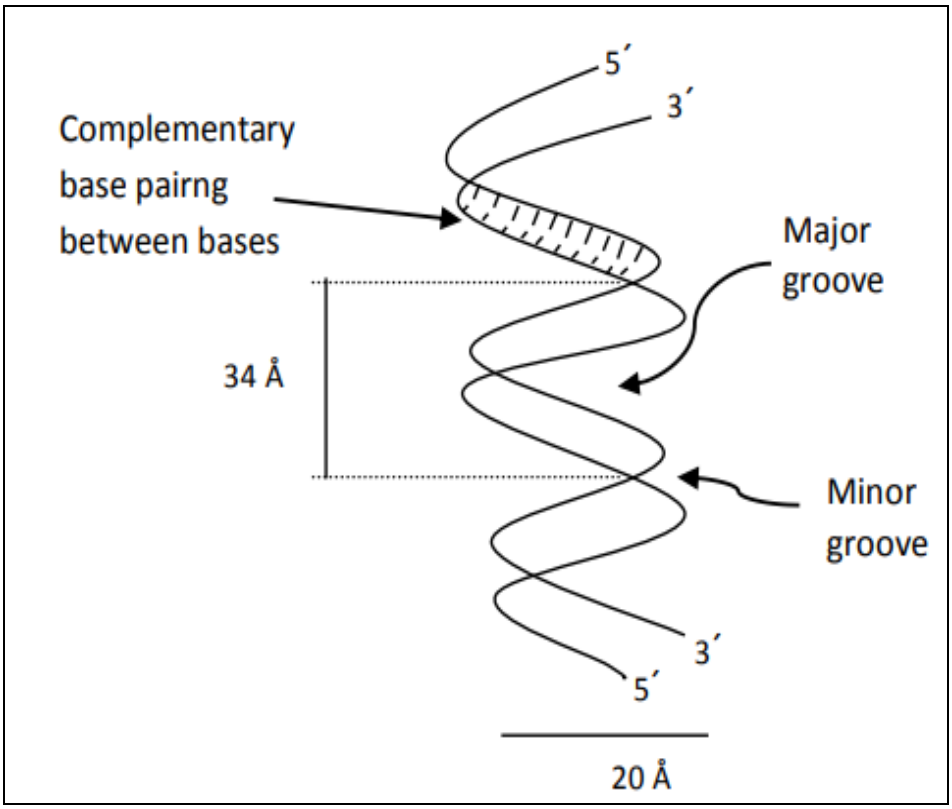


Figure 20.5: Double Helical Structure of DNA

Within the helix, each base on one strand forms specific hydrogen bonds with a complementary base on the opposite strand: adenine (A) pairs with thymine (T) via two hydrogen bonds, and guanine (G) pairs with cytosine (C) via three hydrogen bonds. Due to the additional hydrogen bond in G≡C pairs, regions rich in G-C content require more energy to denature. Though the two strands are not identical, they are complementary - wherever an A is present in one strand, a T will be found in the other, and similarly, G pairs with C.

The distance between stacked base pairs is 3.4 Å, and one complete helical turn spans 34 Å, comprising about 10.5 base pairs per turn. The double helix is stabilized by hydrogen bonding between base pairs and by base-stacking interactions.

This classic DNA structure is known as B-DNA, the most stable form under physiological conditions. Variants include A-DNA - a wider, right-handed helix found in dehydrated environments with 11 base pairs per turn - and Z-DNA, a left-handed helix that occurs in sequences with alternating G and C residues. Z-DNA is slenderer and more elongated, featuring a zigzag-shaped surface and 12 base pairs per turn.

Messenger RNA (mRNA):

While DNA stores genetic information, mRNA functions as the intermediary that conveys genetic instructions from DNA to the protein-synthesizing machinery in the cytosol. mRNA is synthesized from DNA via transcription and serves as a template for translating nucleotide sequences into amino acid sequences of proteins.

Ribosomal RNA (rRNA):

rRNA is a key structural and functional component of ribosomes. In prokaryotes, ribosomes consist of a 30S small subunit (containing 16S rRNA) and a 50S large subunit (containing 23S and 5S rRNAs). Eukaryotic ribosomes comprise a 40S small subunit (with 18S rRNA) and a 60S large subunit (with 28S, 5.8S, and 5S rRNAs). rRNAs facilitate the proper positioning of mRNA and tRNAs and catalyze peptide bond formation. RNA can form duplexes with complementary RNA or DNA strands in antiparallel orientations. Although RNA adopts an A-form helix, unlike the B-form of DNA, it often contains mismatches, bulges, and internal loops, which create complex three-dimensional shapes stabilized by hydrogen bonding and base stacking.

Transfer RNA (tRNA):

acids to the ribosome. Each tRNA has an amino acid covalently linked at its 3′ end and an anticodon region that pairs with the corresponding codon on mRNA. The secondary structure of tRNA resembles a cloverleaf and consists of four stem-loop regions:

- The **acceptor stem** binds the amino acid.
- The **D arm** contains dihydrouridine.
- The **anticodon arm** carries the anticodon sequence.
- The **TψC arm** includes pseudouridine.

The three-dimensional structure of tRNA is an L-shape, with one leg formed by the acceptor and T arms, and the other by the D and anticodon arms. Around 25% of the bases in tRNA are chemically modified, contributing to its stability and function.

20.4 FUNCTIONS OF DNA (DEOXYRIBONUCLEIC ACID):

1) **Genetic Information Storage**: DNA serves as the hereditary material in almost all living organisms. It stores the genetic blueprint that determines the structure, function, and regulation of the body's cells, tissues, and organs.

2) **Transmission of Genetic Information:** DNA is passed from one generation to the next during reproduction, ensuring that offspring inherit characteristics from their parents.

3) **Gene Expression Regulation:** DNA contains regulatory elements (promoters, enhancers, silencers) that control when, where, and how much of a gene is expressed.

4) **Template for RNA Synthesis (Transcription):** DNA acts as a template for the synthesis of RNA molecules during transcription.

5) **DNA Replication:** DNA can make exact copies of itself before cell division, ensuring that each new cell receives an identical copy of the genetic material.

20.5 FUNCTIONS OF RNA (RIBONUCLEIC ACID):

RNA plays a more diverse and dynamic role in cells, especially in **gene expression** and **protein synthesis**:

1) **Messenger RNA (mRNA):**
   - Carries genetic code from DNA in the nucleus to the ribosome in the cytoplasm.
   - Acts as a template for protein synthesis during translation.

2) **Transfer RNA (tRNA):**
   - Delivers the correct amino acids to the ribosome during protein synthesis.
   - Recognizes specific codons on the mRNA through its anticodon.

3) **Ribosomal RNA (rRNA):**
   - A structural and catalytic component of ribosomes.
   - Facilitates the assembly of amino acids into proteins.

4) **Regulatory RNA (e.g., miRNA, siRNA):**
   - Regulates gene expression by degrading mRNA or inhibiting translation.
   - Plays a role in RNA interference and epigenetic regulation.

5) Catalytic RNA (Ribozymes):

- Some RNA molecules have enzymatic activity and can catalyze biochemical reactions, such as self-splicing or cleaving other RNAs.

6) RNA in Reverse Transcription (in some viruses):

- In retroviruses like HIV, RNA is reverse-transcribed into DNA, which integrates into the host genome.

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