



**GEETHANJALI COLLEGE OF ENGINEERING & TECHNOLOGY  
(AUTONOMOUS)  
CHEERYAL (V), KEESSARA (M), MEDCHAL DIST. - 501 301**  
(Approved by AICTE, NEW DELHI, Accredited by NBA)

**DEPARTMENT OF FRESHMAN ENGINEERING**

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**2020-2021**

**COURSE FILE**

**ENGINEERING CHEMISTRY**

**(Subject Code: 20CH11001)**

**B.Tech CSE - DS I Semester**

Prepared by **Faculty of Chemistry**



Please show course files that contain the following:

1. Syllabus copy of the course
2. Vision of the Department
3. Mission of the Department
4. PEOs, POs and PSOs
5. Course objectives and outcomes
6. Course mapping with POs and PSOs
7. Brief notes on the importance of the course, namely, course purpose:
  - a. What role does this course play within the Program?
  - b. How is the course unique or different from other courses of the Program?
  - c. What essential knowledge or skills should they gain from this experience?
  - d. What knowledge or skills from this course will students need to have mastered to perform well in future classes or later (Higher Education / Jobs)?
  - e. Why is this course important for students to take?
  - f. What is/are the prerequisite(s) for this course?
  - g. When students complete this course, what do they need know or be able to do?
  - h. Is there specific knowledge that the students will need to know in the future?
  - i. Are there certain practical or professional skills that students will need to apply in the future?
  - j. Five years from now, what do you hope students will remember from this course?
  - k. What is it about this course that makes it unique or special?
  - l. Why does the program offer this course?
  - m. Why can't this course be "covered" as a sub-section of another course?
  - n. What unique contributions to students' learning experience does this course make?
  - o. What is the value of taking this course? How exactly does it enrich the program?

The "Course Purpose" describes how the course fits into the student's educational experience and curriculum in the program and how it helps in his/her professional career.

8. Prerequisites, if any
9. Instructional Learning Outcomes which refer to
  - Specific knowledge
  - Practical skills
  - Areas of professional development
  - Attitudes
  - Higher-order thinking skills, etc.which faculty members expect students to develop, learn, or master during a course.
10. Class Time Table
11. Individual Time Table
12. Lecture schedule with methodology being used/adopted for each session
13. Detailed notes
14. Additional topics
15. University Question papers of previous years
16. Question Bank
17. Assignment Questions
18. Unit wise Quiz Questions
19. Known gaps, if any and inclusion of the same in lecture schedule
20. Discussion topics, if any
21. References, Journals, websites and E-links if any
22. Quality Measurement Sheets
  - a. Course End Survey
  - b. Teaching Evaluation
23. Student List of the section
24. Group-wise students list for discussion topics, if any

## **1. Syllabus of the course:**

**Geethanjali College of Engineering and Technology**  
**Cheeryal (V), Keesara (M), Medchal Dist., Hyderabad – 501301, Telangana**  
**Department of Freshman Engineering**  
**Engineering Chemistry**

CSE, CSE – AI & ML, CSE - CS, CSE - DS, CSE- IoT, IT

**Subject Code: 20CH11001**

**Semester: I**

L	T	P/D	C
3	-	-	3

**Prerequisite(s):** None.

**Course objectives:** Develop ability to

1. Impart the knowledge of atomic, molecular and electronic modifications for understanding properties of complexes.
2. Acquire the knowledge of various water treatment methods to resolve the problem of water hardness.
3. Understand the essential concepts of electro chemistry and corrosion with a perspective of their industrial applications.
4. Learn the synthetic aspects of drugs and polymers through organic reaction mechanisms.
5. Understand the significance of various spectroscopic techniques and their application in medical and other fields.

### **Course Outcomes:**

At the end of the course, student would be able to

- CO1. Apply the concepts of atomic, molecular and electronic changes for the calculation of CFSE and magnetic moments in complexes.
- CO2. Analyze ground water and choose an appropriate treatment method for domestic and industrial applications.
- CO3. Interpret the concepts of electrochemistry for the construction of batteries and understanding corrosion for its prevention.
- CO4. Explain various reaction mechanisms and apply them in the synthesis of organic compounds of industrial significance.
- CO5. Use the principles of various spectroscopic techniques in medicine and other fields.

### **UNIT – I: Molecular structure and Theories of Bonding (9 hours)**

Atomic and Molecular orbitals. Linear Combination of Atomic Orbitals (LCAO), Molecular orbitals of diatomic molecules, Molecular Orbital Energy Level diagrams of N<sub>2</sub>, O<sub>2</sub> and F<sub>2</sub> molecules. Crystal Field Theory (CFT): Salient Features of CFT – Crystal Field Splitting of transition metal ion d-orbitals in Tetrahedral and Octahedral geometries. Crystal Field Stabilization Energies (CFSE). Applications of CFT- Magnetic Properties of the Octahedral and Tetrahedral Complexes.

### **UNIT - II: Water and its treatment (9 hours)**

Introduction – Hardness of water – Causes of hardness - Types of hardness: temporary and permanent – Expression and units of hardness – Estimation of hardness of water by complexometric method. Potable water and its specifications. Steps involved in treatment of water – Disinfection of water by chlorination and ozonization. Boiler feed water and its treatment – Calgon conditioning, Phosphate conditioning and Colloidal conditioning. External treatment of water – Ion exchange process. Desalination of water - Reverse osmosis. Numerical problems.

### **UNIT - III: Electrochemistry and corrosion (12hours)**

Electrochemical cells – Electrode potential, Standard electrode potential, Types of electrodes – calomel, quinhydrone and glass electrode. Nernst equation, Determination of pH of a solution by using quinhydrone and glass electrode. Electrochemical series and its applications. Numerical problems. Potentiometric titrations. Batteries – Primary (Lithium cell) and secondary batteries (Lead – acid storage battery and Lithium ion battery).

Causes and effects of corrosion – Theories of chemical and electrochemical corrosion – Mechanism of electrochemical corrosion, Types of corrosion: galvanic, water-line and pitting corrosion. Factors affecting rate of corrosion, Corrosion control methods- Cathodic protection – Sacrificial anode and impressed current cathodic methods. Surface coatings – metallic coatings – methods of application. Electroless plating of Nickel.

### **UNIT - IV: Reaction Mechanisms and polymeric materials (9 hours)**

#### **Reaction Mechanisms**

Substitution reactions: Nucleophilic substitution reactions: Mechanism of S<sub>N</sub>1, S<sub>N</sub>2 reactions. Electrophilic and Nucleophilic addition reactions: Addition of HBr to propene. Markovnikov's

and anti-Markovnikov's additions. Grignard additions on carbonyl compounds. Elimination reactions: Dehydrohalogenation of alkyl halides, Saytzeff's rule. Oxidation reactions: Oxidation of alcohols using  $\text{KMnO}_4$  and Chromic acid.

Reduction reactions: Reduction of carbonyl compounds using  $\text{LiAlH}_4$  &  $\text{NaBH}_4$ . Hydroboration of olefins. Structure, synthesis and pharmaceutical applications of Paracetamol and Aspirin.

### **Polymeric materials**

Classification of polymers, Types of Polymerization - addition and condensation, Differences between addition and condensation polymers, Mechanism of free radical addition polymerization. Preparation, properties and engineering applications of PVC, Teflon and Nylon- 6, 6.

### **UNIT - V: Spectroscopic techniques and applications (9 hours)**

Introduction to spectroscopic techniques- Electronic spectroscopy- Beer lambert's law, Principle of UV-Visible spectroscopy, Selection rules, Types of electronic transitions and applications of UV-Visible spectroscopy; Vibrational and rotational spectroscopy- IR spectroscopy-Principle- Mode of vibrations, Selection rules, Applications of IR spectroscopy, Nuclear magnetic resonance Spectroscopy- Principle, Chemical shift, Factors influencing chemical shift, Medical application of NMR spectroscopy - Magnetic Resonance Imaging.

#### **TEXT BOOKS:**

1. Engineering Chemistry by B.Ramadevi, Prasanta Rath and Ch.Venkata Ramana Reddy, Cengage Publications, 2018.
2. A Text Book of Engineering Chemistry by M. Thirumala Chary, E. Laxminarayana and K. Shashikala, Pearson Publishers, 2020.

#### **REFERENCE BOOKS:**

1. Engineering Chemistry by P.C Jain & Monica Jain, Dhanpatrai Publishing Company, 17<sup>th</sup> edition, 2015.
2. Elements of Physical Chemistry by P.W. Atkins 4<sup>th</sup> Edition.
3. Fundamentals of Molecular Spectroscopy, by C.N. Banwell, 4<sup>th</sup> Edition.
4. Selected topics in Inorganic Chemistry by Wahid U. Malik, G.D. Tuli and R.D Madan. S. Chand publications, 17<sup>th</sup> Edition.

## **2. Vision of the CSE Department**

To produce globally competent and socially responsible computer science engineers contributing to the advancement of engineering and technology which involves creativity and innovation by providing excellent learning environment with world class facilities.

## **3.Mission of the CSE Department**

1. To be a centre of excellence in instruction, innovation in research and scholarship, and service to the stake holders, the profession, and the public.
2. To prepare graduates to enter a rapidly changing field as a competent computer science engineer.
3. To prepare graduate capable in all phases of software development, possess a firm understanding of hardware technologies, have the strong mathematical background necessary for scientific computing, and be sufficiently well versed in general theory to allow growth within the discipline as it advances.
4. To prepare graduates to assume leadership roles by possessing good communication skills, the ability to work effectively as team members, and an appreciation for their social and ethical responsibility in a global setting.

## **4.CSE: Program Educational Objectives-PEOs and POs**

### **Program Educational Objectives (PEOs):**

**PEO-I:** To provide graduates with a good foundation in mathematics, sciences and engineering fundamentals required to solve engineering problems that will facilitate them to find employment in industry and / or to pursue postgraduate studies with an appreciation for lifelong learning.

**PEO-II:** To provide graduates with analytical and problem solving skills to design algorithms, other hardware / software systems, and inculcate professional ethics, inter-personal skills to work in a multi-cultural team.

**PEO-III:** To facilitate graduates get familiarized with state of the art software / hardware tools, imbibing creativity and Innovation that would enable them to develop cutting-edge technologies of multi-disciplinary nature for societal development.

## **CSE: Program Outcomes (PO)**

Program Outcomes (POs) describe what students are expected to know and be able to do during the graduation to accomplish Program Educational Objectives (PEOs). The Program Outcomes for Information Technology students are: Engineering Graduates will be able to:

**PO 1: Engineering knowledge:** Apply the knowledge of Mathematics, Sciences, Engineering fundamentals, and an engineering specialization to solve complex engineering problems.

**PO 2: Problem analysis:** Identify, formulate, review research literature, and analyze complex Engineering problems reaching substantiated conclusions using first principles of Mathematics, Sciences, and Engineering sciences.

**PO 3: Design/development of solutions:** Design solutions for complex Engineering problems and design system components or processes that meet the specified needs with appropriate consideration for the public health and safety, and the cultural, societal, and environmental considerations.

**PO 4: Conduct investigations of complex problems:** Use research-based knowledge and research methods including design of experiments, analysis and interpretation of data, and synthesis of the information to provide valid conclusions.

**PO 5: Modern tool usage:** Create, select, and apply appropriate techniques, resources, and modern Engineering and IT tools including prediction and modeling to complex Engineering activities with an understanding of the limitations.

**PO 6: The Engineer and society:** Apply reasoning informed by the contextual knowledge to assess societal, health, safety, legal and cultural issues and the consequent responsibilities relevant to the professional Engineering practice.

**PO 7: Environment and sustainability:** Understand the impact of the professional Engineering solutions in societal and environmental contexts, and demonstrate the knowledge of, and need for sustainable development.

**PO 8: Ethics:** Apply ethical principles and commit to professional ethics and responsibilities and norms of the Engineering practice.

**PO 9: Individual and team work:** Function effectively as an individual, and as a member or leader in diverse teams, and in multidisciplinary settings.

**PO 10: Communication:** Communicate effectively on complex engineering activities with the engineering community and with society at large, such as, being able to comprehend and write

effective reports and design documentation, make effective presentations, and give and receive clear instructions.

**PO 11: Project management and finance:** Demonstrate knowledge and understanding of the Engineering and Management principles and apply these to one's own work, as a member and leader in a team, to manage projects and in multidisciplinary environments.

**PO 12: Life-long learning:** Recognize the need for, and have the preparation and ability to engage in independent and life-long learning in the broadest context of technological change.

**Program specific outcomes (PSOs):**

**PSO 1:** Demonstrate competency in Programming and problem solving skills and apply those skills in solving computing problems

**PSO 2:** Select appropriate programming languages, Data structures and algorithms in combination with modern technologies and apply them in developing innovative solutions

**PSO 3:** Apply techniques of data modeling, analysis and visualization which include statistical techniques to solve real world problems delivering actionable insights for decision making.

## 5. Course Objectives and Course outcomes

**Course objectives:** Develop ability to

6. Impart the knowledge of atomic, molecular and electronic modifications for understanding properties of complexes.
7. Acquire the knowledge of various water treatment methods to resolve the problem of water hardness.
8. Understand the essential concepts of electro chemistry and corrosion with a perspective of their industrial applications.
9. Learn the synthetic aspects of drugs and polymers through organic reaction mechanisms.
10. Understand the significance of various spectroscopic techniques and their application in medical and other fields.

**Course Outcomes:**

At the end of the course, student would be able to

- CO1. Apply the concepts of atomic, molecular and electronic changes for the calculation of CSFE and magnetic moments in complexes.
- CO2. Analyze ground water and choose an appropriate treatment method for domestic and industrial applications.

CO3. Interpret the concepts of electrochemistry for the construction of batteries and understanding corrosion for its prevention.

CO4. Explain various reaction mechanisms and apply them in the synthesis of organic compounds of industrial significance.

CO5. Use the principles of various spectroscopic techniques in medicine and other fields.

## 6. Course Mapping with POs and PSOs

### **Mapping of Course with Programme specific outcomes:**

S. No	Course component	Code	Name of the Course	YEAR	SEM	PSO 1	PSO 2
1	Basic Sciences	<u>20CH11001</u>	Engineering Chemistry	I	I		

### **Mapping of Course outcomes with Programme outcomes:**

1. Slightly/ Low

2. Moderately/ Medium

3. Substantially/ High

PO's	PO 1	PO 2	PO 3	PO 4	PO 5	PO 6	PO 7	PO 8	PO 9	PO 10	PO 11	PO 12	PSO1	PSO2
CO 1	3	2	2			2	2						3	
CO 2	3	2	2			2	2						3	
CO 3	3	2	2			2	2						3	
CO 4	3	2	2			2	2						3	
CO 5	3	2	2			2	2						3	

## 7. Brief notes on the importance of the course, namely, course purpose:

### a) Role that the course play within the program:

Chemistry has a significant contribution in developing various technologies and to understand them, student needs a course in Chemistry.

### b) Course is unique or different from other courses of the program:

This course deals with Chemistry aspect of technology and as a discipline it is unique.

### c) Essential knowledge or skills student will gain from this experience:

Skills they gain from this experience are scientific method, analytical thinking, reasoning skills and ability to apply the concepts of Chemistry as and when required.

**d) Knowledge or skills from this course will students need to have master to perform will in future classes or later (higher education/jobs)**

With continuous development of technology, student needs to develop innovative capability and learn to comprehend the scientific principles used in the technology.

**e) Important of this course:**

In sustainable development of the society, Chemistry plays a very crucial role in addressing societal needs like energy, water resources and health care.

**f) Prerequisites(s) of the course:**

Basic intermediate Chemistry which is a prerequisite for the program.

**g) After completion of the course:**

When students complete this course, what do they need know or be able to do?

Student will know about MRI, water treatment methods, spectroscopic techniques and should be able to apply the knowledge learnt to solve real life problems.

**h) Specific knowledge that the students will need to know in the future:**

Concepts like spectroscopic techniques, batteries, corrosion, water treatment methods etc. have a significant role to play in different sectors for sustainable development.

**i) Practical or professional skills that students will need to apply in the future:**

Water technology and corrosive aspects are some of the governing factors for any industry to run smoothly. In this regard, student needs to understand socio-economic aspects of technology associated.

**j) After five years students will remember from this course:**

Water treatment methods, spectroscopic techniques corrosion and reaction mechanism always strive for innovation to cater the changing needs of the society. So, it is imperative for the student to learn and remember these concepts.

**k) About the course that makes it unique or special:**

Concepts delivered in the course connect the basic fundamental knowledge of science to the technology developed for alleviating the problems of society.

**l) Program offers this course:**

The innovations that take place in science later take the shape of technology. So, to understand innovation, basic concepts of Chemistry are essential.

**m) Why can't this course be covered as a sub-section of another course?**

For delivering, the Chemical and scientific aspects of technology, the student needs to be aware of technical terms and their treatment in that discipline. Hence, it cannot be covered as a sub-section.

**n) Unique contribution to students learning experience does this course make:**

Students learn scientific method to draw a conclusion from the given inferences and develop rational thinking.

**o) Value of taking this course: How exactly does it enrich the program?**

The course paves a way for the student to further pursue higher studies inculcating interest and inquisitiveness towards innovative aspects enriching the program.

**8. Pre-requisites: None**

**9. Instructional learning outcomes**

**Unit wise Learning Outcomes**

**UNIT 1: Molecular structure and Theories of Bonding**

**After completion of this unit Students would be able to**

1. Understand and explain the combination of atomic orbitals to form molecular orbitals.
2. Able to write the molecular energy level diagrams of simple molecules like O<sub>2</sub>, N<sub>2</sub> and F<sub>2</sub>
3. Describe the salient features of crystal field theory.
4. Draw and explain the crystal field splitting of transition metal ions (Tetrahedral and Octahedral geometries).
5. Evaluate the crystal field stabilization energies.
6. Explain the magnetic properties of Octahedral and Tetrahedral complexes.

**UNIT 2: Water and its treatment**

**After completion of this unit Students would be able to**

1. Identify the problem of hardness in real life scenario.
2. Evaluate the basic causes for boiler troubles.
3. Predict the causes and preventive measures.
4. Assess different parameters in the boiler troubles and their removal by different treatment methods.
5. Explore different methods in the treatment of hard water.
6. Analyze different parameters in the treatment of potable water.
7. Predict the action of chlorine and ozone on pathogenic bacteria.
8. Innovate different techniques for converting hard water into soft water.

## **UNIT 3: Electrochemistry and Corrosion**

**After completion of this unit Students would be able to**

1. Define basic terms and their relation in Electrochemistry.
2. Calculate concentration of various solutions.
3. Use them in systems like power back up.
4. Calculate free energy and predict the feasibility of the reaction.
5. Identify the importance of batteries in real life scenario.
6. Design a battery and apply them in real life.
7. Appraise the purpose of usage of fuel cells, instead of conventional resources.
8. Identify the problem of corrosion and their disadvantages.
9. Outline the effect of factors on metal tendency towards corrosion.
10. Compare different metals based on their potentials.
11. Use different techniques in order to reduce the corrosion.
12. Use different methods to control corrosion.
13. Compare different methods used to control corrosion.
14. Select appropriate paint in different fields to control corrosion.

## **UNIT 4: Reaction Mechanisms and molecules of industrial importance**

**After completion of this unit students would be able to**

1. Explain the nucleophile substitution  $S_N^1$  and  $S_N^2$  reactions.
2. Apply Markownikoff and Anti Markownikoff rule to addition reactions.
3. Predict the favored alkene product in elimination reactions by applying Satzeff's rule.
4. Explain the reaction mechanisms of some oxidation and reduction reactions.
5. Synthesize Paracetamol and Aspirin and have the knowledge of their pharmaceutical applications.
6. Classify the polymers into various types.
7. Differentiate between addition and condensation reactions in polymers and explain their mechanisms.
8. Prepare some important polymers and explain their properties/applications.

## **UNIT 5: Spectroscopic techniques and applications**

**After completion of this unit students would be able to**

1. Write the selection rules and explain the applications of electronic, vibrational and rotational spectroscopy
2. Explain the basic concepts of NMR such as Chemical shift, formation of relative peaks in the spectrum etc.
3. Apply required skills of various spectroscopic techniques in medical and other fields.

## **10. Class Time Table**

## **11. Individual Time Table**

<b>NAME OF THE FACULTY:</b>								
<b>Designation:</b>								
<b>Day /</b>	<b>I</b>	<b>II</b>	<b>III</b>		<b>IV</b>	<b>V</b>	<b>VI</b>	<b>VII</b>
<b>Period &amp; Time</b>	<b>9.30 - 10.20</b>	<b>10.20 - 11.10</b>	<b>11:10 -12:00</b>	<b>12:00 -12:40</b>	<b>12:40- 1:30</b>	<b>1:30- 2:20</b>	<b>2:20- 3:10</b>	<b>3:10- 4:00</b>
<b>MON</b>				<b>L</b>				
<b>TUE</b>				<b>U</b>				
<b>WED</b>				<b>N</b>				
<b>THU</b>				<b>C</b>				
<b>FRI</b>				<b>H</b>				
<b>SAT</b>								

## 12. Lecture schedule with methodology being used/adopted

Period Number	Total No of Periods	Topics to be covered	Date of topic	Learning Outcomes	BTL	Mode of Teaching	Remarks
				<b>At the end of the program the Student is expected to acquire an ability to -</b>			
<b>Unit I: Molecular structure and theories of Bonding</b>							
01	9	Atomic and Molecular orbitals		Define and explain Atomic and Molecular orbitals	1	BB	offline
02		Linear combination of atomic orbital		Combine atomic orbital by LCAO method.	2	BB	offline
03		Molecular orbital of diatomic molecules		Draw the molecular orbital configurations of N <sub>2</sub> , O <sub>2</sub> , F <sub>2</sub> molecules. Further explain the salient features of CFT	3	BB	offline
04		Molecular orbital energy level diagrams of N <sub>2</sub> , O <sub>2</sub> , F <sub>2</sub> molecules			3	BB	offline
05		CFT: Salient features			2	BB	offline
06		Splitting of transition metal ion d-orbitals in Tetrahedron geomotry		Explain the splitting of t <sub>2g</sub> and e <sub>g</sub> when four ligands approach.	2	BB	offline
07		Splitting of transition metal ion d-orbitals in Octahedral geomotry		Explain the splitting of t <sub>2g</sub> and e <sub>g</sub> when six ligands approach	3	BB	offline
08		CFSE, Applications of CFT		Calculate CFSE of a complex. State and explain the applications of CFT.	4	BB	online
09		Magnetic properties of Tetrahedron and Octahedral complexes.		Apply the spin only formula to explain the magnetic properties.	3	BB	online
			<b>UNIT - II: Water and its treatment</b>				

12	9	Hardness of Water: types of Hardness- Temporary and Permanent,		Identify the problem of hardness in real life scenario.	2	BB	offline	
13		Units and interrelation between them.		Identify the problem of hardness in real life scenario	1	BB	online	
14		Estimation of Hardness of water by EDTA method		Predict the causes and preventive measures Assess different parameters in the boiler troubles and their removal by different treatment methods.	2	BB	online	
15		Treatment of boiler feed water – Internal treatment (Colloidal and Calgon conditioning)		Predict the causes and preventive measures Assess different parameters in the boiler troubles and their removal by different treatment methods.	2	BB	online	
16		External treatment – ion exchange process.		Explore different methods in the treatment of hard water.	2	BB	offline	
17		Potable water- Steps involved in treatment of potable water		Analyze different parameters in the treatment of potable water.	2	BB	online	
18		Potable water- Steps involved in treatment of potable water		Predict the action of chlorine and ozone on pathogenic bacteria.	2	BB	online	
19		Disinfecting water by chlorination and ozonization		Predict the action of chlorine and ozone on pathogenic bacteria.	2	BB	offline	
20		Reverse osmosis & its significance.		Innovate different techniques for converting Hard water into soft water.	3	BB	online	
			<b>UNIT - III: Electrochemistry and corrosion</b>					
21	12	Introduction to Electrochemistry		Recall the Basics of Electro hemistry	1	BB	offline	
22		Electrode potential, standard electrode potential		Use them in systems like power back up	2	BB	offline	
23		Types of Electrodes : SHE, Calomel		Use them in systems like power back up	1	BB	online	
24		Quinhydrone, glass electrode.			2	BB	offline	
25		Electrochemical series and its applications			3	BB	offline	

26		Numerical problems, Potentiometric titrations		Solve numerical problems in electrochemistry.	4	BB	offline
27						BB	
28		Introduction to batteries; types of batteries, Secondary Batteries, Lead-acid battery Lithium ion battery,		Identify the importance of batteries in real life scenario.	2	BB	offline
29		<b>Corrosion:</b> Introduction, Causes and effects of corrosion.		Identify the problem of corrosion and their disadvantages.	2	BB	online
30		Theories of corrosion: Chemical corrosion		Identify the problem of corrosion and their disadvantages	2	BB	online
31		Electro chemical corrosion mechanism		Identify the problem of corrosion and their disadvantages	3	BB	offline
32		Types of corrosion: Galvanic, waterline and pitting corrosion		Will be able to identify and explain types of corrosion	3	BB	online
33		Factors affecting corrosion		Explain the factors of corrosion	2	BB	online
34		Corrosion control methods: Sacrificial and impressed current cathodic protections		Will gain the knowledge of control methods of corrosion	2	BB	online
35		Metallic coatings, Galvanizing and Tinning, Electroless plating of Nickel.		Will gain the knowledge of control methods of corrosion	2	BB	offline
	<b>UNIT - IV: Reaction Mechanisms and molecules of industrial importance</b>						
36	1 2	Substitution reactions: Nucleophilic substitution reactions: Mechanism of S <sub>N</sub> 1, S <sub>N</sub> 2 reactions.		Have the in-depth knowledge of S <sub>N</sub> 1, S <sub>N</sub> 2 reaction mechanisms	3	BB	offline
437		Electrophilic and nucleophilic addition reactions		Have the in depth knowledge of electrophilic and nucleophilic addition reactions	3	BB	offline

38	Addition of HBr to propene. Markownikoff and anti Markownikoff additions. Grignard additions on carbonyl compounds.		Have Understanding of Markowinkoff and Antimarkowinkof rules for addition reactions.	3	BB	offline
39	Elimination reactions: Dehydro halogenation of alkylhalides. Saytzeff rule. Oxidation reactions: Oxidation of alcohols using $\text{KMnO}_4$ and chromic acid.		Have Understanding of Elimination reactions with some specific examples	3	BB	online
40	Reduction reactions: reduction of carbonyl compounds using $\text{LiAlH}_4$ & $\text{NaBH}_4$ .		Will be able to explain some specific reduction reactions	3	BB	online
41	Hydroboration of olefins. Structure, synthesis and pharmaceutical applications of Paracetamol and Aspirin.		Will gain the knowledge of synthesis of important drugs like Aspirin and paracetamol.	3	BB	online
42	<b>Polymers:</b> Classification of polymers		Will be able to classify polymers with ease	2	BB	online
43	Types of Polymerization—addition and condensation, differences between addition and condensation polymers,		Will gain the ability to differentiate addition and condensation polymers	2	BB	online
44	Mechanism of free radical addition polymerization. Preparation, properties and engineering			3	BB	offline

		applications of PVC, Teflon and Nylon- 6, 6.					
	<b>9</b>	<b>UNIT - V: Spectroscopic techniques and applications</b>					
45		Principles of spectroscopy		Have the knowledge of basics of spectroscopy	2	BB	offline
46		Beer lambert's law, Principle of UV-Visible spectroscopy, selection rules,		Apply the knowledge of Beer-lambert's law principle in interpreting UV spectroscopy Explain the selection rules	3	BB	online
47		applications of electronic spectroscopy		Apply the principles of electronic spectroscopy at appropriate place.	3	BB	online
48		vibrational and rotational spectroscopy		Apply the principles of vibrational and rotational at appropriate place.	2	BB	offline
48		Basic concepts of Nuclear magnetic resonance Spectroscopy		Have understanding of basic concept of NMR	3	BB	offline
49		Introduction to Magnetic resonance imaging		Have the knowledge of basic concept of MRI and its applications.	4	BB	offline

### **13.Detailed notes**

Soft and hard copies are available

#### **Molecular structure and Theories of Bonding:**

Atom consists of a central nucleus surrounded by one or more orbital electrons. The nucleus always possesses positive character, as it contains positively charged proton and neutron which is electrically neutral. Electron has dual character i.e. it behaves both as a particle and as a wave.

#### **Atomic orbital:**

An atomic orbital is a mathematical function that describes the wave-like behavior of electrons in an atom. It can be used to calculate the probability of finding any electron of an atom in any specific region around the nucleus of atom.

Each orbital in an atom is characterized by a unique set of values of the four quantum numbers  $n$ ,  $\ell$ ,  $m$  and  $s$  correspond to the energy, angular momentum, magnetic moment and spin of the electron respectively.

The principal quantum number  $n$  describes the energy of the electron and is always a positive integer. Each atom has many orbitals associated with each value of  $n$ . These orbitals together are called electron shells.

The azimuthal quantum number  $\ell$  describes the orbital angular momentum of each electron and is a non-negative integer. The set of orbitals associated with a particular value of  $\ell$  are collectively called a subshell.

The magnetic quantum number  $m$ , describes the magnetic moment of an electron in an arbitrary direction, and is also an integer.

**Molecular orbital (MO)** is a mathematical function describing the wave-like behavior of an electron in a molecule. This function can be used to calculate chemical and physical properties such as the probability of finding an electron in any specific region.

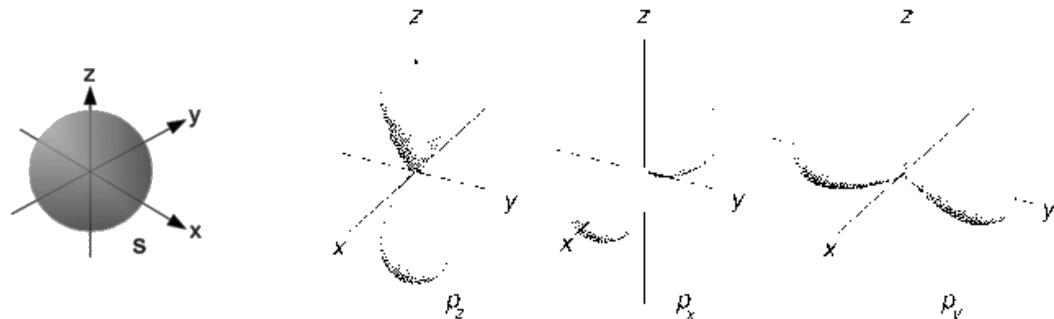
Molecular orbitals are obtained from the combination of atomic orbitals, which predict the location of an electron in an atom.

Molecular orbitals arise from allowed interactions between atomic orbitals that are further allowed if their symmetries are compatible with each other. Efficiency of atomic orbital interactions is determined from the overlap between two atomic orbitals, that is significant if the atomic orbitals are close in energy. Finally, the number of molecular orbitals formed must be equal to the number of atomic orbitals in the atoms being combined to form the molecule.

### **1. Molecular Orbital theory:** This theory was stated by Hund and Mulliken.

#### **Postulates of MOT:**

1. A molecule is considered as a group of nuclei and the orbitals are devised for the molecule as a whole.
2. All the electrons are distributed around the single nucleus in different energy levels in an atom. Those orbitals are called atomic orbitals. They are mono centric.



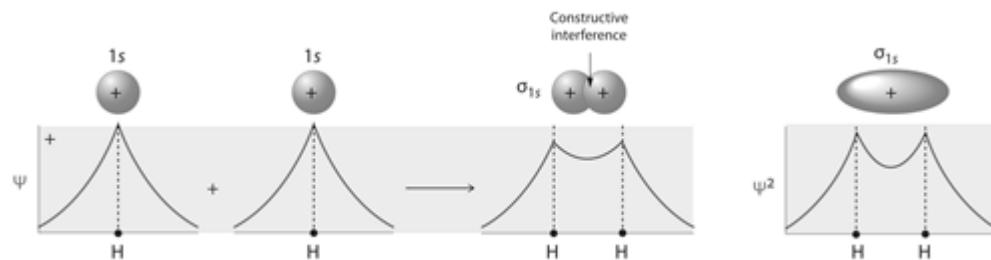
3. When the electrons are distributed around a group of nuclei in different energy levels of a molecule. They are called molecular orbitals, which are polycentric.
4. Each orbital in the molecule is described by wave function. The value of wave function is obtained by a method called LCAO.
5. Each molecular orbital contain definite amount of energy. It can be calculated by applying Schrodinger equation.
6. The size, shape and energy of molecular orbitals depend upon that of corresponding atomic orbitals.
7. Atomic orbitals with same symmetry and comparable energies may combine to form molecular orbitals.
8. The electrons are filled in molecular orbitals as per the same rules followed by atomic orbitals, viz. Aufbau principle, Pauli exclusion principle and Hunds rule of maximum multiplicity.

## Bonding, antibonding, and nonbonding MOs

When atomic orbitals interact, three types of molecular orbitals can be formed- bonding, anti bonding, or nonbonding.

### Bonding MOs:

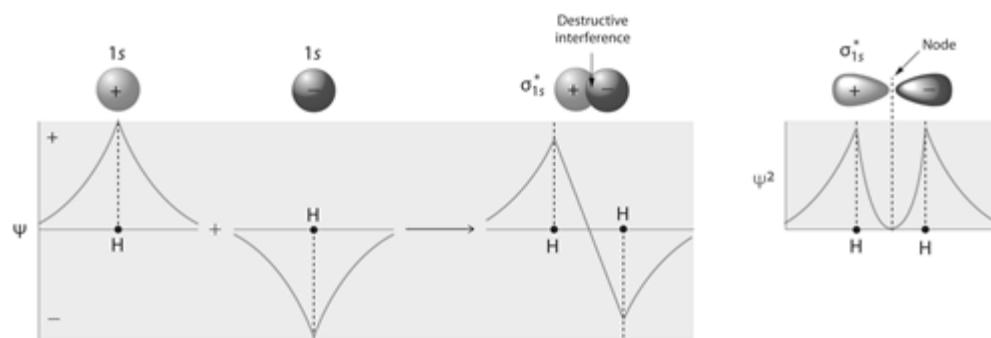
Bonding MOs are lower in energy than that of combining atomic orbitals. The interactions between atomic orbitals are constructive. These are formed when the lobes of combining atomic orbitals overlap with the same sign.



### Anti bonding MOs:

Antibonding MOs are higher in energy than the atomic orbitals that are combining. Interactions between atomic orbitals are destructive where the wave function of the anti-bonding orbital is zero between the two interacting atoms.

These are formed when the lobes of combining atomic orbitals are of opposite sign and the overlapping orbitals will be out of phase.



### Nonbonding MOs:

Nonbonding MOs will have the same energy as that of the atomic orbitals in the molecule. Nonbonding MOs are the result of no interaction between atomic orbitals because of lack of compatible symmetries.

**Linear Combination of atomic orbitals (LCAO):** The linear combination of atomic orbitals (LCAO) approximation for molecular orbitals was introduced by Sir John Lennard-Jones in 1929.

The wave function of molecular orbital can be constructed by Linear Combination of atomic orbitals (LCAO) method.

In this method the linear combination of wave functions of two atomic orbitals is brought about either by adding or by subtracting the two wave functions.

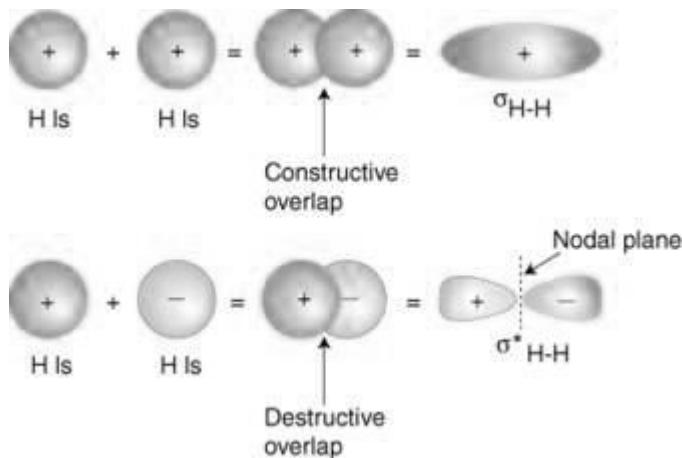
$$\therefore \Psi = \psi_A \mp \psi_B$$

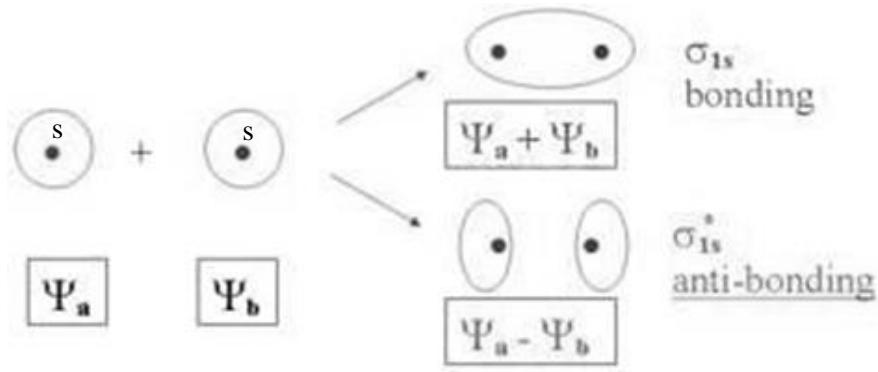
Where ‘ $\Psi$ ’ is the wave function of molecular orbital, $\psi_A$  and  $\psi_B$  are the wave functions of two atoms A and B.

The atomic orbitals  $\psi_A$  and  $\psi_B$  will combine effectively, only when they have similar energy, same symmetry and when they overlap. The function  $\Psi^+$  or  $\Psi_g$  is a bonding molecular orbital and is associated with decrease in energy, while  $\Psi^-$  or  $\Psi_u$  is an antibonding orbital which is associated with an increase in energy. (where ‘g’ stands for gerade (even) and ‘u’ stands for un gerade (odd) both refer to the symmetry of orbital.)

Consider the wave functions  $\psi_A$  &  $\psi_B$  of two atoms A & B which contain atomic orbitals. A pair of atomic orbitals ( $\psi_A$  &  $\psi_B$ ) combine to form a pair of molecular orbitals  $\psi_g$  &  $\psi_u$ . The number of molecular orbitals formed always be equal to the number of atomic orbitals involved. The wave function  $\psi_g$  leads to increased electron density in between the nuclei and therefore a bonding orbital. It is lower in energy than the original atomic orbital. The function  $\psi_u$  results in zero electron density as two lobes of opposite sign cancel each other. Therefore the anti bonding molecular orbital is higher in energy.

A pictorial representation of LCAO procedure is as follows





When the two 1s orbitals are added they reinforce each other, mostly in the region between the nuclei. The building up of electron density between the nuclei helps to lower the coulombic potential energy resulting a bond, denoted as  $\sigma$  1s.

When one atomic orbital is subtracted from the other, they exactly cancel each other in a plane midway between the nuclei, there by producing a nodal plane. The resulting electron density is zero at nodal plane. This deficiency of electron density helps to raise the coulombic potential energy of the system resulting antibonding orbital (denoted as  $\sigma^*$  1s).

#### **Rules for Linear combination of atomic orbitals**

The following rules must be considered to decide the combination of atomic orbitals in to molecular orbitals.

1. The atomic orbitals must be roughly of the same energy.
2. The orbitals must overlap one another as much as possible. This is done only when the atoms are close enough and radial distribution functions of two atoms are similar.
3. In order to produce bonding and anti bonding MO's, either the symmetry of the two atomic orbitals must remain unchanged when rotated about the inter nuclear axis, or both atomic orbitals must change symmetry in an identical manner.
4. Aufbau principle is used to fill the molecular orbitals with electrons. Lowest energy orbitals should be filled first. Each orbital may hold up to two electrons of opposite spins.
5. Hunds rule is to be followed to fill the electrons in molecular orbitals. When several orbitals are degenerate (Having same energy) electrons will be arranged so as to give maximum number of unpaired spins.

## Molecular orbital treatment of homo nuclear diatomic molecules

Homo nuclear diatomic molecules have two identical atoms linked together. Examples are H<sub>2</sub>, O<sub>2</sub>, and N<sub>2</sub>.

Key points to be remembered while drawing molecular orbital diagram of homonuclear diatomic molecules.

The number of molecular orbitals produced is the same as the number of atomic orbitals used to create them.

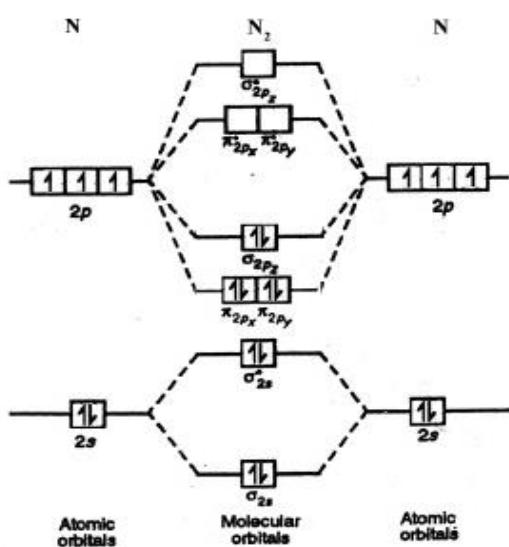
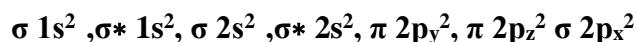
As the overlap between two atomic orbitals increases, the difference in energy between the resulting bonding and antibonding molecular orbitals increases.

When two atomic orbitals combine to form a pair of molecular orbitals, the bonding molecular orbital is stabilized about as much as the antibonding molecular orbital is destabilized.

The interaction between atomic orbitals is greatest when they have the same energy.

### N<sub>2</sub> Molecule:

A nitrogen atom has 7 electrons as its electronic configuration is 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>3</sup>. Therefore N<sub>2</sub> molecule has 14 electrons. These are arranged in the molecular orbitals as follows.



Assume that inner shell does not participate in bonding. Therefore the bonding & antibonding 2s levels cancel. One  $\sigma$  & two  $\pi$  bonding pairs remain giving a total of 3 bonds. This is in agreement with the valence bond for mutation as N=N.

### O<sub>2</sub> Molecule:

A nitrogen atom has 7 electrons as its electronic configuration is 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>4</sup>. Therfore O<sub>2</sub> molecule has 16 electrons. These are arranged in the molecular orbitals as follows.

$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_x^2, \pi 2p_y^2, \pi 2p_z^2, \pi^* 2p_y^1, \pi^* 2p_z^1$

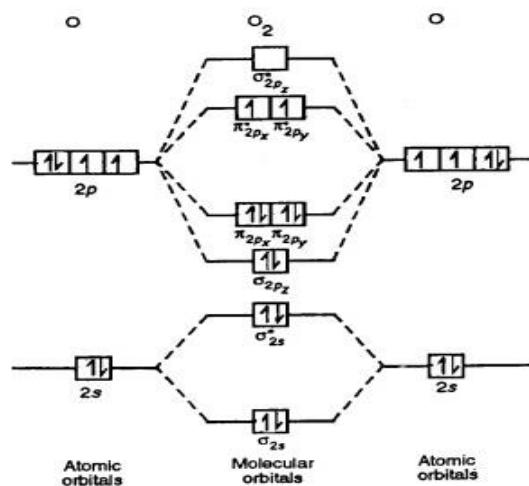
As per Hund's rule, the two anti-bonding orbitals,  $\pi^* 2p_y^1$  &  $\pi^* 2p_z^1$  are singly occupied. Unpaired electrons with parallel signs lead to paramagnetism. This is the reason why O<sub>2</sub> molecule is diamagnetic.

Assuming inner shell does not participate in bonding &anti-bonding 2s orbitals cancel each other. A  $\sigma$  bond results from the filling of  $\sigma 2p_x^2$ .Half the effect of the completely filled  $\pi 2p_z^2$ . Half the effect of the completely filled  $\pi 2p_y^2$  orbital is cancelled by half-filled  $\pi^* 2p_y^1$  and therefore half of a  $\pi$  bond remains. Similarly another half of the  $\pi$  bond arises from  $\pi 2p_z^2$  and  $\pi^* 2p_z^1$  giving a total of  $1 + \frac{1}{2} + \frac{1}{2} = 2$  bonds. Thus the bond order as above it can also be calculated by the equation.

$$\text{Bond order} = \frac{(\text{No. of electrons occupying Bonding orbitals}) - (\text{No. of electrons occupying anti-bonding orbitals})}{2}$$

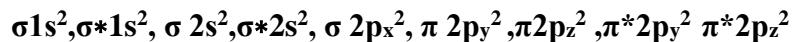
of O<sub>2</sub> molecule,

bond order can be calculated as =  $(10-6)/2 = 2$ . It corresponds to double bond.



## **F<sub>2</sub> Molecule:**

Fluorine atom has 2+7 (1s<sup>2</sup>2s<sup>2</sup>2p<sup>5</sup>) electrons. Thus Fluorine molecule contains 18 electrons. These electrons are arranged in the following order.



The inner shell is non bonding and the filled bonding 2s, 2p<sub>y</sub> and 2p<sub>z</sub> are cancelled by the equivalent antibonding orbitals. This leads to a  $\sigma$  bond from the filled  $\sigma$  2p<sub>x</sub><sup>2</sup> and thus a bond order of one.

In case of F<sub>2</sub> molecule, bond order can be calculated as = (10-8)/2=1, which corresponds to single bond.

**Advantages of MO theory:** MO theory extended to cover  $\pi$  bonding, in consequence it helps to explain how metals in low oxidation states (ex: [Ni<sup>0</sup>(CO)<sub>4</sub>] can form complexes.  $\pi$  bonding also helps to explain the position of some ligands in spectro chemical series.

There are two cases of  $\pi$  bonding:

**$\pi$  acceptors:** Ligands such as CO, CN<sup>-</sup> and NO<sup>+</sup> have empty  $\pi$  orbitals with the correct symmetry to overlap with the metal t<sub>2g</sub> orbitals giving  $\pi$  bonds. Normally the  $\pi$  orbital of ligand has higher in energy than metal t<sub>2g</sub> orbital. Though no more electrons are added as the ligand  $\pi$  orbitals are empty, but the  $\pi$  interaction increases the value of  $\Delta$ . This makes them as strong field ligands and accounts for the position of these ligands at the right of spectro chemical series.

**$\pi$  donors :** When the ligands with filled  $\pi$  orbitals overlap with the metal t<sub>2g</sub> orbitals giving  $\pi$  bond, electron density is transferred from ligand to the metal. Such cases arise when the central metal has high oxidation state and devoid of electrons.  $\pi$  orbitals of ligand has lower in energy than metal t<sub>2g</sub> orbitals. Delocalizing  $\pi$  electrons from the ligand to the metal reduces the value of  $\Delta$ .

**Disadvantages** The enthalpies of formation and bond energies cannot be calculated directly.

**Crystal Field Theory (CFT):** To explain the nature of bonding in transition metal complexes especially ionic crystals, Brethe and Vanvleck suggested a theory called Crystal Field Theory (CFT).

### **Main Features of the CFT are**

1. Any complex is a combination of a central metal ion surrounded by other ions or molecules called ligands.
2. Ligands can either be negatively charged ions or neutral molecules. Hence they are considered as point charges or point dipoles.

3. If the ligands are negatively charged, they approach closer to the central metal ion with negative poles or ends. If they are neutral molecules, they are polarised by positive charge of the cation and thus appear as negatively charged dipoles.
4. The bonding between metal cation and ligands arises due to an electrostatic attraction between the nucleus of metal cation and negatively charged ligands, represented as point charges or point dipoles.
5. The metal ion and the ligands do not mix their orbitals and share electrons. i.e. there is no orbital overlap between the metal ion and ligands.
6. As the interaction between electrons of metal ion and those of ligands is repulsive, it causes splitting of d-orbitals of the metal cation. The bond is purely ionic.

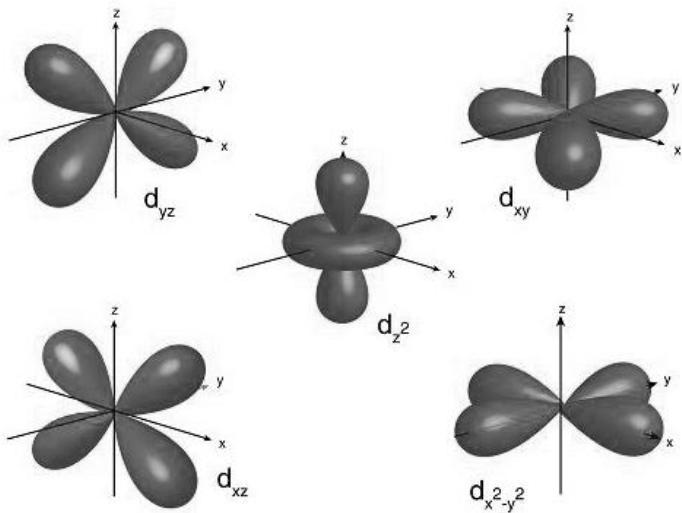
### **Crystal field splitting of transition metal ion d- orbitals**

Based on the orientation of the lobes of the five d- orbitals, they are divided in to two groups.

1. **Axial Orbitals:** The group of orbitals which contain their lobes along the axes are called axial orbitals. According to group theory, these are also called  $e_g$  orbitals, where ‘e’ represents doubly degenerate. Two  $e_g$  orbitals are  $d_{z^2}$  and  $d_{x^2-y^2}$ .
2. **Non axial orbitals:** The group of orbitals whose lobes lie in between the axes are called non axial orbitals. These are also called  $t_{2g}$  orbitals where ‘t’ represents triply degenerate.

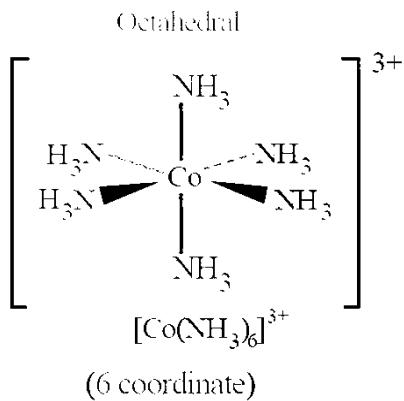
The three  $t_{2g}$  orbitals are  $d_{xy}$ ,  $d_{xz}$  and  $d_{yz}$ .

In case of a transition metal ion in free space, all the five d orbitals are degenerate, as their energies are same. The degeneracy of the d-Orbitals is removed in the electrostatic field created by the presence of the ligands. The symmetrical field caused by the ligands is similar to the electrostatic field around ions in ionic crystals. Ligands are placed symmetrically around the central metal ion. But when the ligands come close to the central metal ion, the energy of the entire system decreases due to electrostatic attraction between them. The five d orbitals of the metal ion are no longer spatially equivalent. Two  $e_g$  orbitals,  $d_{z^2}$  and  $d_{x^2-y^2}$  have greater electron density in directions that lie along the axes. The other three  $t_{2g}$  orbitals,  $d_{xy}$ ,  $d_{xz}$  and  $d_{yz}$  have greatest electron density in the region between the axes. The stronger the field due to the ligands, the greater the splitting of the energy levels ( $10Dq$ ).



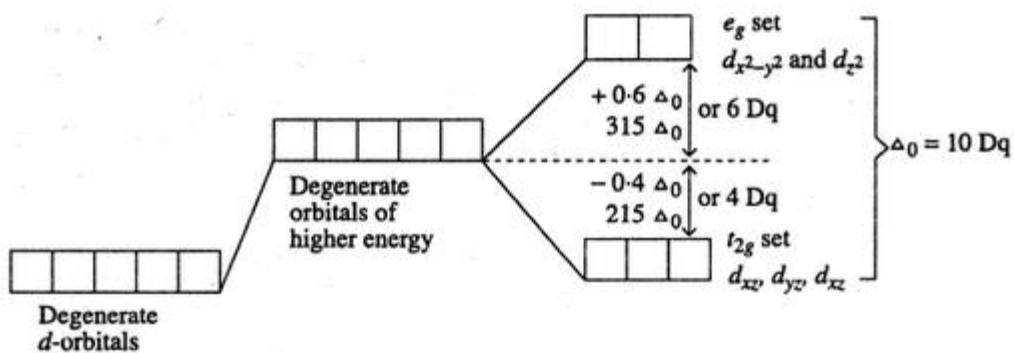
### Crystal field splitting in octahedral complexes:

Let us consider an example of octahedral complex  $[\text{CO}(\text{NH}_3)_6]^{3+}$ , in which the central metal cobalt cation is placed at the centre of the octahedron and is surrounded by six  $\text{NH}_3$  ligands, which are located at the six corners of the octahedron.

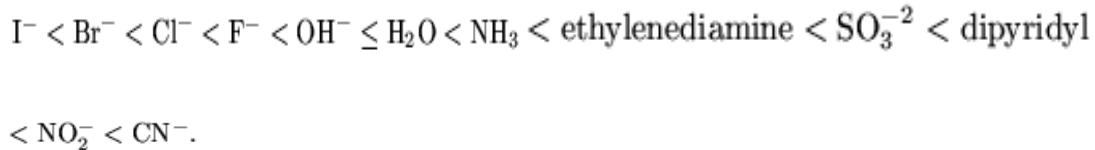


As the negative ligands (i.e. negative point charges in case of ionic ligands and negative dipoles in case of neutral ligands) brought near the central metal ion, electrons feel repulsion. This repulsion will raise the energy of all the five d orbitals. Since the lobes of the two  $e_g$  orbitals are concentrated along the path of the approaching ligands, electrons in the  $e_g$  orbitals feel stronger electron repulsion from the ligand than do electrons in the  $t_{2g}$  orbitals, whose lobes are located in between the path of approaching ligands. Because the  $e_g$  orbitals are more concentrated along the axes where ligands are located. Thus, the degeneracy of five d orbitals is removed in presence of ligands and split into high energy and lower energy  $t_{2g}$  orbitals.

"The splitting up of five d-orbitals of the metal ion into two sets of orbitals containing different  $e_g$  energies is called Crystal field splitting."



For octahedral splitting in order of increasing  $\Delta_0$ , some common species are:

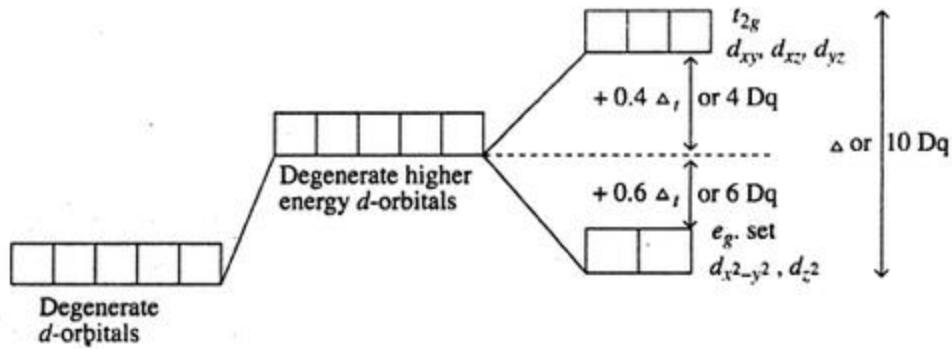


### Crystal field stabilisation energy:

The decrease in energy caused by the splitting of the energy levels is the crystal field stabilisation energy or Crystal field stabilisation energy(CFSE). i.e. The energy gap between  $t_{2g}$  and  $e_g$ , which arises due to the electro static field exerted by the ligands on  $t_{2g}$  and  $e_g$  sets. It is denoted by  $\Delta_o$  (where 'o' represents octahedral arrangement of ligands) or  $10 \text{ Dq}$ . The energy of  $t_{2g}$  orbitals is  $0.4 \Delta_o$  less than that of hypothetical degenerate orbitals and the energy of  $e_g$  orbitals is  $0.6 \Delta_o$  more than that of hypothetical degenerate orbitals. It is clear that,  $t_{2g}$  orbitals loose energy equivalent to  $0.4 \Delta_o$  or  $4 \text{ Dq}$  and  $e_g$  orbitals gain energy equal to  $0.6 \Delta_o$  or  $6 \text{ Dq}$ . The loss and gain of energies can be shown by positive and negative signs respectively.

### Crystal field splitting in tetrahedral complexes:

Let us consider an example of a tetrahedral complex  $[\text{CoCl}_4]^{2-}$



3. The four negative ligands are located at the four corners of the cubes. Thus, they are placed in between the three axes, x,y,z. The lobes of  $t_{2g}$  orbitals ( $d_{xy}$ ,  $d_{xz}$  and  $d_{yz}$ ) are placed between the axes i.e. directly in the path of ligands. Therefore they experience greater force of repulsion from the ligands than those of  $e_g$  orbitals ( $d_{z^2}$  and  $d_{x^2-y^2}$ ). Hence  $t_{2g}$  orbitals have high energy and  $e_g$  orbitals have low energy.
4. The energy difference between  $t_{2g}$  and  $e_g$  sets of orbitals for tetrahedral complex is represented as  $\Delta_t$ .  

$$\therefore \Delta_t < \Delta_0$$

$$\Delta_t = 0.45\Delta_0$$

#### Distribution of d-electrons in $t_{2g}$ and $e_g$ orbitals in octahedral complexes

The distribution of d-electrons in  $t_{2g}$  and  $e_g$  orbitals takes place based on the nature of ligands (i.e. whether they are weak or strong)

**Strong Ligands:** Ligands with donor atoms like halogens, oxygen and sulphur act as strong ligands.

**Ex:**  $F^-$ ,  $Cl^-$ ,  $Br^-$ ,  $I^-$ ,  $OH^-$ ,  $SCN^-$ ,

**Weak Ligands:** Ligands with donor atoms like Carbon, nitrogen and phosphorus act as weak ligands.

**Ex:**  $CN^-$

When the ligands are weak, the energy difference between  $t_{2g}$  and  $e_g$  orbitals is relatively small and the distribution of d-electrons in  $t_{2g}$  and  $e_g$  sets obey Hund's rule.

Consider a complex  $[COF_6]^{2-}$  where Fluorine is a weak ligand. The distribution will be as follows. First three electrons (1,2,3) go to  $t_{2g}$  level and 4,5 electrons go to  $e_g$  level and then the pairing starts (i.e. 6<sup>th</sup> electron will occupy  $t_{2g}$  set). The complexes containing weak ligands are called high spin complexes.

In the formation of such complexes  $\Delta_o < P$  where 'P' is the pairing energy i.e. energy required to pair two electrons in the same orbital.

When ligands are strong ,distribution of d-electrons in  $t_{2g}$  and  $e_g$  orbitals does not obey hund's rule. Consider an example of  $[CO(NH_3)]^{2+}$  complex which contains strong ligands. The distribution of electrons will be as follows.



All the six electrons (1,2,3,4,5,6) enter in to  $t_{2g}$  set and the  $e_g$  set is empty.

For these complexes  $\Delta_o > P$

### **Applications of Crystal field theory (CFT):**

#### **Magnetic Properties of transition metal complexes.**

Number of techniques can be used to determine magnetic susceptibilities of transition metal complexes. These include the Gouy method, the Faraday method, and the NMR method. Of these, the Faraday and NMR techniques are suitable for micro scale samples ( $\leq 50$  mg). Generally, the magnetic moment can be measured using a Gouy method, which involves weighing a sample of the complex in the presence and absence of a magnetic field and observing the difference in weight.

From quantum mechanics point of view, magnetic moment  $\mu$ , results from both the spin and orbital contributions of unpaired electrons.

$$\mu_{S+L} = \sqrt{4S(S+1) + L(L+1)}$$

But, the presence of ligands around the metal ion quenches the orbital contribution, making the spin contribution most important. Therefore, contribution towards orbital magnetic moment can be ignored in transition metal complexes. Assuming the magnetic moment arises entirely from unpaired electron spins, 'spin only formula' can be used to estimate the number of unpaired electrons.

$$\mu_S = g \sqrt{S(S+1)}$$

In the above equation,  $g$  = gyromagnetic ratio ( $g = 2.00023$ ),  $S = n (1/2)$ , where  $n$  is the number of unpaired electrons.

Substituting  $g = 2$  and  $S = n (1/2)$  into equation, we get

$$\mu_s = \sqrt{[n(n+2)]}$$

Calculation of magnetic moment through Spin only formula gives reasonable agreement with the complexes of first row transition elements.

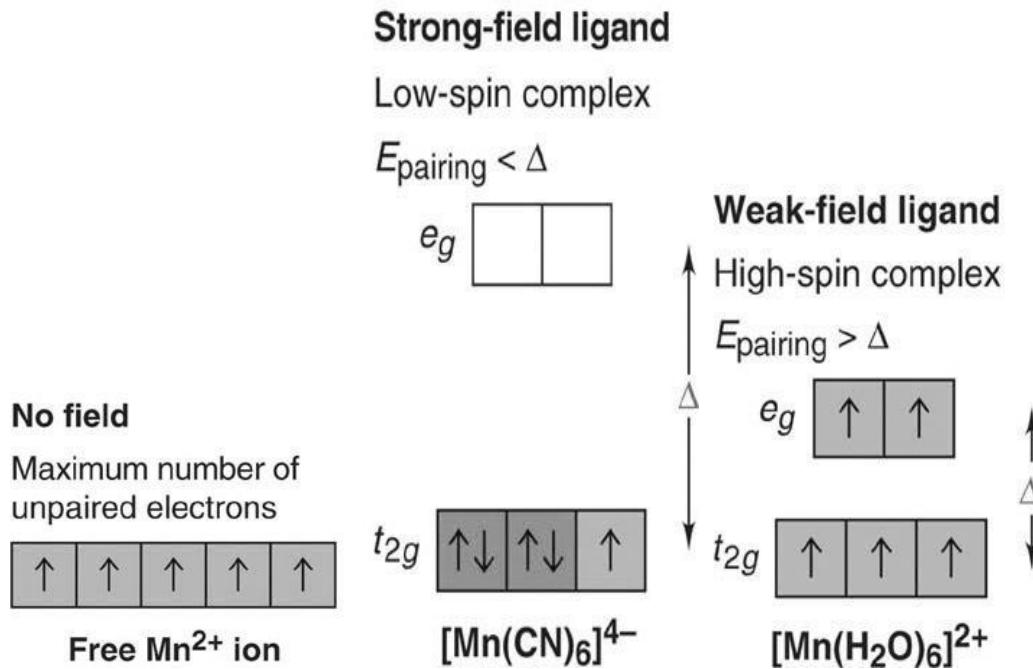
When an electron in an atom or ion is unpaired, the magnetic moment due to its spin makes the entire atom or ion paramagnetic. The strength of the magnetism of a coordination complex increases with the number of unpaired electrons. The greater the number of unpaired electrons, the larger is the magnetic moment. A higher-spin complex is more paramagnetic. The occurrence and relative strength of magnetism can be predicted by determining whether the compound is coordinated to a weak field ligand or a strong field ligand.

Crystal field theory is helpful in determining the number of unpaired electrons in a given high spin (HS) and low spin(LS) octahedral complex. Since the number of unpaired electrons in the central metal ion with  $d^4$  to  $d^7$  configuration in HS and LS complexes is different,  $\mu_s$  values are also different. Experimental evidence of magnetic measurements supports the theory of high- and low-spin complexes.

Hunds rule states that electrons fill all available orbitals with single electrons before pairing up, while maintaining parallel spins (paired electrons have opposing spins). For a set of five degenerate d-orbitals in a metal atom, electrons fill all orbitals before pairing to conserve pairing energy. After the addition of ligands, the splitting energy between the d-orbitals increases the energy required to place single electrons into the higher-energy orbitals. Once the lower-energy orbitals have been half-filled, the strength of the ligands decide, whether the next electron is to be placed in a higher-energy orbital or paired with an electron in a lower-energy orbital.

If the splitting energy is greater than the pairing energy, the electrons will pair up, as in complexes with strong field ligand (Low spin complexes). These complexes, such as  $[\text{Mn}(\text{CN})_6]^{4-}$  are more often diamagnetic or weakly paramagnetic.

If the pairing energy is greater, unpaired electrons will occupy higher energy orbitals as in complexes with weak field ligand (high-spin complexes). High-spin complexes are often paramagnetic. The unpaired electrons in paramagnetic compounds create tiny magnetic fields. For example, Complexes such as  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ , containing weak field ligands are paramagnetic.



### Limitations of CFT

1. CFT considers only the metal ion d-orbitals. It does not explain the formation of  $\pi$  bonding in complexes.
2. According to CFT the bond between metal and ligand is purely ionic. It does not explain the partly covalent nature of metal-ligand bond.

## UNIT- II

### Water and its treatment

#### Introduction:

Water is nature's most wonderful, abundant, useful compound and is an essential without it one cannot survive. It occupies a unique position in industries. Its most important use is as an engineering material in the *steam generation*. Water is also used as *coolant* in power and chemical plants. It is also used in other fields such as production of steel, rayon, paper, atomic energy, textiles, chemicals, ice and for air-conditioning, drinking, bathing, sanitary, washing, irrigation, etc.

#### Occurrence:

Water is widely distributed in nature. It has been estimated that about 75% matter on earth's surface consists of water. The body of human being consists of about 60% of water. Plants, fruits and vegetables contain 90-95% of water.

#### Sources of Water:

Different sources of water are:

1. **Surface Waters:** Rain water (purest form of natural water), River water, Lake Water, Sea water (most impure form of natural water).

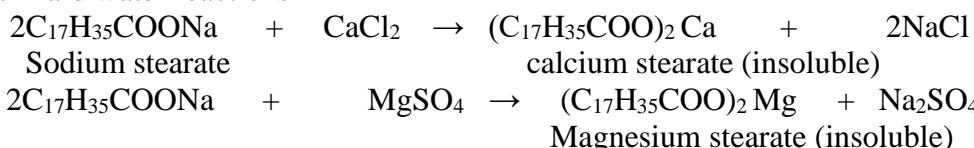
**Underground Waters:** Spring and Well water. Underground waters have high organic impurity.

**Hardness of water :** Hardness of water defined as which prevent the lathering of soap. This is due to presence of in water of certain salts of  $\text{Ca}^{+2}$ ,  $\text{Mg}^{+2}$  and other Heavy metals dissolved in it.

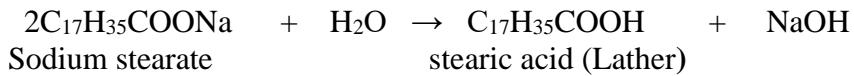
Soaps are Sodium or Potassium salts of higher fatty acids like Oleic acid or Palmitic acid or stearic acids.

**Hard water:** Water which does not produce lather with soap solution is called hard water.

Soap with hard water reactions



**Soft water:** Water which produce lather easily on shaking with soap solution is called soft water. Such water does not contain dissolved calcium and magnesium salts in it.



**Degree of hardness:** Hardness of water is expressed in terms of calcium carbonate equivalents. The weights of different salts causing hardness are converted to weight equivalent to that of  $\text{CaCO}_3$ .

If a sample of water contains two or more than two salts, their quantities are converted in equivalent to that of  $\text{CaCO}_3$  and then the sum will give the total hardness.  $\text{CaCO}_3$  is selected for expression of the degree of hardness, because the mol.wt. of  $\text{CaCO}_3$  is 100, which is easy for calculation and  $\text{CaCO}_3$  is an insoluble salt. All the dissolved salts of calcium are precipitated as  $\text{CaCO}_3$ .

Hardness of the water causing salt in terms of  $\text{CaCO}_3$  =  $\frac{\text{Amount of the hardness causing salt} \times 100}{\text{mol. wt. of the hardness causing salt}}$

**Different types of water have different degrees of hardness:**

Hardness	Name of water
0-70 mg/liter	Soft water
70-150 mg/liter	Moderate hard water
150-300 mg/liter	Hard water
300 mg/liter & above	Very hard water

**Equivalents of  $\text{CaCO}_3$ :** 100 parts by weight of  $\text{CaCO}_3$  hardness must be equivalent

- 162 parts by weight of  $\text{Ca}(\text{HCO}_3)_2$  hardness .
- 146 parts by weight of  $\text{Mg}(\text{HCO}_3)_2$  hardness.
- 136 parts by weight of  $\text{CaSO}_4$  hardness.
- 111 parts by weight of  $\text{CaCl}_2$  hardness.
- 164 parts by weight of  $\text{Ca}(\text{NO}_3)_2$  hardness.
- 120 parts by weight of  $\text{MgSO}_4$  hardness.
- 95 parts by weight of  $\text{MgCl}_2$  hardness

**Units of hardness:-**

1. Parts Per Million (ppm):- is the parts of  $\text{CaCO}_3$  equivalent hardness per  $10^6$  parts of water i.e.,  
 $1\text{ppm} = 1$  part of  $\text{CaCO}_3$  equivalent hardness in  $10^6$  parts of water.
2. Milligrams Per Litre (mg/L):- number of milligrams of  $\text{CaCO}_3$  equivalent hardness present per liter of water.

$1\text{mg/L} = 1\text{mg of CaCO}_3$  equivalent hardness of  $1\text{L}$  of water =  $1\text{kg} = 1000\text{g} = 10^6\text{mg}$ .

$\therefore 1\text{mg/L} = 1\text{mg of CaCO}_3 \text{ eq per } 10^6 \text{ mg of water} = 1\text{ppm}$ .

3. Clarke's degree ( ${}^0\text{Cl}$ ):- the no. of grains ( $1/7000\text{lb}$ ) of  $\text{CaCO}_3$  equivalent hardness per gallon ( $10\text{lb}$ ) of water or it is parts of  $\text{CaCO}_3$  equivalent hardness per 70,000 parts of water.  
 $\therefore 1 {}^0\text{Cl} = 1$  grain of  $\text{CaCO}_3$  eq hardness per gallon of water

= 1 part of  $\text{CaCO}_3$  hardness eq per  $10^5$  parts of water.

4. Degree French ( ${}^\circ\text{Fr}$ ):- parts of  $\text{CaCO}_3$  equivalent hardness per  $10^5$  parts of water.  $\therefore 1 {}^\circ\text{Fr} = 1$  part of  $\text{CaCO}_3$  equivalent hardness per  $10^5$  parts of water.

5. Milli-equivalent per liter (meq/L):- is the number of milli-equivalents of hardness present per liter.  $1\text{ meq/L} = 1\text{ meq of CaCO}_3$  per liter of water  
 $= 10^{-3} \times 50 \text{ g of CaCO}_3 \text{ eq. per liter}$   
 $= 50 \text{ mg of CaCO}_3 \text{ eq. per liter} = 50 \text{ mg/L of CaCO}_3 \text{ eq.} = 50\text{ppm.}$

### Relationship between various units of hardness:

$$1 \text{ ppm} = 1 \text{ mg/L} = 0.1 {}^\circ\text{Fr} = 0.07 {}^\circ\text{Cl} = 0.02 \text{ meq/L}$$

$$1 \text{ mg/L} = 1 \text{ ppm} = 0.1 {}^\circ\text{Fr} = 0.07 {}^\circ\text{Cl} = 0.02 \text{ meq/L}$$

$$1 {}^\circ\text{Cl} = 1.433 {}^\circ\text{Fr} = 14.3 \text{ ppm} = 14.3 \text{ mg/L} = 0.0286 \text{ meq/L}$$

$$1 {}^\circ\text{Fr} = 10 \text{ ppm} = 10 \text{ mg/L} = 0.7 {}^\circ\text{Cl} = 0.2 \text{ meq/L}$$

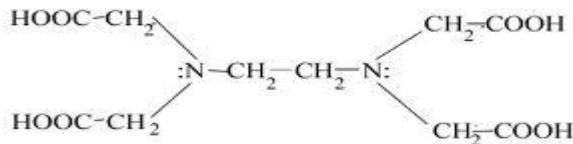
$$1 \text{ meq/L} = 50 \text{ mg/L} = 50 \text{ ppm} = 5 {}^\circ\text{Fr} = 0.35 {}^\circ\text{Cl}$$

### ESTIMATION OF HARDNESS BY EDTA METHOD:

The analysis is done by complexometric titration using standard EDTA and EBT as an indicator.

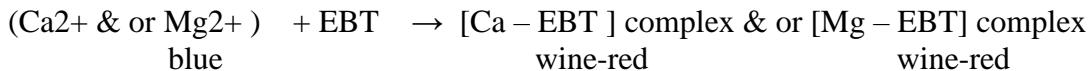
**PRINCIPLE:** In this complexometric Titration, the water sample is titrated with standard solution of Di sodium salt of EDTA using EBT indicator. EBT indicator when added to hard water at pH = 10, forms weak complexes with calcium and magnesium present in hard water. It results in the formation of wine-red Ca-EBT or Mg-EBT complexes which are unstable. When hard water comes in contact with EDTA, at PH 9-10,  $\text{Ca}^{+2}$  and  $\text{Mg}^{+2}$  forms stable, colorless complex with EDTA, releasing the free indicator(blue) so, the colour changes from wine-red to blue at the endpoint.

Ethylene diamine tetra acetic acid



structure of EDTA

EDTA can form 4 to 6 dative bonds with cations like Calcium Magnesium.



**PROCEDURE:**

**1. Preparation of standard hard water:** dissolve 1g of pure, dry  $\text{CaCO}_3$  in minimum quantity of dil. $\text{HCl}$  and then evaporate the solution to dryness on a water bath. Dissolve the residue in distilled water to make 1 Litre solution. Each ml of this solution thus contains 1mg of  $\text{CaCO}_3$  equivalent hardness.

1 mL hard water solution = 1mg of  $\text{CaCO}_3$  equivalent hardness.

$$\text{Molarity of standard hard water } (M_1) = \frac{\text{Weight of } \text{CaCO}_3}{\text{Mol. Wt. Of } \text{CaCO}_3} \times \frac{1000}{100}$$

**2. Standardization of EDTA solution:** - Pipette out 20 ml of standard hard water into a conical flask. Add 5ml of buffer solution and few drops of Eriochrome Black-T indicator, which is originally blue, would assume a wine red colour. Titrate it with EDTA solution taken in the burette, till the wine red colour changes to blue.

This is the end point. Let the burette reading be  $V_2$  ml

$$\frac{M_1 V_1}{n_1} = \frac{M_2 V_2}{n_2} \quad n_1 = n_2 = 1$$

$$\text{Molarity of EDTA } (M_2) = \frac{M_1 V_1}{V_2}$$

**3.Determination of total hardness:** - Pipette out 20 ml of tap water into a conical flask. Add 2ml of buffer solution and 2 to 3 drops of EBT indicator. Colour changes to wine red colour. Titrate with EDTA solution. Wine red colour changes to blue colour. Note burette reading .let the volume of the solution be  $V_2$  ml . Repeat the titration 2 or 3 times.

$$M_3 V_3 = M_2 V_2$$

$$\text{Molarity of sample water } (M_3) = \frac{M_2 V_2}{V_3}$$

$$\text{Total hardness of sample water} = M_3 \times 100 \times 1000 \text{ (ppm)}$$

**4. Determination of permanent hardness:** - Take 100ml of hard water into a conical flask and boil the water till the volume reduces to 50 ml .Add 50 ml of distilled water to it and pipette out 20 ml of this hard water into a comical flask and add 2ml of buffer solution,3 drops of EBT indicator. Colour changes to wine red colour. Titrate with EDTA solution wine red colour changes to blue colour. Note the burette reading at the volume of EDTA solution,  $V_2$  (zml). Repeat the titration 2 or 3 times.

$$M_4 V_4 = M_2 V_2$$

$$\text{Molarity of sample water } (M_4) = \frac{M_2 V_2}{V_4}$$

V<sub>4</sub>

$$\text{Permanent hardness of water} = M_4 \times 100 \times 1000 \text{ (ppm)}$$

$$\text{Temporary hardness} = \text{Total hardness} - \text{Permanent hardness}$$

#### **Advantages of EDTA method:**

This method is definitely preferable to the other methods, because of the

1. Greater accuracy
2. Convenience

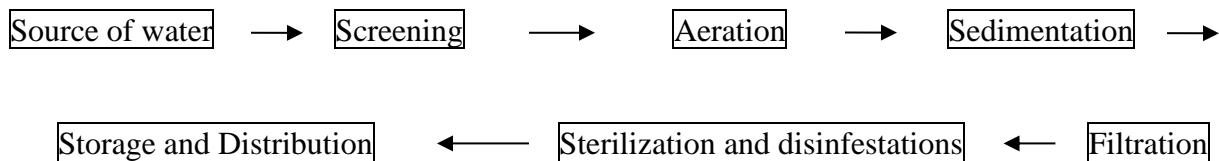
### **POTABLE WATER:**

#### **Specifications:**

1. The water should be clear, colourless and odourless.
2. The water must be free from pathogenic bacteria and dissolved gases like H<sub>2</sub>S.
3. The optimum hardness of water must be 125 ppm and pH must 7- 8.5.
4. The turbidity in drinking water should not exceed 25 ppm.
5. The recommended maximum concentration of total dissolved solids in portable water must not exceed 500 ppm.

#### **Steps involved in the treatment of portable water:**

The treatment includes the removal of suspended impurities, colloidal impurities and harmful pathogenic bacteria, the following is the flow diagram of water treatment for domestic purposes and various stages involved in purification are given as:

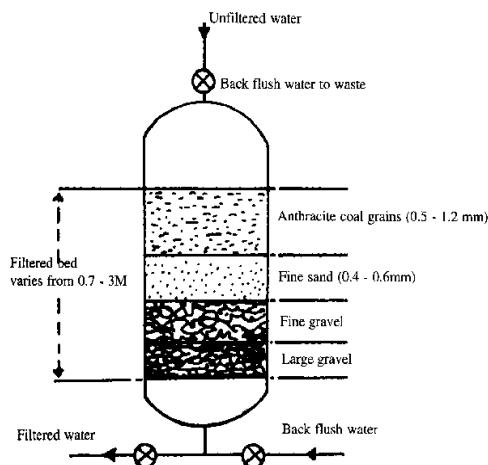


#### **Flow diagram of treatment of water for municipal supply**

1. **Screening:** The water is passed through screens having large number of holes in it to remove floating impurities.
2. **Aeration:** The water is then subjected to aeration which
  - i) Helps in exchange of gases between water and air
  - ii) Increase the oxygen content of water
  - iii) Removes the impurities like Fe and Mn by precipitating as their hydroxides.
3. **Sedimentation with Coagulation:** The suspended and colloidal impurities are allowed to settle under gravitation. The basic principle of this treatment is to allow water to flow at a very slow velocity, so that the heavier particles settle under gravitation. For settling of fine particles, coagulants like Alums, Sodium aluminate and salts of iron are added which produces gelatinous precipitates like floc. Floc attracts and helps accumulation of the

colloidal particles resulting in setting of the colloidal particles. The following is the sedimentation tank used for the removal of colloidal impurities.

- Filtration:** It helps in removal of the colloidal and suspended impurities not removed by sedimentation. Usually sand filters are employed. There are 2 types of sand filters, slow sand filters and rapid sand filters or pressure filters. In slow sand filter the filter bed consists of 3 layers of sand of different particle size. A fine sand layer on the top supported by coarse sand layer, which is supported by gravel. The colloidal impurities are retained by the fine sand layer resulting a very slow filtration of water. The top layers of the fine sand layer is scraped off, washed, dried and introduced into the filter bed for reuse. Rapid sand filters make use of compressed air for fast filtration.



### Rapid Sand Filter

- Sterilisation and Disinfection:** Destruction of harmful pathogenic bacteria from drinking water is carried out by sterilisation and disinfection. The following are the methods adopted for this process.

- Boiling:** By boiling water for 15- 20 min, harmful bacteria are killed. This is not possible for the municipal supply of water. This method of sterilisation is adopted for domestic purpose.
- Passing Ozone:** Ozone when passed into water acts as disinfectant. Ozone is an unstable isotope of oxygen, produced nascent oxygen which is a powerful disinfectant.



This treatment is costly and ozone is unstable and cannot be stored for long time.

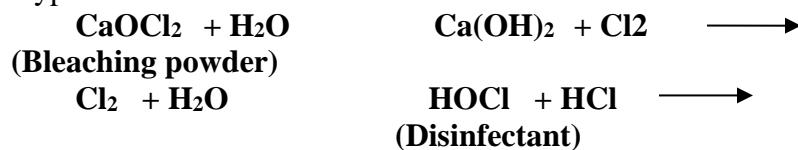
- Chlorination:** The process of utilising chlorine as a powerful disinfectant is called chlorination. They are 3 types of chlorinating reagents .

i) **By passing Chloramines:** Chlorine is mixed with ammonia in the ratio 2:1 by volume to form a stable chloramines which generates hypochlorous acid a powerful disinfectant

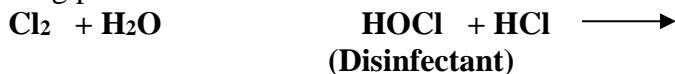


Hypochlorous acid inactivates the enzymes of bacteria and kills bacteria. Chloramine is useful for disinfecting swimming pools.

ii) **By bleaching powder:** Bleaching powder contains 80% chlorine. When bleaching powder is used as disinfectant, it is called hypochlorination because the disinfection is due to Hypochlorous acid.



iii) **Chlorination:** The process of applying calculated amount of Chlorine to water in order to kill the pathogenic bacteria is called chlorination. Chlorine also reacts with water and generates Hypochlorous acid, which kills bacteria. Chlorine is a powerful disinfectant than chloramine and bleaching powder.



Calculated amount of chlorine must be added to water because chlorine after reacts with bacteria and organic impurities or ammonia, remains in water as residual chlorine which gives bad taste, odour and toxic to humans. The amount of chlorine required to kill bacteria and remove organic matter is called breakpoint chlorination.

The water sample is treated with chlorine and estimated for the residual chlorine in water and plotted a graph shown below which gives the breakpoint chlorination.

From Graph it is clear that

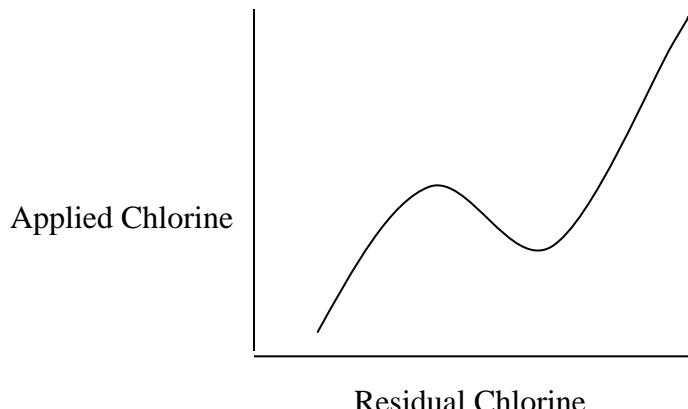
'a' gms of chlorine added oxidizes reducing impurities of water

'b' gms chlorine added forms chloramines and other chloro compounds

'c' gms of chlorine added causes destruction of bacteria.

'd' gms of chlorine is residual chlorine

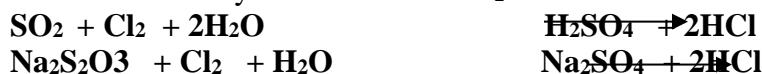
'c' gms is the breakpoint for the addition of chlorine to water. This is called breakpoint chlorination.



### **Advantages of Break point Chlorination:**

1. It removes taste, color, and oxidizes completely organic compounds, ammonia and other reducing impurities.
2. It destroys completely all disease producing bacteria.
3. It prevents growth of any weeds in water.

**Dechlorination:** over chlorination after ‘Break point’ produces unpleasant taste, odor, and toxicity to water. The over chlorination is removed by passing the water through a bed of granular carbon and also by the addition of  $\text{SO}_2$  and sodium thio sulphate.

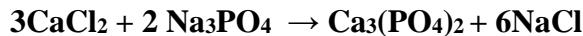


### **Boiler feed water and its treatment:**

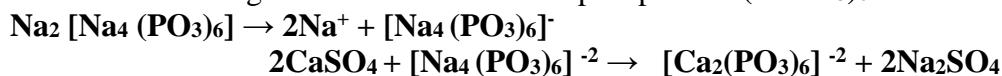
Some of the internal treatment methods used for the removed of scale formation in boilers are -

**1. Colloidal conditioning:** The addition of organic substances such as Kerosene, tannin, Gel etc., to the surface in low pressure boilers may prevent the scale formation. These substances gets coated over the scale forming precipitates and gives a loose and non-sticky precipitates which can be removed by using blow-down operation.

**2. Phosphate Conditioning:** The addition of sodium phosphate in hard water reacts with the hardness causing agents and gives calcium and magnesium phosphates which are soft and non-adhere and can be removed easily by blow-down operation. In this way, scale formation is removed in highpressure boilers.



**3.. Calgon conditioning:** Involves in adding calgon to boiler water. It prevents the scale and sludge formation by forming soluble complex compound with  $\text{CaSO}_4$ .



### **Ion exchange process :**

Ion exchange process also known as demineralization or de-ionization process. Ion-Exchange resins are insoluble. Cross linked long chain organic polymers with a micro porous structure, and the “functional Groups” attached to the chains are responsible for the ion-exchanging properties. In De-ionization process all the ions present in water are eliminated by using ion-exchange resins. Resins are classified as

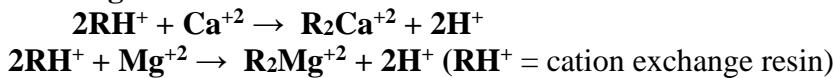
- 1. Cation Exchange Resins**
- 2. Anion Exchange Resins**

**1. Cation Exchange Resins:** These are mainly styrene divinyl benzene co-polymers, which on sulphonation or carboxylation. These are capable of exchanging their hydrogen ions with cations in water.

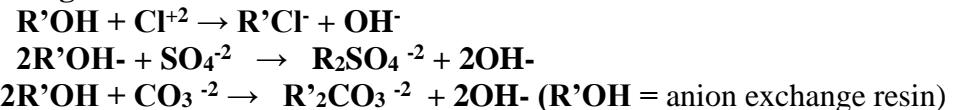
**2. Anion Exchange Resins:** Anion exchange resins are styrene-divinyl benzene or amine formaldehyde copolymers, which contains amino, quaternary ammonium groups as an internal parts of the resin matrix. These after treatment with dilute NaOH solution. Become capable of exchanging their OH<sup>-</sup> ions with anions in water.

In ion-exchange process, hard water is allowed to pass through cation exchange resins, which remove Ca<sup>+2</sup> and Mg<sup>+2</sup> ions and exchange equivalent amount of H<sup>+</sup> ions. Anions exchange resins remove bicarbonates, chlorides and sulphates from water exchange equivalent amount of OH<sup>-</sup> ions. Thus by passing hard water through cation hardness is observed by the following reactions.

### Cation Exchange Resins



### Anion Exchange Resins

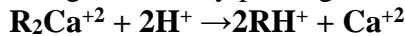


H<sup>+</sup> and OH<sup>-</sup> ions, thus released in water from respective cation and anion exchange columns, get combined to produce water molecules.

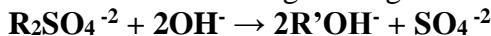


The water coming out from the exchanger is ion free i.e., free from anions and cations. Thus water of zero hardness is obtained.

**REGENERATION:** When cation exchanger losses capacity of producing H<sup>+</sup> ions and exchanger losses capacity of producing OH<sup>-</sup> ions, they are said to be exhausted. The exhausted cation exchanger is regenerated by passing it through dilute sulphuric acid.



The exhausted anion exchanger is regenerated by passing a dilute solution of NaOH.



### Merits of Ion-exchange process:

- The process can be used to soften highly acidic or alkaline water.
- It produces water of very low hardness (2 ppm)
- So it is very good for treating water for use in high-pressure boilers.

### Demerits of Ion-exchange process:

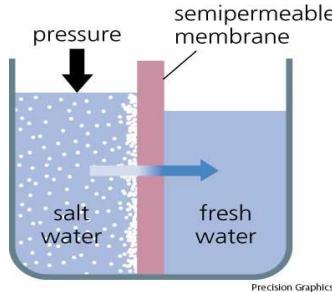
- The equipment is costly and more expensive chemicals are needed.
- If water contains turbidity, the output of the process is reduced. The turbidity must be below 10 ppm; else it has to be removed by coagulation and filtration.

**Desalination of Brackish water:** The process of removing common salt from the water is known as desalination. The water containing dissolved salts with a peculiar salty taste is called brackish water. Sea water, containing on an average about 3.5% salts, comes under this category. Commonly used methods for the desalination of brackish water is:

1. Reverse Osmosis & 2. Electrodialysis.

**1. Reverse Osmosis:** Osmosis is the phenomenon by virtue of which flow of solvent takes place from a region of low concentration to high concentration when two solutions of different concentrations are separated by a semi-permeable membrane. The flow continues till the concentration is equal on both the sides. The driving force for osmosis is osmotic pressure. However, if a hydrostatic pressure in excess of osmotic pressure is applied on the concentrated

side, the flow of solvent reverses as it is forced to move from concentrated side to dilute side across the membrane. This is the basis of reverse osmosis.



### **Method of purification:**

The reverse Osmosis cell consists of a chamber fitted with a semi-permeable membrane which is made of thin films of cellulose acetate, polymethyl acrylate and polyamide polymers . Above the semi permeable membrane sea water or impure water is taken and a pressure of the order of 15-40 kg/cm<sup>2</sup> is applied on the sea water for separating the water from its contaminants. Pure water is forced through semi permeable membrane. The process is also known as super or hyper filtration.

### **Advantages:**

- a. Colloidal SiO<sub>2</sub> can be removed by reverse osmosis which even cannot be removed by demineralization.
- b. It is simple and reliable process.
- c. Capital and operating expenses are low.
- d. The life of the semi-permeable membrane is about 2 years and it can be easily replaced within a few minutes, thereby nearly uninterrupted water supply can be provided.

## **UNIT III- Electrochemistry and Corrosion**

**Introduction:** Electro chemistry is the study of process involving interconversion of electrical energy and chemical energy i.e. it deals the applications of electricity.

### **Electrode potential:**

Potential difference is developed between the metal ions from metal to the solution (or) from solution to the metal. At equilibrium the potential difference remains constant, this is known as electrode potential of metal.

The electrode potential of a metal is defined as the direct measure of its tendency to get reduced is called reduction potential, its value is  $+x$  volts. Similarly the tendency of an electrode to lose electrons is a measure of its tendency to get oxidized is called oxidation potential, its value is  $-x$  volts.

### **Standard Electrode Potential:**

In an electrochemical cell, an electric potential is created between two dissimilar metals. This potential is a measure of the energy per unit charge which is available from the oxidation/reduction reactions to drive the reaction.

The standard reduction potential is the reduction potential of a molecule under specific, standard conditions. Standard reduction potentials can be useful in determining the directionality of a reaction. The reduction potential of a given species can be considered to be the negative of the oxidation potential.

**Electrochemical cells:-** An electrochemical cell is a device for the conversion of electrical energy into chemical energy or vice versa. It can be divided into 2 classes.

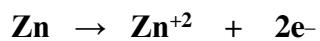
- (1). Galvanic cell
- (2). Electrolytic cell.

### **Differences between electrolytic cell and galvanic cell:**

<b>Electrolytic cell</b>	<b>Galvanic cell</b>
<ul style="list-style-type: none"><li>1. It is a device to convert electrical energy into chemical energy.</li><li>2. The electrodes taken may be of same material or of different material.</li><li>3. Anode is positive and cathode is negative.</li><li>4. Both the electrodes are dipped in the same container having solution of the electrolyte.</li><li>5. Free energy increases during operation of the cell.</li><li>6. Work is done on the electrolytic cell.</li></ul>	<ul style="list-style-type: none"><li>1. It is a device used to convert chemical energy into electrical energy.</li><li>2. The electrodes taken are of different materials.</li><li>3. Anode is negative and cathode is positive.</li><li>4. Two electrodes are immersed into two separate containers having different electrolytes. Salt bridge is used to have connections between the solutions of two electrolytes.</li><li>5. Free energy decreases during operation of the cell.</li><li>6. Work is obtained from this type of cell.</li></ul>

**Galvanic cell:** - The practical application of galvanic cell is Daniel cell. It consists of Zn electrode dipping in  $\text{ZnSO}_4$  solution and a copper electrode dipping in  $\text{CuSO}_4$  solution taken in two different beakers. The two solutions are connected by means of a salt bridge. Salt bridge is an inverted U-tube containing an aqueous solution of electrolyte such as  $\text{KCl}$ ,  $\text{KNO}_3$  or  $\text{K}_2\text{SO}_4$  (which does not react chemically during the process).

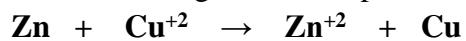
When the two electrodes are connected by a wire, oxidation takes place at the anode (negative electrode) and reduction takes place at the cathode (positive electrode). The electrons flow from anode to cathode. I.e. passes into the solution as  $\text{Zn}^{+2}$  liberating 2 electrons because of its higher oxidation potential than copper.



The electrons thus liberated travel along the external circuit to the copper electrode where copper ions ( $\text{Cu}^{++}$ ) gain these electrons and converted to metallic copper.



The movement of electrons from Zinc to Copper produces a current in the circuit and the net chemical changes can be represented as



Representation of a Galvanic cell:



The negative electrode is at the extreme left and the positive electrode on the extreme right. The double vertical line between the two liquids signifies the salt bridge.

The emf of the Daniel cell is 1.09V.

**Emf of cell = reduction potential of cathode – reduction potential of anode**

Or

$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$

Or

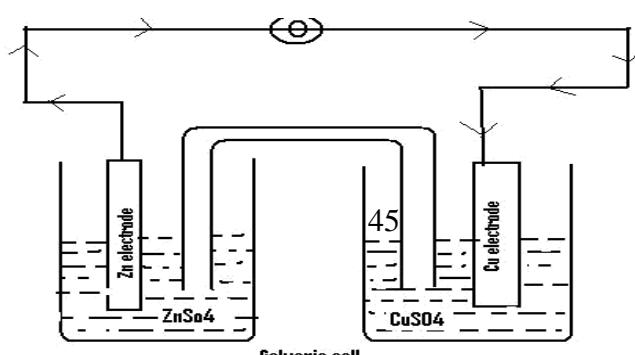
$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}}$

The cell reaction is feasible only when  $E_{\text{cell}}$  has positive value.

For Galvanic cell  $\text{Zn (s)} | \text{Zn}^{+2}(\text{aq}) || \text{Cu}^{+2}(\text{aq}) | \text{Cu(s)}$

$E_{\text{cell}} = E_{\text{Cu}^{+2}/\text{Cu}} - E_{\text{Zn}^{+2}/\text{Zn}}$

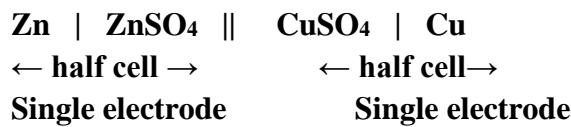
**Daniel cell:**



**Single electrode potential:-** Each electrochemical cell is made up of two electrodes, at one electrode electrons are liberated and at other electrode they are used up.

Each electrode, which is dipped in its salt solution, is called half cell. The potential of half cell i.e. the potential difference between the metal and its salt solution in which it is dipped is called single electrode potential.

It cannot be directly measured.



But the potential difference between two electrodes can be accurately measured. Thus standard electrode (reference electrode) must be chosen to determine the potential of the electrode. The total cell emf is equal to the sum of the single potentials.

$$E_{\text{cell}} = E_{\text{cathode}} + E_{\text{anode}}$$

(Or)

$$E_{\text{cell}} = E_{\text{ox}} + E_{\text{red}}$$

(Or)

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}}$$

**Ex:**  $E_R$  of  $\text{Cu}+2 \mid \text{Cu}$  is  $0.337V$  ;  $E_L$  of  $\text{Zn} \mid \text{Zn}+2$  is  $-0.763 V$

$$\begin{aligned} E_{\text{cell}} &= E_{\text{right}} - E_{\text{left}} \\ &= 0.337V - (-0.763 V) \\ &= 0.337 + 0.763 \\ &= 1.1 V \end{aligned}$$

**EMF or cell potential:** The difference in potential of the two half cells of a cell is known as electro motive force (EMF) or cell potential.

To derive an expression for the EMF of the concentration cell the electrode potential of the two electrodes are considered.

$$\text{Electrode potential of anode} = E = E^0 + 2.303 RT / nF \log_{10} [M_1]$$

$$\text{Electrode potential of cathode} = E = E^0 + 2.303 RT / nF \log_{10} [M_2]$$

$$\begin{aligned} \text{EMF of cell} &= \text{Electrode potential of cathode} - \text{Electrode potential of anode} \\ &= [E^0 + 2.303 RT / nF \log_{10} [M_2]] - [E^0 + 2.303 RT / nF \log_{10} [M_1]] \\ &= 2.303 RT / nF \log_{10} [M_2] / [M_1] \end{aligned}$$

By substituting values for F,R and T , we get

$$E_{\text{cell}} = 0.0591 \log_{10} [M_2] / [M_1]$$

n

**Standard electrode potential:** The Standard electrode potential of a metal may be defined as the potential difference in volts at 25°C developed in a cell consisting of two electrodes, the pure metal in contact with a molar solution of one of its ions and normal hydrogen electrode

**NERNST EQUATION:** The derivation of a mathematical relationship between the standard electrode potentials, temperature and the concentration of ions is known as the Nernst equation.

For the general reduction reaction occurring at an electrode



$$E_{cell} = E^{\circ} - \frac{2.303 RT}{nF} \log \frac{[M]}{[M^{n+}]}$$

Where  $E^{\circ}$  = Standard EMF of the cell for 1 M solution at 298 K

$R$  = Gas constant

$T$  = Kelvin temperature (298 K)

$n$  = number of electrons involved in the cell reaction

$F$  = Faraday of electricity, i.e., 96500 coulomb charge

$E$  = electrode potential of the metal

$[M]$  = activity of metal in the metal phase and is taken as unity

$[M^{n+}]$  = activity of metal ions in the solution is taken equal to their molarities

At 298K,  $2.303 RT / F = 0.059$

$$\begin{aligned} E &= E^{\circ} - 0.059 / n \log [M] / [M^{n+}] \\ &= E^{\circ} - 0.059 / n \log [\text{Products}] / [\text{Reactants}] \end{aligned}$$

**APPLICATIONS:** Nernst equation enables us to calculate

- (i) Half cell potential or single electrode potential
- (ii) Cell potential or EMF of the cell
- (iii) Equilibrium constant for the cell reaction

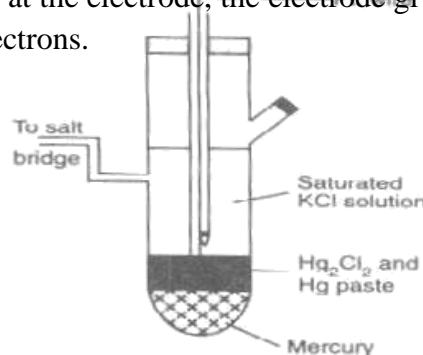
## TYPES OF ELECTRODES:

### A. REFERENCE ELECTRODES:

**Calomel electrode:** (Metal-metal salt ion electrode): An electrode of this type consists of a metal and a sparingly soluble salt of the same metal, dipping in a solution of a soluble salt having the same anion (KCl).

It is represented as  $Hg, Hg_2Cl_2(s); KCl$  (solution)

Mercury of high degree purity is placed at the bottom of a glass tube with a side tube on both the sides. It is connected to the outer circuit by means of a platinum wire sealed in a glass tube. The surface is covered with a paste of mercurous chloride (calomel). A saturated normal or deci normal KCl solution is introduced through the side tube present in the right side. If this electrode acts as anode i.e. when oxidation takes place at the electrode, the electrode gives mercurous ions ( $\text{Hg}_2^{2+}$ ) into solution with the liberation of electrons.



These  $\text{Hg}_2^{2+}$  ions combine with  $\text{Cl}^-$  ions (from KCl) to form sparingly soluble mercurous chloride with the result the concentration of chloride ions falls in the solution.

On the other hand, when electrode acts as cathode i.e. reduction occurs, which results in an increase in the concentration of chloride ions. Hence the calomel electrode is reversible with respect to chloride ions.

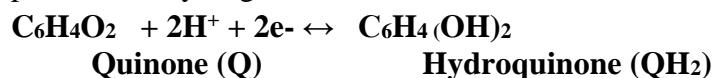
This electrode is connected with the help of the side tube on the left through a salt bridge with the other electrode, the potential of which is to be determined. The potential of the calomel electrode depend upon the concentration of the KCl solution.

For 0.1 N KCl  $E = -0.3338$  V;

For Saturated KCl solution  $E = -0.2415$  V

### B. REDOX ELECTRODE:

**Quinhydrone electrode:-** Quinine and hydroquinone form a reversible redox system in the presence of hydrogen ions.



**Construction of electrode:** - Add a pinch of Quinhydrone to the solution under examination and immerse a clean platinum electrode in it. The potential 'E' developed when an inert electrode (platinum electrode) is immersed in this system is given by the Nernst reduction equation.

$$E = E^0 + 2.303 \frac{RT}{nF} \log_{10} [\text{QH}_2]/[\text{Q}][\text{H}^+]^2$$

$$\begin{aligned} E &= E^0 + 2.303 \frac{RT}{2F} \times \log_{10} [\text{QH}_2]/[\text{Q}] \\ &= E^0 - 2.303 \frac{RT}{2F} \log_{10} [\text{H}^+]^2 \end{aligned}$$

The rate  $[\text{QH}_2]/[\text{Q}]$  is maintained constant at unity by saturating the solution with the substance 'Quinhydrone' (which is 1:1 molar Q & QH<sub>2</sub>).

Since  $\log_{10} 1 = 0$  &  $\log_{10}[H^+]^2 = 2 \log_{10}[H^+]$

We have  $E = E^0 - \frac{2.303 RT}{2F} \times 2 \log_{10} [H^+]$

$$E = E^0 - \frac{2.303 RT}{F} \log_{10} [H^+]$$

$$E = E^0 - 0.0591 PH. \quad (E^0_Q = 0.6994V)$$

Since the electrode potential of the Quinhydrone electrode depends upon the concentration of hydrogen ions, it can be used for the determination of PH value just like a hydrogen electrode.

### Advantages:

1. The electrode is very easy to setup.
2. The PH value obtained is very accurate.
3. Very small quantities of the solution are sufficient for the measurement.

**Limitations:** The electrode cannot be used in alkaline solutions and the solutions which react with Quinhydrone or quinine. (Ex:  $Fe^{+2}$ ,  $MnO_2$  etc.)

**C. ION SELECTIVE ELECTRODES:** Ion selective electrodes have the ability to respond to certain specific ions(present in a mixture while ignoring others) and develop a potential. The potential developed is a measure of the concentration of the species of interest. These electrodes use a membrane which is sensitive to a particular chemical species. Generally 3 types of membranes are used.

They are:

- (1) Glass membrane (sensitive to  $H^+$  ions)
- (2) Solid membrane (sensitive to  $F^-$  ions)
- (3) Liquid membrane (sensitive to alkali and alkaline earth cations )

Measurement of concentration of cations: The cell constructed for the measurement of concentration of cation  $[M^+]$  is

**Reference electrode 1 / Solution to be analysed  $[Mn^+]$  =**

**$C_1 // Internal\ standard\ solution\ [C_2] / Reference\ electrode\ 2$**

The membrane potential is given by  $E = RT/n F \log C_2 / C_1$

Suppose reference electrode is anode and membrane electrode is cathode

Then the cell potential  $E_{cell} = E_{Mn^+} - \Delta E_{Ref}$

Here  $\Delta E_{Ref}$  is zero if identical electrodes were used. As the concentration of  $Mn^+$  in the internal reference electrode is cathode the  $E_{cell}$  is given by

$$E = RT/n F \log C_1$$

Where  $C_1$  is the concentration of  $Mn^+$  in the solution to be analysed.

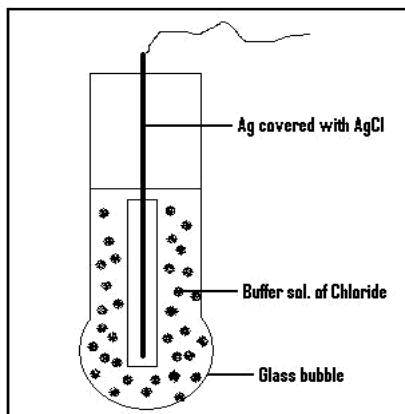
### Applications of ion selective electrodes:

1. To determine the concentration of gas levels like  $\text{CO}_2$  level in blood samples.
2. To determine the concentration of a number of cations like  $\text{H}^+$ ,  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ag}^+$ ,  $\text{NH}_4^+$ ,  $\text{Pb}^{+2}$ ,  $\text{Cd}^{+2}$ ,  $\text{Ca}^{+2}$ ,  $\text{Mg}^{+2}$  etc.
3. To determine the PH of a solution by using  $\text{H}^+$  ion selective electrode.
4. To find the concentration of anions like  $\text{F}^-$ ,  $\text{NO}_3^-$ ,  $\text{CN}^-$ ,  $\text{S}_2^-$  and halide ions.

**D. GLASS ELECTRODE:** **Construction of electrode:** A glass electrode is made up of a special glass of relatively low melting point and high electrical conductivity. It consists of thin walled glass bulb filled with 0.1 M HCl and a silver wire coated with silver chloride ( $\text{AgCl}$ ) is immersed in it. Here  $\text{Ag} / \text{AgCl}$  acts as the internal reference electrode. The glass electrode is represented by

**$\text{Ag} / \text{AgCl (s)} / \text{HCl (0.1 M)} / \text{glass}$ .**

**Principle:** When the glass electrode is immersed in another solution, whose PH value is to be determined, there develops a difference of potential between the two surfaces of the membrane. The potential difference developed is proportional to the difference in PH value.



**Theory:** The glass membrane functions as an ion-exchange resin, and an equilibrium is set up between the  $\text{Na}^+$  ions of glass and  $\text{H}^+$  ions in solution. For a particular type of glass, the potential difference varies with  $\text{H}^+$  ion concentration

$$E_G = E_{0G} + 0.0592 \text{ PH (25}^\circ\text{C)}$$

#### **Advantages of glass electrode:**

1. Glass electrode is the most convenient and simple to use.
2. The results are accurate.
3. It can be used in turbid, colored and colloidal solutions.

4. It can be used in both alkaline and oxidising solutions.

**Limitations:** the glass electrode can be used up to a PH of 13 but becomes sensitive to Na<sup>+</sup> ions above PH =9 resulting in an alkaline error.

**Electro chemical series:** When the metals are arranged in the order increasing reduction potentials or decreasing oxidation potentials with respect to 1 molar solution of their ions and measured on the hydrogen scale, resulting series is known as galvanic series or electro chemical series.

**Main features of the series are:**

1. Metals more active than hydrogen are placed at the top. These metals can give electrons to H<sup>+</sup> ions, and can reduce them to hydrogen gas. They displace hydrogen from water and acid solutions.
2. Metals less active than hydrogen are placed at the bottom. Their cations can be reduced by hydrogen to the metal state. They do not displace hydrogen from acids or water.
3. Various oxidising agents are arranged in the increase order, i.e. oxidant at the top is the weakest oxidising agent and the one at the bottom is the strongest oxidising agent. It means greater the reduction potential, stronger is the oxidising agent and lower the reduction potential, stronger is the reducing agent.

#### Standard Reduction potentials at 25°C

ELECTRODE	HALF CELL REACTION	E <sup>0</sup> VOLTS
Li/ Li <sup>+</sup>	Li <sup>+</sup> + e <sup>-</sup> ↔ Li	-3.045
K/K <sup>+</sup>	K <sup>+</sup> + e <sup>-</sup> ↔ K	-2.925
Ca <sup>2+</sup> /Ca	Ca <sup>2+</sup> + 2e <sup>-</sup> ↔ Ca	-2.866
Na <sup>+</sup> /Na	Na <sup>+</sup> + e <sup>-</sup> ↔ Na	-2.714
Mg <sup>2+</sup> /Mg	Mg <sup>2+</sup> + 2e <sup>-</sup> ↔ Mg	-2.363
Al <sup>3+</sup> /Al	Al <sup>3+</sup> + 3e <sup>-</sup> ↔ Al	-1.662
Zn <sup>2+</sup> /Zn	Zn <sup>2+</sup> + 2e <sup>-</sup> ↔ Zn	-0.763
Fe <sup>2+</sup> /Fe	Fe <sup>2+</sup> + 2e <sup>-</sup> ↔ Fe	-0.440
Sn <sup>2+</sup> /Sn	Sn <sup>2+</sup> + 2e <sup>-</sup> ↔ Sn	-0.136

<b>Pb<sup>2+</sup>/Pb</b>	<b>Pb<sup>2+</sup> +2e-↔ Pb</b>	<b>-0.126</b>
<b>H<sup>+</sup>;H<sub>2</sub>,Pt</b>	<b>2H<sup>+</sup> +2e-↔ H<sub>2</sub></b>	<b>0.000</b>
<b>Cu<sup>2+</sup>/Cu</b>	<b>Cu<sup>2+</sup> + 2e-↔ Cu</b>	<b>0.340</b>
<b>Ag<sup>+</sup>/Ag</b>	<b>Ag<sup>+</sup> +2e-↔ Ag</b>	<b>+0.800</b>
<b>Cl/Cl<sub>2</sub></b>	<b>Cl<sup>2+</sup> 2e-↔ 2Cl-</b>	<b>+1.36</b>
<b>Au<sup>3+</sup>/Au</b>	<b>Au<sup>3+</sup> + 3e-↔ Au</b>	<b>+1.50</b>
<b>F/F<sub>2</sub>,Pt</b>	<b>F<sup>2-</sup> +2e-↔ 2F-</b>	<b>+2.87</b>

Active (Anodic)

- 1. Mg
- 2. Mg alloys
- 3. Zn
- 4. Al
- 5. Cd
- 6. Al alloys
- 7. Mild steel
- 8. Cast Iron
- 9. high Ni cast Iron
- 10. Pb-Sn solder
- 11. Pb
- 12. Sn
- 13. Ni-Mo-Fe alloys
- 14. Brass
- 15. Silver solder
- 16. Cu
- 17. Ni
- 18. Cr stainless steel
- 19. 18-8 stainless steel
- 20. 18-8 Mo stainless steel
- 21. Ag
- 22. Ti
- 23. Graphite
- 24. Au
- 25. Pt

Noble (Cathodic)

**Applications of electrochemical series:** The electrochemical series give more information on

1. The relative corrosion tendencies of the metals.
2. Relative ease of oxidation or reduction of metals.
3. Replacement of tendency of metals.
4. Calculating the equilibrium constant.

**POTENTIOMETRIC TITRATIONS:** A titration in which the equivalent or end point of a reaction is determined with the help of measurement of the potentials of the reaction mixture is known as potentiometric titration.

**1. Acid-Base Titrations:** The acid solution whose strength has to be determined is taken in a beaker and the hydrogen electrode and calomel electrode were dipped in the solution. The electrodes are connected to the potentiometer and the EMF is measured. A known volume of standard alkali solution is added from a burette, stirred thoroughly and the EMF of the cell is recorded. Like this 10-15 readings are recorded by repeating the procedure of the addition of alkali. The volume of alkali added is plotted against EMF observed. The steepest portion of the curve indicates the equivalent point of the titration.

**2. Oxidation – Reduction titrations:** The EMF of the electrode is determined by the activity of ratio of the substance being oxidised or reduced. For example  $\text{Fe}^{+2}$  titrated against  $\text{K}_2\text{Cr}_2\text{O}_7$  ferrous iron solution is taken in the beaker, treated with dil.  $\text{H}_2\text{SO}_4$  and platinum electrode and calomel electrode are dipped. The electrodes are connected to the potentiometer and EMF of the solution after the addition of  $\text{K}_2\text{Cr}_2\text{O}_7$  is recorded. A graph is plotted with EMF and volume of  $\text{K}_2\text{Cr}_2\text{O}_7$ . The steep rise is the end point of the titration.

**3. Precipitation reactions:** The EMF of the electrode is determined by the precipitation of product. For example titration of silver nitrate with sodium chloride where silver chloride precipitates out .Silver chloride is used along with calomel electrode. The silver nitrate is placed in the burette and added sodium chloride taken in the beaker, containing electrodes. The EMF of the cells measured and plotted against volume of silver nitrate added. The steep rise in the curve shows the end point of the titration.

**4. Determination of PH by EMF method:** the EMF of a solution depends on the concentration of  $\text{H}^+$  ions or PH of the solution. A hydrogen electrode containing solution of unknown PH is paired with a standard calomel electrode.

**Pt,  $\text{H}_2$  (1 atm) /  $\text{H}^+$  (unknown) //  $\text{KCl}$  (sat. sol) /  $\text{Hg}_2\text{Cl}_2, \text{Hg}$**

The EMF of this cell is measured by potentiometer, and the PH of the unknown solution can be calculated.

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} ;$$

$$E_{\text{cell}} = 0.2415 - (-0.0591 \times \text{PH})$$

$$E_{\text{cell}} = 0.2415 + 0.0591 \times \text{PH}$$

## **ADVANTAGES:**

1. Colored solutions where the use of indicator is impossible are estimated by potentiometric titrations.
2. Solutions more than one halide can be analyzed in a single titration against silver nitrate.

**BATTERIES:** Battery is an electrochemical cell or several electrochemical cells connected in series that can be used as a source of direct electric current at constant voltage.

Batteries are of 3 types: **1. Primary cell**  
**2. Secondary cell**

### **1. Primary cell:**

**Lithium cell:** Lithium cell consists of lithium anode and either solid electrolyte or liquid electrolyte and solid or liquid cathode. A thin protective insulating film is formed on the lithium anode protecting the anode against corrosion as it is conductive to lithium ions but not electrons. Water and alcohol do not form such a protective film and hence cannot be used as solvents. Organic solvents such as dioxane, tetrahydrofuran, propylene carbonate ether, etc., and electrolyte salts of lithium such as per chlorate, tetrafluoroborate or hexafluorophosphate are used.

Lithium-iodide solid cathode cell consists of iodine-PVP (polyvinyl pyrrolidone) cathode with voltage of 3V. it has low current densities but is highly stable and dependable and hence used in medical source for electronic flash guns of cameras.

Lithium-sulphur dioxide cell consists of a liquid cathode of a mixture of acetonitrile or propylene carbonate with sulphur dioxide. Instead of the solvents acetonitrile or propylene carbonate, thionyl chloride has been found to be better as it generates a potential of 3.5 V and has high energy density.

### **2. Secondary cell:**

#### **Basics of Lead Acid Battery:**

**A) Lead acid storage cell:** It consists of lead –antimony alloy coated with lead dioxide as cathode and spongy lead as anode. The electrolyte is a 20% solution of  $\text{H}_2\text{SO}_4$ .

- Anode: Spongy lead on lead grid.
- Cathode: Porous  $\text{PbO}_2$ .
- Electrolyte:  $\text{H}_2\text{SO}_{4(\text{aq})}$ ( 20 %)
- Cell Scheme:  $\text{Pb}/\text{PbSO}_4;\text{H}_2\text{SO}_{4(\text{aq})};\text{PbSO}_4;\text{PbO}_2/\text{Pb}$

A lead accumulator for car consists of six lead-acid storage cells in series which undergoes both discharging and recharging process.

**Discharging:** when the lead accumulator is used for supplying electrical energy, it is said to be discharging. During this process

- Anode: Spongy lead on lead grid.
- Cathode: Porous PbO<sub>2</sub>.
- Electrolyte: H<sub>2</sub>SO<sub>4(aq)</sub>( 20 %)
- **Overall Reaction:**  $Pb_{(s)} + PbO_2_{(s)} + 4H^+_{(aq)} + 2SO_4^{2-}_{(aq)} \rightarrow 2PbSO_4_{(s)} + 2H_2O_{(l)} + \text{energy}$
- The voltage of each cell is about 2.0 V.

**Charging reactions:** During the discharging, PbSO<sub>4</sub> is precipitated at both the electrodes. When PbSO<sub>4</sub> covers completely both anode and cathode, the cell stops functioning as a voltaic cell. For further use, it needs to be re-charged. Recharging is done by passing an external EMF greater than 2 volts so that the reactions taking place during discharging are reversed.

- Cathode: Spongy lead on lead grid.
- Anode: Porous PbO<sub>2</sub>.
- Electrolyte: H<sub>2</sub>SO<sub>4(aq)</sub>( 20 %)
- **Overall reaction:**  $2PbSO_4_{(s)} + 2H_2O_{(aq)} \rightarrow Pb_{(s)} + PbO_2_{(s)} + 2H_2SO_4$

### **Advantages:**

1). A lead storage battery is highly efficient. The voltage efficiency of the cell is defined as follows.

$$\text{Voltage efficiency} = \frac{\text{Average voltage during discharge}}{\text{Average voltage during charge}}$$

The voltage efficiency of the lead – acid cell is about 80 %.

2). A lead – acid battery provides a good service for several years.

3). It can be recharged. The number of recharges possible range from 300 to 1500, depending on the battery's design and conditions. The battery's own internal self – discharging is low.

4). The length of time that is generally required for re-charging process is less i.e. recharge time is 2-8 hours depending on the status of battery.

**B) Lithium cells OR Lithium ion cells:** These are secondary cells. In this cathode consists of a layered graphite into which the lithium is intercalated.

- **Anode:** graphite.
- **Cathode:** Oxides of Lithium (LiCoO<sub>2</sub> Or LiNiO<sub>2</sub> Or LiV<sub>2</sub>O<sub>5</sub>)
- **Electrolyte:** LiPF<sub>6</sub> , LiBF<sub>4</sub>
- **Net Reaction:**  $2 \text{LiCoO}_2 + 6\text{C} \leftrightarrow \text{Li}_2\text{C}_6 + 2 \text{CoO} + \text{Li}_2\text{O}$

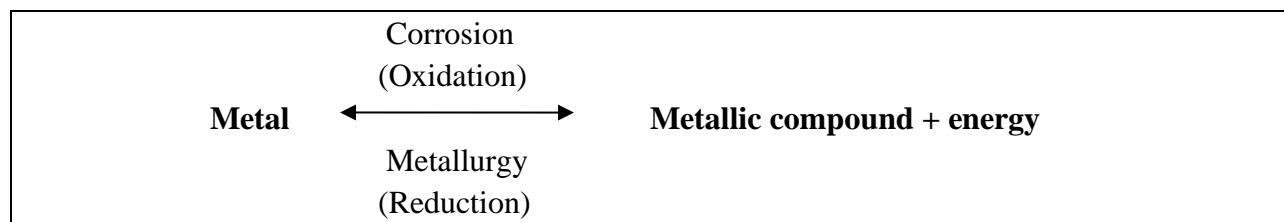
Intercalation keeps the small ions such as lithium into the interstitial spaces in a graphite crystal. This makes the graphite is conductive, dilute the Li for safety.

**Applications:** They are used in laptops, cellular phones, electric vehicles

### **Differences between primary and secondary cells:**

<b>Primary Batteries</b>	<b>Secondary Batteries</b>
1. Cell reaction is irreversible	1. Cell reaction is reversible.
2. Must be discarded after use.	2. May be recharged.
3. Have relatively short shelf life .	3. Have long shelf life.
4. Function only as galvanic cells.	4. Functions both galvanic Cell & as electrolytic cell.
5. They cannot be used as storage devices	5. They can be used as energy storage devices (e.g. solar/ thermal energy converted to electrical energy)
6. They cannot be recharged	6. They can be recharged.
7. Ex: Dry cell, Li-MnO <sub>2</sub> battery.	7. Ex:Lead acid storage cell, Ni-Cd battery.

**CORROSION:** Any process of deterioration and loss of solid metallic material by chemical or electrochemical attack by its environment, starting at its surface is called corrosion.  
Corrosion is the reverse process of metallurgy.

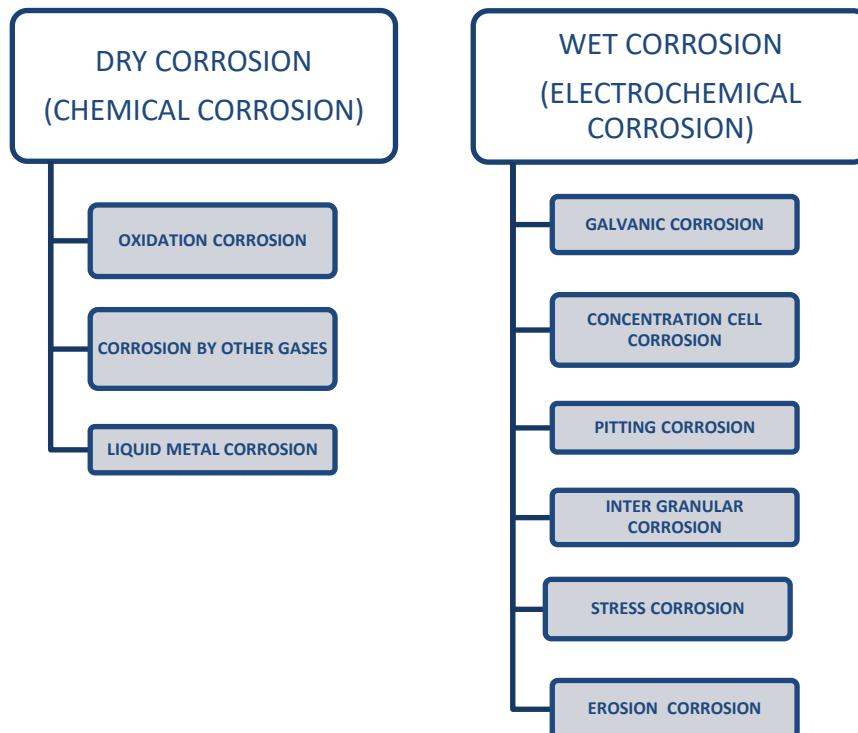


- 1) Ex: rusting of iron when exposed to atmospheric conditions. Rust is hydrated oxide ( $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ ).
- 2) Ex: formation of green film of basic carbonate ( $\text{CuCO}_3 + \text{Cu(OH)}_2$ ) on the surface of copper,when exposed to moist air containing  $\text{CO}_2$ .

### **Disadvantages of Corrosion:**

- It reduces the strength of the structure, making it likely to collapse.
- It reduces the beauty or attractiveness of the device.
- It increases the maintenance cost.
- It is dangerous. Rusty pin pricks can cause tetanus

**TYPES OF CORROSION:** Corrosion is of two types.



**1. Dry (or) Chemical Corrosion:** This type of Corrosion occurs mainly through the direct chemical action of atmospheric gasses ( $O_2$ , halogen,  $H_2S$ ,  $SO_2$ ,  $N_2$  or anhydrous inorganic liquid) with metal surface.

There are three types of chemical Corrosion.

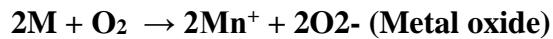
**a. Oxidation Corrosion:** This is carried out by the direct action of oxygen low or high temperatures on metals in absence of moisture. Alkali metals and Alkaline earth metals are rapidly oxidized at low temperatures. At high temperature all metals are oxidized (except Ag, Au, Pt).



**(Metal ion)**



### (Oxide ion)



**Mechanism:** At the surface of metal oxidation occurs and the resulting metal oxide scale forms a barrier which restricts further oxidation. For oxidation to continue either the metal must diffuse outwards through the scale to the surface or the oxygen must diffuse inwards through the scale to the underlying metal. Both the cases are possible. But the outward diffusion of metal is generally more rapid than inward diffusion of oxygen since metal ion is appreciably smaller than the oxygen ion and hence more mobile. Nature of the oxide film decides further corrosion.

If the film is,

i) **Stable** it behaves has a protective coating in nature e.g., the oxide films on Al, Pb, Cu, Pt etc., are stable and therefore further oxidation correction of prohibited.

ii) **Unstable** that is the oxide layer formed decomposes back into metal and oxygen. So, oxidation Corrosion is not possible.

e.g., Ag, Au and Pt do not undergo oxidation Corrosion.

iii) **Volatile** that is oxide layer volatilizes after formation and as such leaves the underlying metal surface exposed further attack. This causes continuous which is excessive.

e.g. Molybdenum oxide ( $MoO_3$ )

iv) **Porous** that is the oxide layer formed having pores or cracks. In this case the atmospheric oxygen passes through the pores or cracks of the underlying metal surface. This causes continuous corrosion till complete conversion of metal into its oxide.

Ex: alkali and alkaline earth metals, Fe.

**b. Corrosion by other gases like  $SO_2$ ,  $CO_2$ ,  $Cl_2$ ,  $H_2S$ ,  $F_2$  :-** In this the extent of corrosive effect depends mainly on the chemical affinity between the metal and the gas involved. The degree of attack depends on the formation of protective or non protective films on the metal surface.

a).if the film formed is protective or non porous, the intensity of attack decreases, because the film formed protects the metal from further attack.

Ex:  $AgCl$  film due to  $Ag$  &  $Cl_2$

b) if the film formed is non protective or porous, the surface of the whole metal is gradually destroyed.

1 ex: Sn is attacked by  $Cl_2$  gas forming volatile  $SnCl_4$  which volatilizes immediately.

Ex: in petroleum industry,  $H_2S$  at high temperature steel forming a  $FeS$  scale.

**c. Liquid metal corrosion:** - this corrosion is due to chemical action of flowing liquid metal at high temperatures on solid metal or alloy. The corrosion reaction involves either:

- (i) dissolution of a solid metal by a liquid metal.
- (ii) or internal penetration of the liquid metal into the solid metal.

Ex: coolant (sodium metal) leads to corrosion of cadmium in nuclear reactors

## 2. Wet or Electrochemical Corrosion.-

This type of Corrosion occurs:

- i) Where a conducting liquid is in contact with the metal or
- ii) When two dissimilar metals or alloys are dipped partially in a solution.

This corrosion occurs due to the existence of separate anodic and cathodic parts, between which current flows through the conducting solution. At anodic area, oxidation reaction occurs thereby destroying the anodic metal either by dissolution or formation of compounds. Hence corrosion always occurs at anodic parts.

### Mechanism:

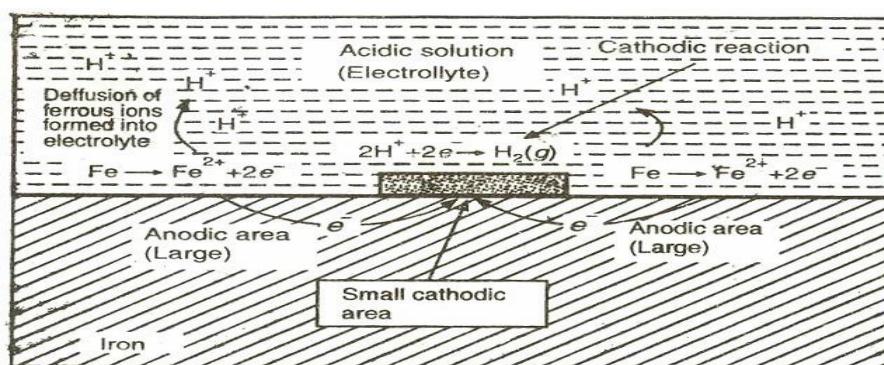
Electrochemical corrosion involves flow of electrons between anode and cathode.

The anodic reaction involves dissolution of metal liberating free electrons.

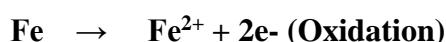


The cathodic reaction consumes electrons with either evolution of hydrogen or absorption of oxygen which depends on the nature of corrosive environment.

**Evolution of hydrogen:** This type of corrosion occurs in acidic medium



e.g., considering the metal Fe, anodic reaction is dissolution of iron as ferrous ions with liberation of electrons.

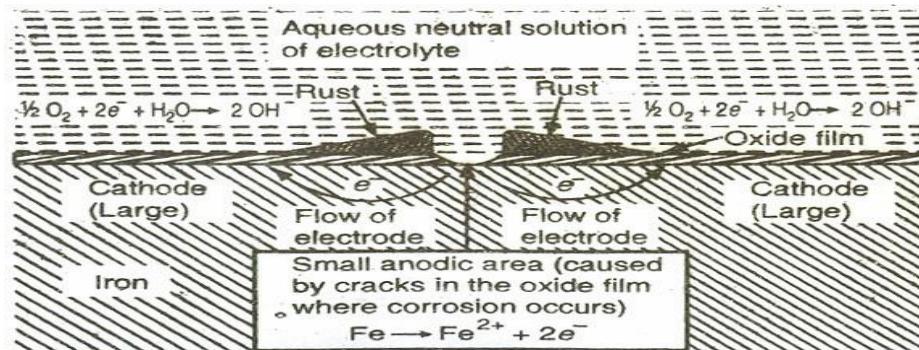


The electrons released flow through the metal from anode to cathode, whereas H<sup>+</sup> ions of acidic solution are eliminated as hydrogen gas.

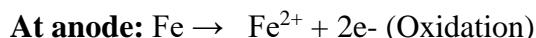


This type of corrosion causes displacement of hydrogen ions from the solution by metal ions. All metals above hydrogen in electrochemical series have a tendency to get dissolved in acidic solution with simultaneous evolution of H<sub>2</sub> gas. The anodes are large areas, whereas cathodes are small areas.

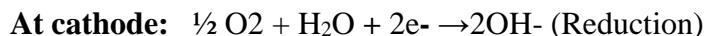
### Absorption of oxygen: -



For example, rusting of iron in neutral aqueous solution of electrolytes in presence of atmospheric oxygen. Usually the surface of iron is coated with a thin film of iron oxide. If the film develops cracks, anodic areas are created on the surface. While the metal parts act as cathodes. It shows that anodes are small areas, while the rest metallic part forms large cathodes.



The released electrons flow from anode to cathode through iron metal.



If oxygen is in excess, ferrous hydroxide is easily oxidized to ferric hydroxide.



The product called yellow rust corresponds to Fe<sub>2</sub>O<sub>3</sub>. xH<sub>2</sub>O.

If the supply of oxygen is limited, the corrosion product may be black anhydrous magnetite Fe<sub>3</sub>O<sub>4</sub>.

**Galvanic Corrosion :** When two dissimilar metals are electrically connected and exposed to an electrolyte, the metal higher in electrochemical series undergoes corrosion. This type of corrosion

is called Galvanic corrosion .e.g., Zinc (higher in electrochemical series) forms the anode and is attacked and gets dissolved; whereas copper (lower in electrochemical series) acts as cathode.

**Mechanism:** If the solution is acidic then corrosion occurs by hydrogen evolution process and if the solution is neutral or slightly alkaline in nature then corrosion occurs by oxygen absorption process. The electrons flow from the anodic metal to the cathodic metal.



Thus the corrosion is a localized accelerated attack resulting in the formation of pits, holes or cavities. Pitting corrosion therefore results in the formation of pinholes, pits and cavities in the metal. The pitting corrosion may be due to following reasons:

1. Metal surface are not homogeneous.
2. External environment is not homogeneous
3. Films are not perfectly uniform.
4. Crystallography directions are not equal in the reactivity.
5. Environment is not uniform with respect to concentration.

Pitting is usually the result of the breakdown or cracking of the protective film on a metal at specific points. This gives rise to the formation of small anodic and large cathodic areas. In process of correct environment this produces corrosion current.

e.g., Stainless steel and aluminum show characteristic pitting on chloride solution. Pitting is caused by the presence of sand, dust scale and other extraneous impurities present on the metal surfaces. Because of differential amount of oxygen in contact with the metal, the small part (underneath the impurity) becomes the anodic areas and the surrounding large parts become the cathodic areas. Intense corrosion takes place in the anodic areas underneath the impurity. Once a small pit is generated, the rate of corrosion will be increased.

**Waterline Corrosion:** This is also known as differential oxygen concentration corrosion. In general, when water is stored in a steel tank, it is observed that the maximum amount of corrosion takes place along a line just beneath the level of the water meniscus. The area above the waterline (highly oxygenated) acts as cathodic and is not affected by corrosion. However, if the water is relatively free from acidity, little corrosion occurs. The problem of waterline corrosion is a matter of concern for marine engineers. This type of corrosion is prevented to a great extent by painting the sides of the ships by antifouling paints.

**FACTORS INFLUENCING CORROSION:** The rate and extent of corrosion depends on the

1. Nature of the metal
2. Nature of corroding environment.

### NATURE OF METAL:

**a. Position in galvanic series:** when two metals or alloys are in electrical contact in presence of an electrolyte the more active metal having higher position in the galvanic series undergoes corrosion. The greater is the difference in position, the faster is the corrosion.

### Position in Galvanic Series & rate of Corrosion

**b. Over voltage:** Reduction in overvoltage of the corroding metal accelerates the corrosion rate. E.g. Zn in 1N H<sub>2</sub>SO<sub>4</sub> undergoes corrosion slowly because of high overvoltage of zinc metal (0.7 V) which reduces the effective potential to a small value. In presence of CuSO<sub>4</sub> the corrosion rate of zinc is accelerated.

**Over voltage  $\propto 1/RC$**

**c. Relative areas of anodic and cathodic parts:** When two dissimilar metals are in contact, the corrosion of the anodic part is directly proportional to the ratio of areas of cathodic part and the anodic part. Corrosion is rapid and localized if anodic area is small, because the current density at a smaller anodic area is greater.

**Small Anode  $\propto RC$**

**d. Purity of Metal :** Impurities in a metal generally cause heterogeneous state forming minute electrochemical cells resulting corrosion of anodic part. E.g. Zinc metal with impurities Pb or Fe. Corrosion resistance of a metal may be improved by increasing its purity.

**Metal purity  $\propto 1/RC$**

**e. Physical state of Metal:** The rate of corrosion is influenced by physical state of the metal such as grain size, stress; orientation of crystals etc., The smaller the grain size of even in pure metal becomes the anode undergoing corrosion.

**Small Grain size  $\propto RC$**

**f. Nature of surface film:** In aerated atmosphere, all metals get covered with a thin surface film of metal oxides. The ratio of the volumes of metal oxides to the metal is known as specific volume ratio. Greater is this value lesser is the oxidation corrosion rate.

Ex: Specific volume ratios of Ni = 1.6 ; Cr = 2.0 ; W = 3.6 ;

**SVR  $\propto RC$**

#### **NATURE OF CORRODING ENVIRONMENT:-**

**a. Temperature:** As the temperature of environment is increased, the reaction rate is increased thereby accelerating corrosion.

**Temperature  $\propto RC$**

**b. Humidity of air:** Critical humidity is defined as the relative humidity above which the atmosphere corrosion rate of metal increases sharply. The value of critical humidity depends on nature of metal and corrosion products.

Corrosion of a metal is furnish in humid atmosphere because gases (CO<sub>2</sub>, O<sub>2</sub>) and vapours present in atmosphere furnish water to the electrolyte essential to establish an electrochemical corrosion cell. The oxide film on the metal surface has the property to absorb moisture. In presence

of this absorbed moisture, corrosion rate is enhanced. Rain water may also wash away the oxide film from the metal surface. This leads to enhanced atmospheric attack. The exceptions are Cr, Al.

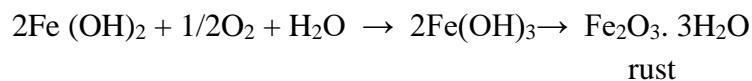
### **Humidity $\alpha$ RC**

**c. Effect of pH:** Generally, acid is more corrosive than neutral or alkaline solutions. Exceptions to the rule are amphoteric metals, aluminum, zinc and lead, which form anions as well as cations. In acid solutions, these react quickly like other metals but in alkaline solutions, they form complex ions and go into solution.

Consequently these metals most resistant to corrosion in neutral solutions. In the case of other metals, the corrosion rate is higher in acidic solutions than in alkaline solutions. The corrosion of iron or steel is quite slow in alkaline solutions and gradually increases as acidity increases and becomes rapid when the pH value is below, say, 4.5 to 3. This is the reason why the pH value of water for boiler feed or for cooling systems is kept in the alkaline range.

### **P<sup>H</sup> $\alpha$ 1/ RC**

**d. Amount of oxygen in atmosphere:** As the percentage of oxygen in atmosphere increases, the rate of corrosion also increases due to the formation of oxygen concentration cell. The decay of metal occurs at the anodic part and the cathodic part of the metal is protected.



### **Amount O<sub>2</sub> $\alpha$ RC**

**CORROSION CONTROL METHODS:** The corrosion methods are as follows:

1. Proper Designing
2. Using Pure metal
2. Using Metal alloys
3. Cathodic Protection
4. Modifying the Environment
5. Use of Inhibitors
6. Application of Protective coatings

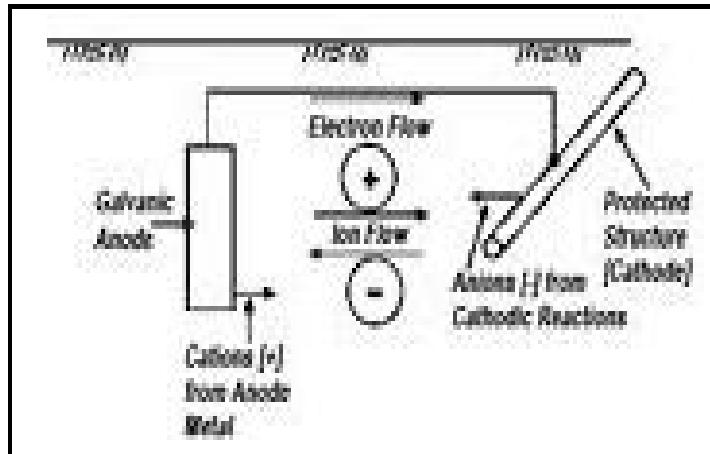
### **CATHODIC PROTECTION:**

The cathodic protection of metals is used to control corrosion metals where it is impracticable to alter the nature of the corrosion medium. The principle involved in this method is to protect metals and alloys from corrosion by making them completely cathodic. Since there will not be any anodic area on the metal, therefore corrosion does not occur.

The following are 2 types of cathodic protections.

1. Sacrificial anodic protection
  2. Impressed current cathodic protection
- a. Sacrificial Anodic Protection Method:**

anodic metal, so



ected by a wire to a more metal. The more anodic

metal itself is corroded slowly, while the parent structure (cathodic) is protected. The more active metal so employed is called "sacrificial anode". A fresh one, when consumed completely replaces the corroded sacrificial anode. Metals commonly employed as sacrificial anode are Mg, Zn, Al and their alloys.

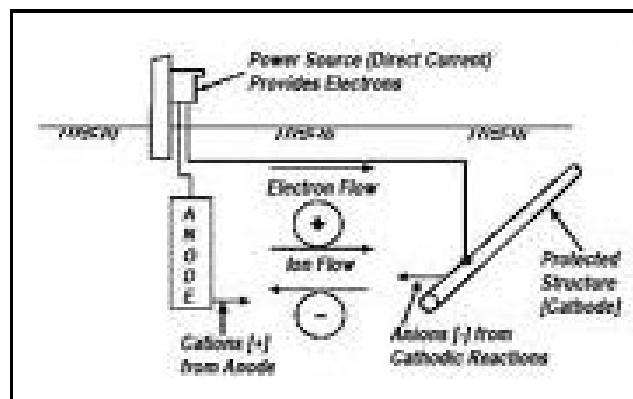
**Applications:** Protection of buried pipe lines, Underground cables, marine structures, ship hulls, water tanks etc.

**b. Impressed Current Cathodic Protection:**

In this method, an impressed current is applied in opposite direction to nullify the corrosion current, and convert the corroding metal from anode to cathode.

Thus the anodic corroding metal becomes cathodic and protected from corrosion.

The impressed current is taken from a battery or rectified on A.C. line.



**Applications:** protection of open water box coolers , water tanks , buried water or oil pipe line, condensers, transmission line towers, marine pipes. Elements with high oxygen content are those that stifle the corrosion reaction occurring at the anode, by forming a sparingly soluble compound with a newly produced metal ion.

## **PROTECTIVE (OR) SURFACE COATINGS:**

Protective coatings are coverings that are intended to provide a layer of protection from anything that could damage the function or integrity of an item. The application of a surface coating is common with a number of different products, ranging from [electrical wiring](#) to printed labels. The coatings are also helpful in preventing rust or enhancing the function of the product, as in the case of coated cookware.

**APPLICATION OF PROTECTIVE COATINGS:** Generally, there are two types of metallic coatings are protection from corrosion.

1. Anodic coatings
2. Cathodic coatings

**1. Anodic coatings:** Anodic coatings are those in which, the metal used is more anodic than the metal which is to be protected.

EX: Coating of Aluminum, Cadmium and Zinc on steel surface are anodic, because their electrode potentials are lower than that of the base metal iron. Therefore sacrificially, anodic coatings protect the underlying base metal.

**2. Cathodic coatings:** Cathodic coatings are obtained by coating a more noble metal (i.e. having higher electrode potential) than the metal. They protect the base metal, because they have higher corrosion resistance than the base metal.

### **Methods of application of metal coatings:-**

**1. Hot-dipping:** Hot dipping process is applicable to the metals having higher melting point than the coating metal. It consists of immersing well cleaned base metal in a bath containing molten coating metal, and a flux layer. The flux cleans the surface of the base metal and prevents the oxidation of the molten coating metal.

Eg. Coating of Zn, Pb, Al on iron, steel surfaces. Most widely used hot dip process are:

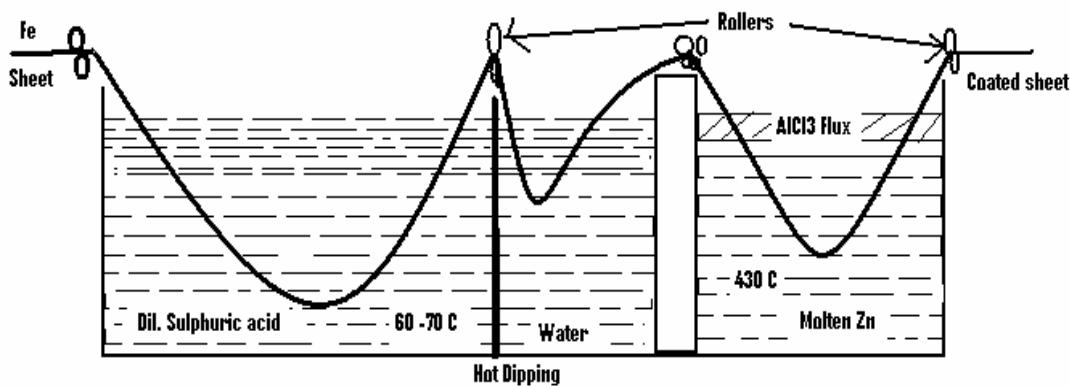
- a). Galvanizing
- b). Tinning

**a). Galvanizing:** Galvanizing is a process in which the iron article is protected from corrosion by coating it with a thin layer of zinc. In this process, at first iron or steel is cleaned by pickling with dilute sulphuric acid solution ( $H_2SO_4$ ) at a temperature range of 60-900C for 15 to 20 minutes.

Therefore, it removes scale, rust and other impurities present if any and then washed well and dried.

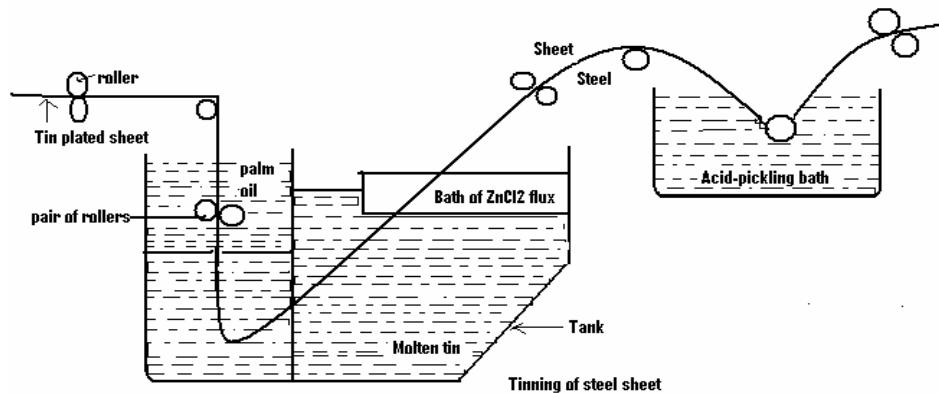
Then after, dipped in the bath molten zinc which is at  $425\text{-}450^{\circ}\text{C}$ . To prevent it from oxide formation, the surface of bath is covered with a flux ( $\text{NH}_4\text{Cl}$ ). When the iron piece is taken out it is coated with a thin layer of zinc. And to remove excess zinc, it is passed through a pair of hot rollers; lastly, it is annealed at a temperature of  $450^{\circ}\text{C}$  and then cooled slowly.

Galvanizing is widely used for protecting iron exposed to the atmosphere, as is the case with roofs, wire fences, pipes and articles fabricated from galvanized sheets like buckets, tubes, etc., Galvanized ware is not used for keeping eatables because of the solubility of zinc. The popularity of galvanizing is due the low cost of zinc. Easy application and the anodic protection offered by the zinc.



**b). Tinning:** The process of coating tin over the iron or steel articles to protect it from corrosion is known as tinning. Tin is a nobler metal than iron, therefore, it is more resistance to chemical attack. In this process, at first Iron sheet is treated in dilute sulphuric acid (pickling) to remove any oxide film if present.

A cleaned Iron sheet is passed through a bath molten flux. Like Zinc chloride, then through molten tin and finally through a suitable vegetable oil. Tinning of mild steel plates is done mostly for the requirements of the foodstuff industry. Tin is a nobler metal than iron, therefore, it is more resistant to chemical attack. As already been explained, if the coating formed does not cover the surface completely during use and leaves iron exposed, more rapid corrosion of iron will take place.

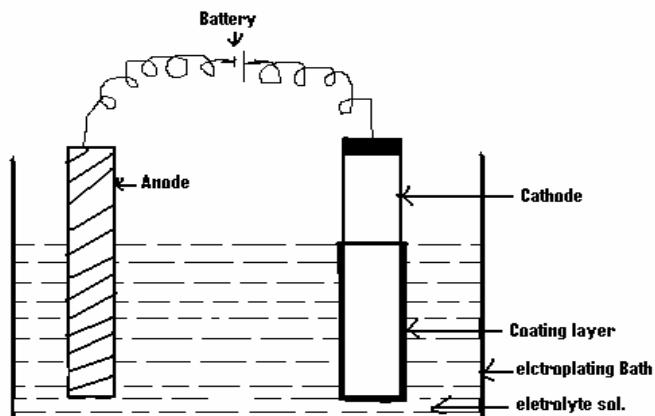


A cleaned iron sheet is passed through a bath of molten flux, like zinc chloride, then through molten tin and finally through a suitable vegetable oil. Lastly it is passed between rolls to adjust then thickness of the tin layer, which may be about 0.002 mm thick.

**ELECTROPLATING:** Electroplating is the process or method of coating metals and non-metals, to change their surface properties such as to improve the appearance, to properties such as to improve the appearance to corrosion and wear or chemical attack. Electroplating is the electro-deposition of metal, by means electrolysis over surface of metals, alloys or non-metals.

The wear resistance of a metal part can be improved by electroplating a harder metal on its surface. The metals most often plated on base metals or materials are chromium, Nickel and Rhodium.

EX: Metals like Iron which are easily corroded by atmospheric air, moisture and CO<sub>2</sub> are coated electrolytic ally with base metals such as nickel or chromium which are more resistant to wear or chemical attack.



Some of the applications of electroplating are:

- Plating for protection from corrosion and chemical attack.
- Plating for decoration.
- Plating for special for special surface and engineering effects.
- Electroforming
- Plating on non-metallic materials.

### **Applications:**

Therefore, this process is widely used in automobiles, aircrafts, refrigerators, jewellery, radios, cameras, type-writers, umbrellas, watches etc.

### **ELECTROLESS PLATING:**

Electro less plating, also known as chemical or auto-catalytic plating, is a non-galvanic plating method that involves several simultaneous reactions in an aqueous solution, which occur without the use of external electrical power. The reaction is accomplished when hydrogen is released by a reducing agent, normally sodium hypophosphite (the hydrogen leaves as a hydride ion), and oxidized, thus producing a negative charge on the surface of the part. The most common Electroless plating method is Electroless nickel-plating, although silver, gold and copper layers can also be applied in this manner, as in the technique of Angel gilding.

### **NICKEL PLATING**

Electro less nickel plating is self-catalyzing process, the resultant nickel layer is NiP compound, with 7–11% phosphorus content. Properties of the resultant layer hardness and wear resistance are greatly altered with bath composition and deposition temperature, which should be regulated with 1 °C precision, typically at 91 °C.

During bath circulation, any particles in it will become also nickel plated, this effect is used to advantage in processes which deposit plating with particles like silicon carbide (Sic) or Polytetrafluoroethylene (PTFE). While compared to many other plating processes, it is expensive because the process is complex. Moreover, the process is lengthy even for thin layers. When only corrosion resistance or surface treatment is of concern, very strict bath composition and temperature control is not required and the process is used for plating many tons in one bath at once.

Electroless nickel plating layers are known to provide extreme surface adhesion when plated properly. Electroless nickel plating is non-magnetic and amorphous. Electroless nickel plating layers are not easily solder able, nor do they seize with other metals or another electroless nickel plated work piece under pressure. This effect benefits electroless nickel plated screws made out of malleable materials like titanium. Electrical resistance is higher compared to pure metal plating.

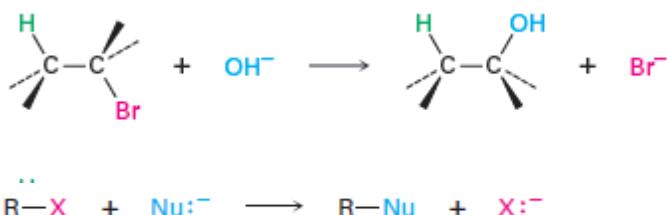
### **Advantages:**

- Uniform layer thickness over most complicated surfaces
- Direct plating of ferrous metals (steel)
- Superior wear and corrosion resistance to electroplated nickel or chrome.
- Much of the chrome plating done in aerospace industry can be replaced with electroless nickel plating, again environmental costs, costs of hexavalent chromium waste disposal and notorious tendency of uneven current distribution favor electroless nickel plating.

## UNIT IV- Reaction Mechanisms and molecules of industrial importance

### Substitution reactions: Nucleophilic substitution reactions: Mechanism of S<sub>N</sub>1, S<sub>N</sub>2 reactions.

Alkyl halides when react with a nucleophile, they undergo substitution of the X group with the nucleophile. Nucleophilic substitution reactions were discovered by German Chemist Paul Walden in 1896.



#### Mechanism of S<sub>N</sub>2

S<sub>N</sub>2 stands for substitution nucleophilic bimolecular

Consider the simple nucleophilic substitution reaction between CH<sub>3</sub>Br and OH<sup>-</sup> to yield CH<sub>3</sub>OH and Br<sup>-</sup>



In this reaction, the rate depends on the concentration of both the reactants. In rate determining step, both RX and OH<sup>-</sup> are present. The reaction is a second order reaction.

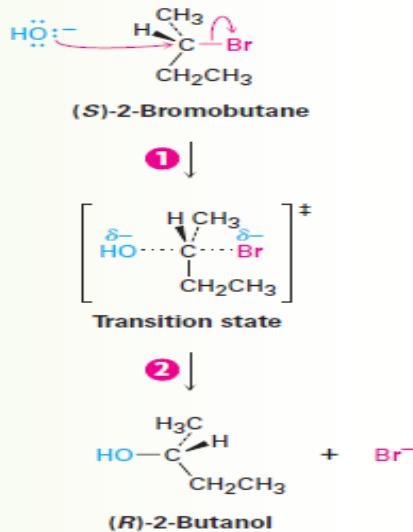
S<sub>N</sub>2 reaction takes place in a single step without formation of intermediates. As the nucleophile attacks from the backside and forms bond with the carbon, halide departs from the other side.

Backside attack of the nucleophile causes inversion in the stereochemical configuration.

### MECHANISM

The mechanism of the  $S_N2$  reaction. The reaction takes place in a single step when the incoming nucleophile approaches from a direction  $180^\circ$  away from the leaving halide ion, thereby inverting the stereochemistry at carbon.

- 1 The nucleophile  $\text{^-OH}$  uses its lone-pair electrons to attack the alkyl halide carbon  $180^\circ$  away from the departing halogen. This leads to a transition state with a partially formed C-OH bond and a partially broken C-Br bond.
- 2 The stereochemistry at carbon is inverted as the C-OH bond forms fully and the bromide ion departs with the electron pair from the former C-Br bond.



### Factors affecting $S_N2$

1. Polar aprotic solvents like DMSO, acetone favor  $S_N2$
2. Reaction rate is slowest for tertiary alkyhalides and fastest for primary alkyl halides. Reaction rate follows the order,  $1 > 2 > 3^\circ$ .
3. Basic, negatively charged nucleophiles favors  $S_N2$ .
4. Good leaving groups, i.e more stable anions favors  $S_N2$ . Weak bases like  $\text{Cl}^-$ ,  $\text{Br}^-$  form good leaving groups when compared to strong bases like  $\text{OH}^-$ ,  $\text{NH}_2^-$ . For halogens the order is,  $\text{F}^- < \text{Cl}^- < \text{Br}^- < \text{I}^-$

### Mechanism of $S_N1$

$S_N1$  stands for substitution nucleophilic unimolecular.

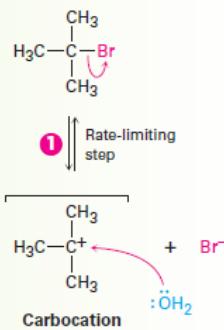
$S_N1$  reaction of  $(\text{CH}_3)_3\text{CBr}$  with  $\text{H}_2\text{O}$  has a rate that depends only on the alkyl halide concentration and is independent of the  $\text{H}_2\text{O}$  concentration. In other words, the reaction is a first-order reaction.

## Mechanism of reaction

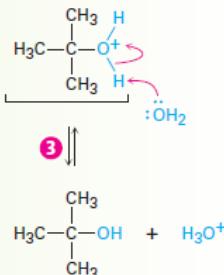
### MECHANISM

The mechanism of the  $S_N1$  reaction of 2-bromo-2-methylpropane with  $H_2O$  involves three steps. Step ①—the spontaneous, unimolecular dissociation of the alkyl bromide to yield a carbocation—is rate-limiting.

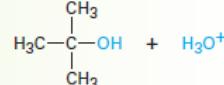
- ① Spontaneous dissociation of the alkyl bromide occurs in a slow, rate-limiting step to generate a carbocation intermediate plus bromide ion.



- ② The carbocation intermediate reacts with water as a nucleophile in a fast step to yield protonated alcohol as product.



- ③ Loss of a proton from the protonated alcohol intermediate then gives the neutral alcohol product.



## Factors affecting $S_N1$

1. Polar protic solvents like alcohols favor  $S_N1$
2. Reaction rate is slowest for tertiary alkyl halides and fastest for primary alkyl halides. Reaction rate follows the order,  $3 > 2 > 1^\circ$ .
3. Involves the formation of carbocation, which is  $SP^2$  hybridised.
4. Carbocation can react with a nucleophile equally well from either side, leading to a racemic mixture.

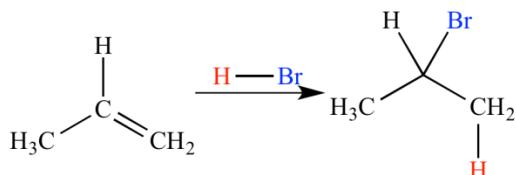
## Electrophilic and nucleophilic addition reactions: Addition of HBr to propene. Markownikoff's and anti Markownikoff's additions.

Conversion of multiple bonds, such as a double or a triple bond, into other functional groups is usually achieved using addition reactions.

## **Electrophilic addition reactions**

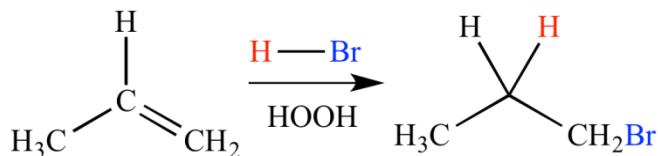
### **Markownikoff's rule**

Addition of hydrogen to an unsymmetrical olefin occurs at those carbon atoms with maximum number of hydrogen atoms. (i.e., the carbon with least substitution). Electronegative group goes to more substituted carbon atom.



### **anti Markownikoff's addition**

In the presence of peroxides, addition reaction between hydrogen atom of HX gets bonded with the carbon atom that has least number of hydrogen atoms. Anti Markownikoff's addition refers to the fact that reaction does not follow Markownikoff's rule.



## **Nucleophilic addition reactions**

For nucleophilic addition to take place, alkene should be attached with an electron withdrawing group, which can withdraw electron density from the pi bond of the alkenes. Examples for this class of reactions are hydroamination and conjugate addition reactions.

### **Hydroamination**

The addition of nucleophilic amino group across double bond are called hydroamination reactions.

### **Nucleophilic conjugate addition**

The addition reaction of  $\alpha,\beta$ -unsaturated carbonyl compounds and  $\alpha,\beta$ -unsaturated nitriles with nucleophiles at 1,4 position is called nucleophilic conjugate addition.

Alkene having carbonyl or nitrile group in conjugation increases reactivity toward nucleophiles by resonance stabilisation.

1,2 additions are also known as direct addition.

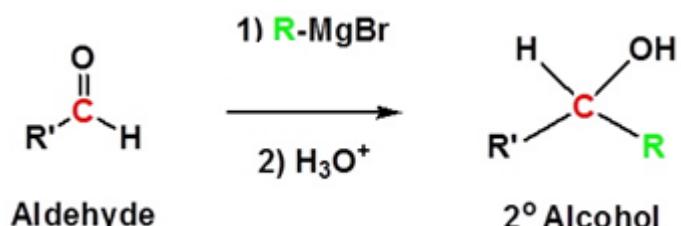
1,4 additions are also known as conjugate addition.

### **Grignard additions on carbonyl compounds.**

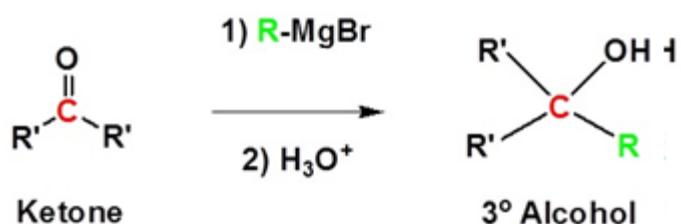
Addition of Grignard reagent to formaldehyde gives 1° alcohols



Addition of Grignard reagent to aldehydes gives  $2^\circ$  alcohols



Addition of Grignard reagent to ketones gives  $3^\circ$  alcohols

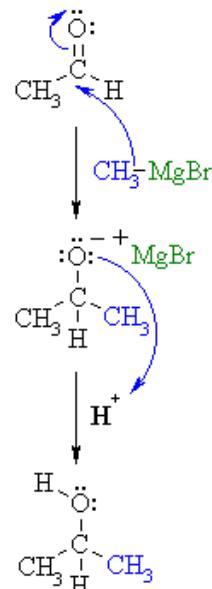


### Mechanism of nucleophilic addition of $\text{RMgX}$ to

#### Step

**1:**

The nucleophilic C in the organometallic reagent adds to the electrophilic C in the polar carbonyl group, electrons from the  $\text{C}=\text{O}$  move to the electronegative O creating an intermediate metal alkoxide complex.



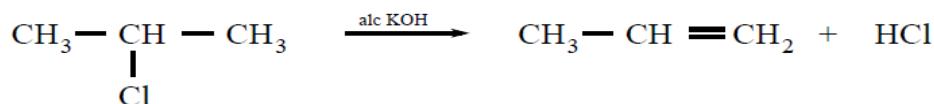
**Step**

**2:**

Protonation of the alkoxide oxygen creates the alcohol product from the intermediate complex.

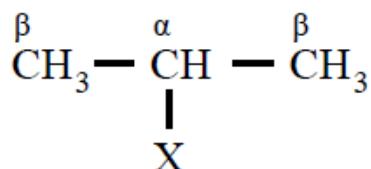
### Elimination reactions: Dehydro halogenation of alkylhalides. Saytzeff rule.

In elimination reaction, some molecules leave the compound leading to the formation of double or triple bond.



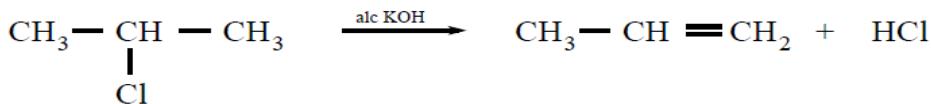
### $\alpha$ and $\beta$

- **$\alpha$ -carbon :** The carbon atom which carries the halogen is called an alpha-carbon ( $\alpha$ -carbon).
- **$\beta$ -carbon :** The carbon atom next to the  $\alpha$ -carbon is called a  $\beta$ -carbon.
- **$\beta$ -hydrogen :** The hydrogen atoms attached to the  $\beta$ -carbon are called  $\beta$ -hydrogens.



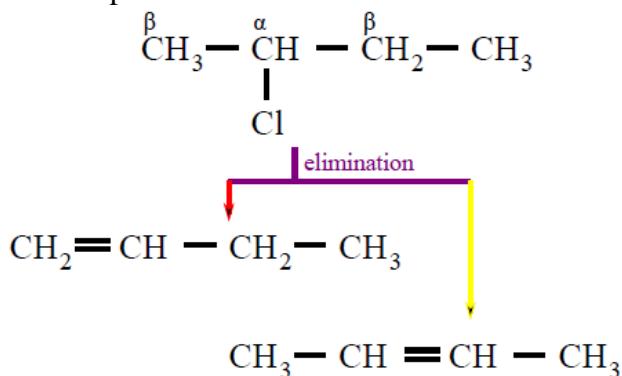
### Dehydrohalogenation

When alkyl halides having  $\beta$ -hydrogen are heated with some base such as alcoholic KOH or alkoxide etc., the halogen is eliminated from  $\alpha$ -position and a hydrogen from  $\beta$ -position leading to the formation of alkenes.

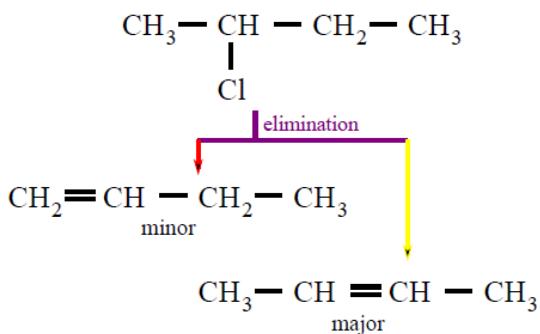


Saytzeff's rule

Let us take the example of 2-chlorobutane. 2-Chlorobutane has two  $\beta$ -carbon atoms, and gives two different products on elimination.



In such reactions, the major product is that alkene which has lesser number of hydrogen atoms on the doubly bonded carbon atoms. This rule is known as **Saytzeff's rule**. Let us apply Saytzeff's rule to the above example:



### Ease of dehydrohalogenation

The alkyl halide that gives alkene with lesser number of hydrogen atoms on the doubly bonded carbon atoms undergoes elimination faster.

In general, the ease of dehydrohalogenation follows the order :

tertiary > secondary > primary

For a given halogen, the order is :

$\text{R-I} > \text{R-Br} > \text{R-Cl}$

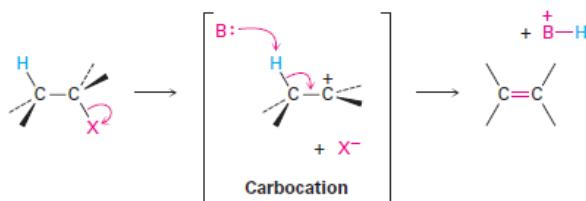
### Reaction Mechanism

Dehydrohalogenation can take place through E1, E2, and E1cB mechanisms. Here, we will consider E1, E2 mechanisms.

E1 mechanism:

In the E1 reaction, the C-X bond breaks first to give a carbocation intermediate, this undergoes subsequent base abstraction of  $\text{H}^+$  to yield the alkene.

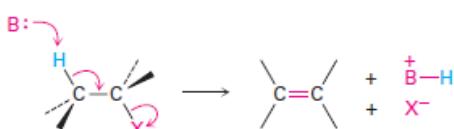
**E1 Reaction:** C-X bond breaks first to give a carbocation intermediate, followed by base removal of a proton to yield the alkene.



### E2 Mechanism:

In the E2 reaction, base-induced C - H bond cleavage is simultaneous with C - X bond cleavage, giving the alkene in a single step.

**E2 Reaction:** C-H and C-X bonds break simultaneously, giving the alkene in a single step without intermediates

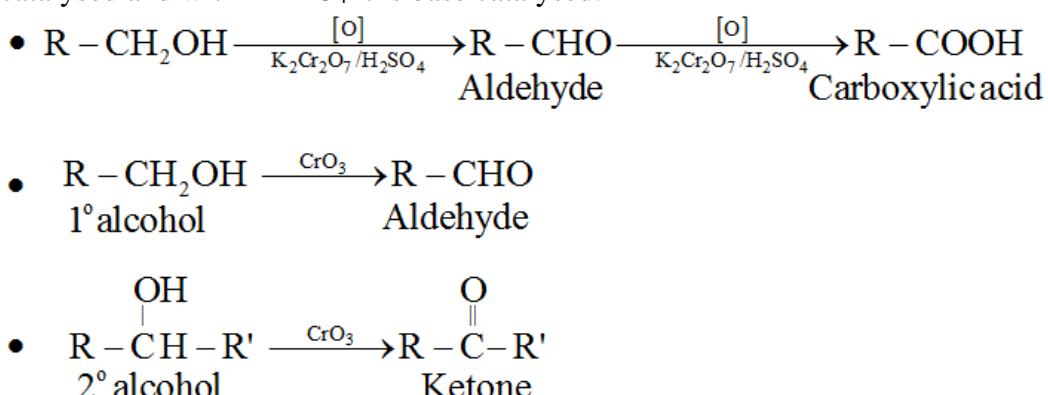


### Oxidation reactions: Oxidation of alcohols using KMnO<sub>4</sub> and chromic acid.

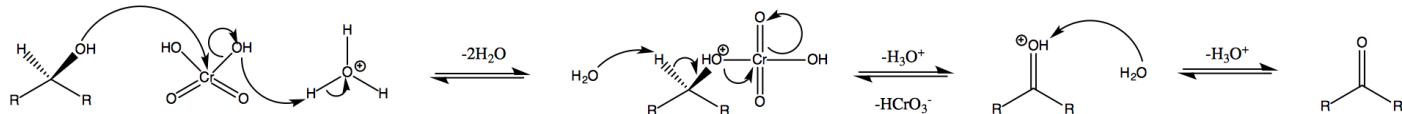
**a. Oxidation of alcohols using chromic acid.**

Depending upon the structure of the alcohol and the type of oxidising agent used, oxidation of alcohol gives different products. Jones reagent is used for the oxidation of primary and secondary alcohols to carboxylic acids and ketones respectively. The Jones reagent is prepared by adding chromium trioxide to dilute sulfuric acid in acetone and is added to the alcohol at 0-25°C. Chromium trioxide with dilute H<sub>2</sub>SO<sub>4</sub> in situ forms chromic acid. Chromic acid and alcohol then through chromate ester gives carbonyl compound in presence of base.

For both chromic acid and  $\text{KMnO}_4$ , oxidation of primary and secondary alcohols gives carboxylic acids and ketones respectively. The difference is in mechanism, with chromic acid, it is acid catalysed and with  $\text{KMnO}_4$  it is base catalysed.

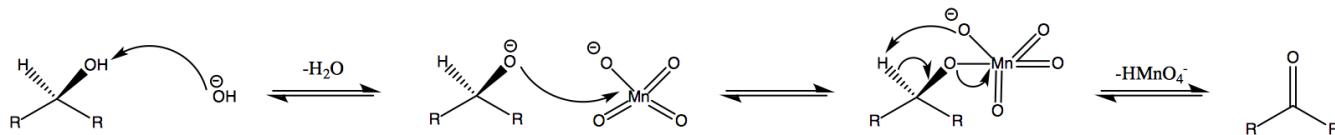


### **Reaction Mechanism:**



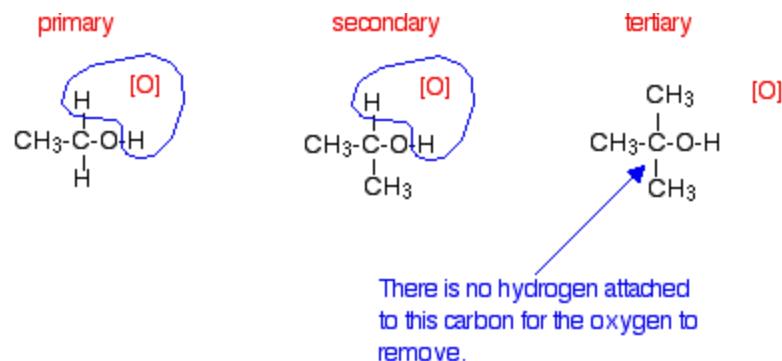
- b. Oxidation of alcohols using  $\text{KMnO}_4$ : Manganese can function as oxidant when it is in +7 oxidation state.  $\text{KMnO}_4$  is one such strong oxidizing agent.

### Reaction Mechanism:



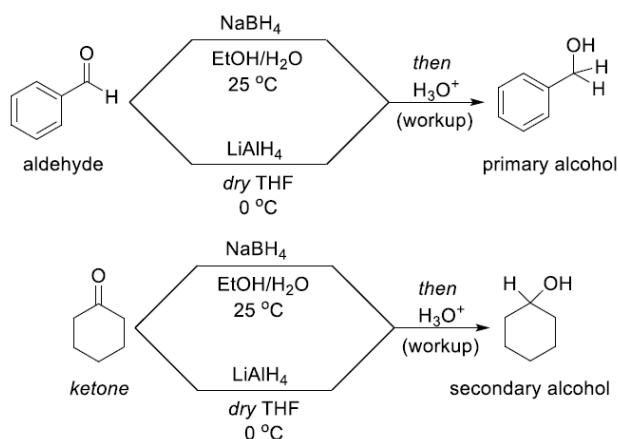
### Tertiary alcohols do not get oxidized- why

In primary and secondary alcohols, the oxidizing agent is removing the hydrogen from the  $-\text{OH}$  group, and a hydrogen from the carbon atom attached to the  $-\text{OH}$ . Tertiary alcohols don't have a hydrogen atom attached to that carbon.



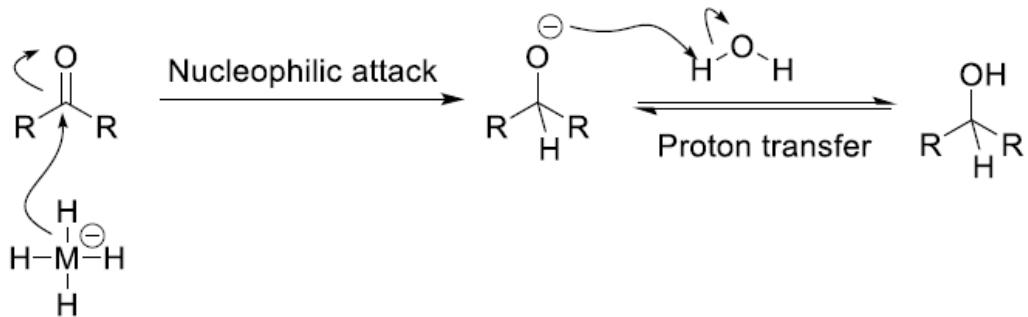
### Reduction reactions: reduction of carbonyl compounds using $\text{LiAlH}_4$ & $\text{NaBH}_4$ .

Reduction of Aldehydes and Ketones using  $\text{NaBH}_4$  or  $\text{LiAlH}_4$ . Aldehydes are converted to primary alcohols, and ketones to secondary alcohols, by treatment with either  $\text{NaBH}_4$  (sodium borohydride) or  $\text{LiAlH}_4$  (lithium aluminum hydride).



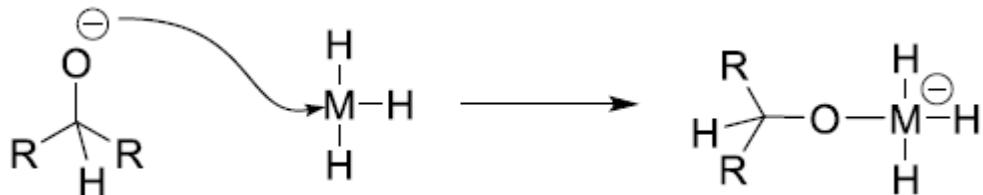
## Mechanism

Even though reaction conditions are different, fundamentally both the mechanisms are same. In the following generic mechanism, 'M' depicts either Boron or Aluminium. There are essentially two steps. Nucleophilic attack of a hydride ion on the electrophilic carbonyl carbon and protonation of the resulting alkoxide by water or some other acid.



Both  $\text{BH}^{4-}$  and  $\text{AlH}^{4-}$  deliver hydride as a nucleophile to the carbonyl carbon.

After donating a hydride to the carbonyl carbon,  $\text{BH}^{4-}$  is converted to  $\text{BH}_3$  and  $\text{AlH}^{4-}$  is converted to  $\text{AlH}_3$ . These two are lewis acids (e- deficient) and form complexes with any lewis base. Hence an alkoxide is formed by attack of hydride on the carbonyl.



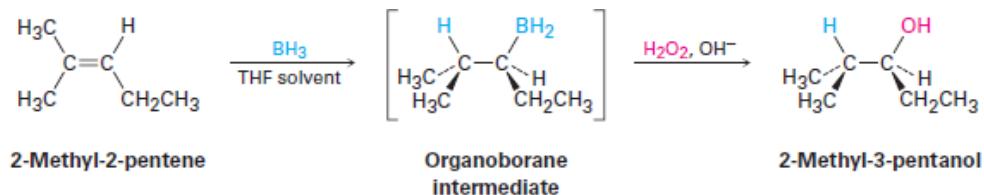
## How $\text{LiAlH}_4$ & $\text{NaBH}_4$ differ

Even though they follow the same mechanism,  $\text{LiAlH}_4$  &  $\text{NaBH}_4$  differ in terms of reactivity.  $\text{NaBH}_4$  is much less reactive as a base or nucleophile than  $\text{LiAlH}_4$ .  $\text{LiAlH}_4$  being stronger hydride donor, shows greater reactivity i.e., it is capable of reducing less reactive functional groups which will not be reduced by  $\text{NaBH}_4$ .

## Hydroboration of olefins.

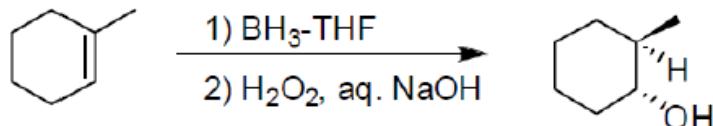
The addition of water to alkene in the presence of boron reagent are known as hydroboration-oxidation reaction. The addition follows syn addition with cis stereoselectivity. Unlike other addition reactions, here the hydroxyl group get added to the least substituted carbon. No carbocation intermediate is involved in this reactions suggesting that a concerted addition take place. If  $\text{BH}_3$  is used as reagent it can hydroborate three alkene units.

The number of alkenes undergoing hydroboration are equal to no. of hydrogens attached directly to boron in the borane reagent. The product obtained in such reactions are a racemic mixture, the stereoselectivity can be improved by using chiral borane reagents.



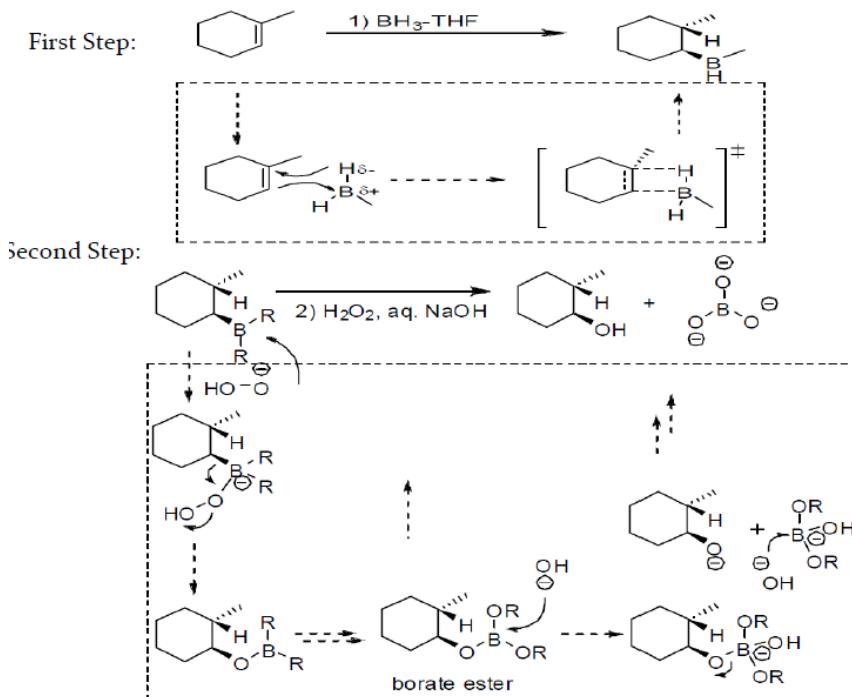
### Mechanism of Hydroboration

Consider the reaction,



In the first step, alkene acts as a nucleophile and attacks on electrophilic boron.

In the second step, peroxide acts as nucleophile & attack the electrophilic boron followed by migration of C-B bond to form C-O bond. Hydrolysis results in the formation of alcohol.



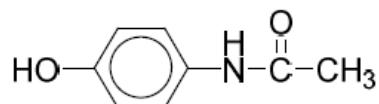
**Structure, synthesis and pharmaceutical applications of Paracetamol and Aspirin.**

**Structure, synthesis and pharmaceutical applications of Paracetamol**

**Paracetamol** and **acetaminophen** are two official names of the same chemical compound derived from its chemical name: **N-acetyl-para-aminophenol**. This drug has a long history was found by

chance. In the 80s of the 19<sup>th</sup> century, two young doctors at the University of Strasburg, in order to eradicate worms, by mistake dispensed acetanilide to a patient instead of naphthalene. They noticed that the drug had a small impact on intestinal parasites, however, it significantly decreased high temperature.

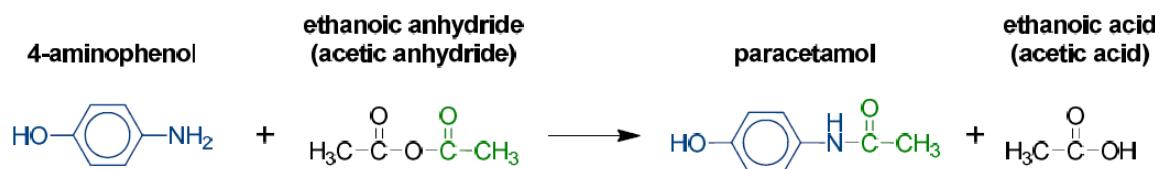
### Structure



### Paracetamol

### Synthesis

Paracetamol is made by reacting 4-aminophenol with ethanoic anhydride (acetic anhydride). This reaction forms an amide bond and acetic acid is the by-product.



### Applications of paracetemol

- Used as Antipyretic, analgesic agent. It has negligible anti-inflammatory action.
- It is suitable substitute for the analgesic and antipyretic effects of NSAIDs for those patients with gastric complaints/ risks, in those whom a prolongation of bleeding time is not desirable, as well as those who do not require the anti-inflammatory action of NSAIDs.
- It is the analgesic/antipyretic of choice for children with viral infections or chickenpox (due to the risk of Reye syndrome with aspirin).
- Paracetamol is one of the most commonly used ‘over-the-counter’ analgesic for headache, mild migraine, musculoskeletal pain, dysmenorrhoea etc. but is relatively ineffective when inflammation is prominent.
- It is recommended as first choice analgesic for osteoarthritis by many professional bodies.
- It is one of the best drugs to be used as antipyretic, especially in children (no risk of Reye’s syndrome).

### Why should we use Paracetamol instead of Aspirin ?

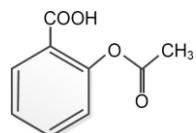
- Paracetamol is much safer than aspirin in terms of gastric irritation, ulceration and bleeding (can be given to ulcer patients), does not prolong bleeding time.

- Hypersensitivity reactions are rare.
- No metabolic effects or acid-base disturbances.
- Can be used in all age groups (infants to elderly), pregnant/lactating women, in presence of other disease states and in patients in whom aspirin is contraindicated.
- It does not have significant drug interactions.  
Thus, it may be preferred over aspirin for most minor conditions.

## Structure, synthesis and pharmaceutical applications of Aspirin

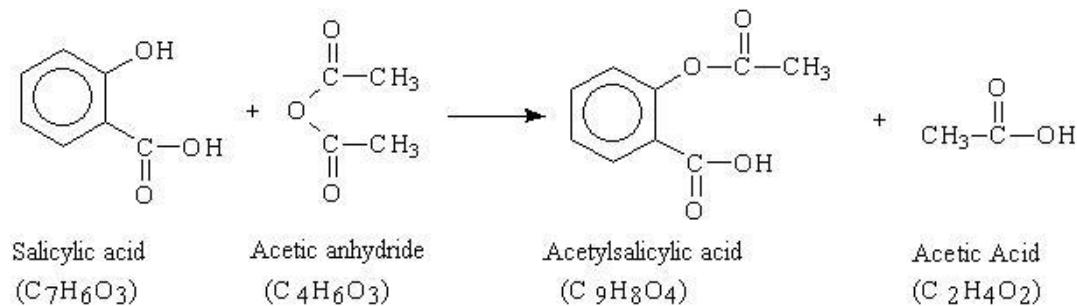
Aspirin (acetylsalicylic acid) is a synthetic organic derived from salicylic acid. Salicylic acid is a natural product found in the bark of the willow tree and was used by the ancient Greeks and Native Americans, among others, to counter fever and pain. However, salicylic acid is bitter and irritates the stomach.

A German chemist named Felix Hoffman is credited with being the first to synthesize aspirin in 1897. Hoffman's father had severe arthritis but could not tolerate salicylic acid he was taking for pain relief. The name given for Hoffman's new compound was **A-spirin**. Apparently this comes from acetylation (**A-**), together with **Spirin**, part of the name for Meadow-sweet (*Spiraea ulmaria*), a plant rich in salicylates.



## Synthesis

To synthesise aspirin, an excess of acetic anhydride ( $C_4H_6O_3$ ) is added to a measured mass of salicylic acid ( $C_7H_6O_3$ ) in the presence of a catalyst, sulfuric acid ( $H_2SO_4$ ). The mixture is heated to form the acetylsalicylic acid ( $C_9H_8O_4$ ) and acetic acid ( $C_2H_4O_2$ ).



## Applications of Aspirin

1. It is used to reduce fever and relieve mild to moderate pain from conditions such as muscle aches, toothaches, common cold, and headaches.
2. It may also be used to reduce pain and swelling in conditions such as arthritis.

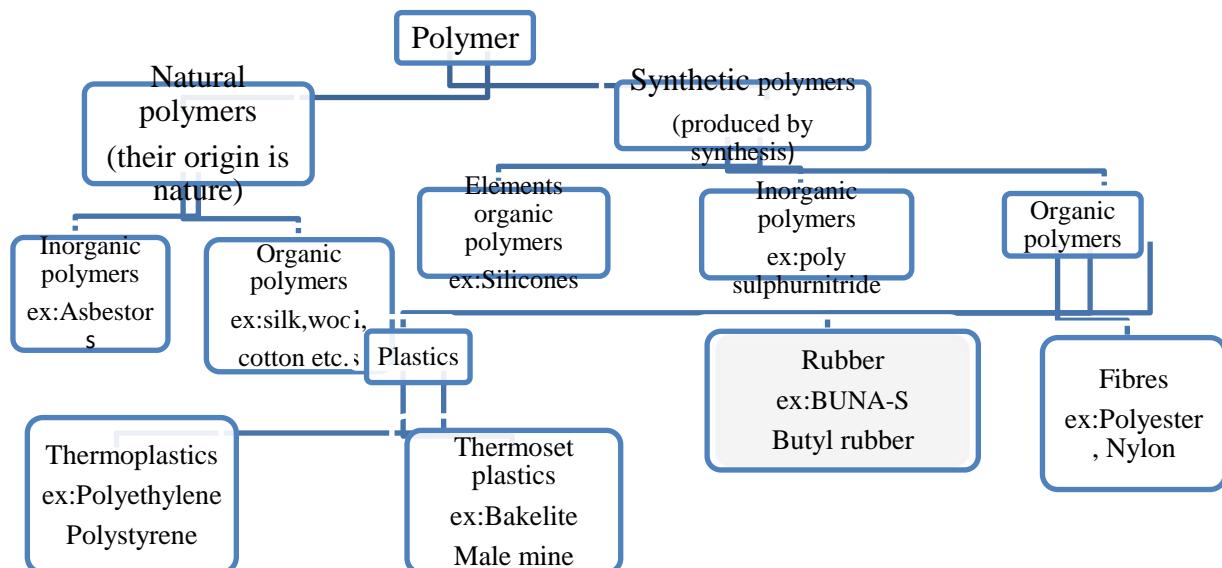
3. It is known as a salicylate and a nonsteroidal anti-inflammatory drug (NSAID). alvanizing
4. It works by blocking a certain natural substance in your body to reduce pain and swelling.
5. It can be used in low doses as a "blood thinner" to prevent blood clots.

**Note:** Reactions mechanisms are taken from various internet resources and from Organic chemistry 9e John Mc Murry. This document will be used only for educational purpose.

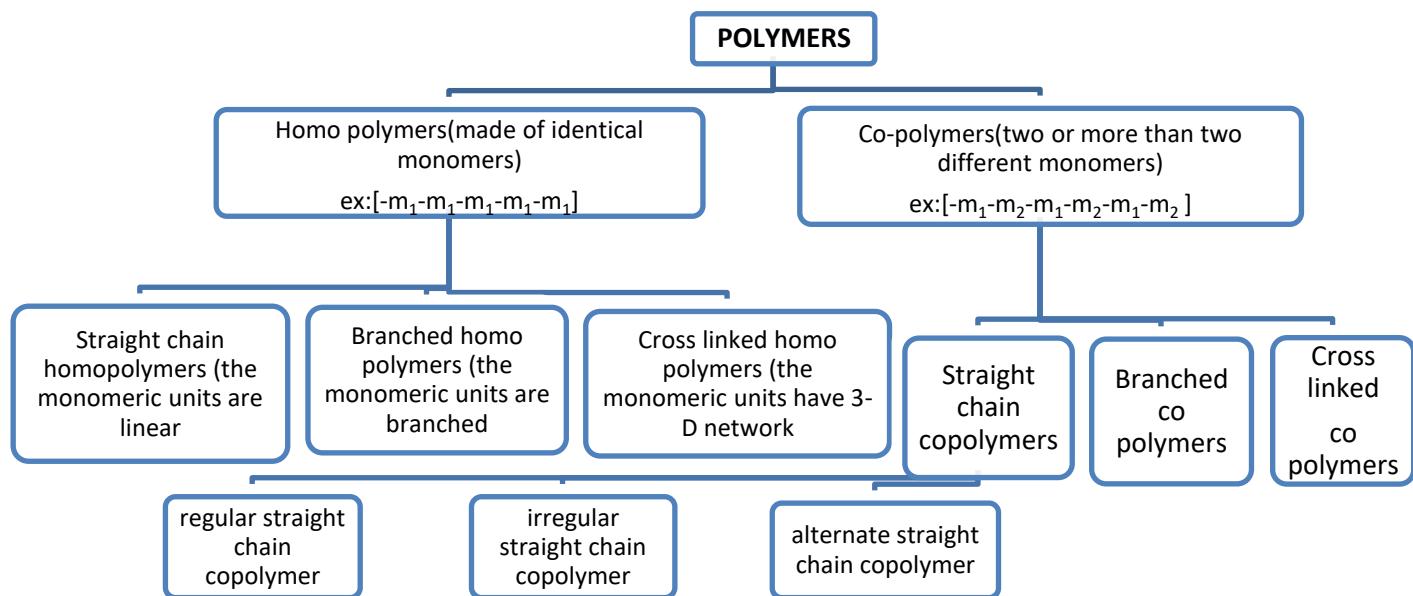
## Polymers

### Classification of the polymers:

#### (a). Based on their origin:



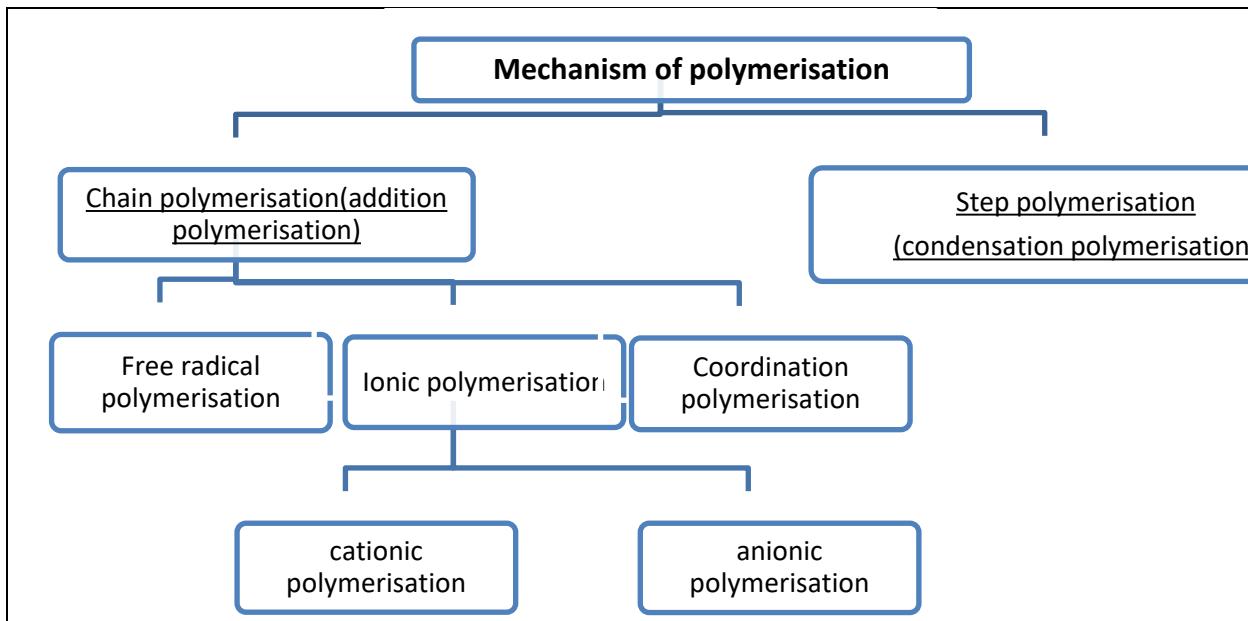
#### b). Based on nature of polymerisation



**Types of Polymerisation:-** The mechanism of polymerization takes place by 2 ways:

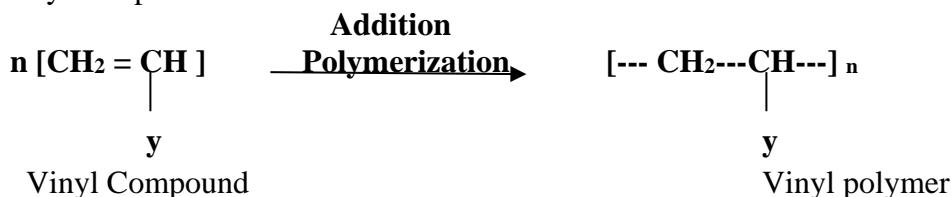
1. Chain/ Addition polymerization
2. Step/ Condensation polymerization

### Mechanism of Polymerisation:



**1. Chain/ Addition Polymerisation:** A chain polymerisation is a reaction in which rapid self addition of several bifunctional monomers to each other takes place by chain reaction without the elimination of any by-product. It yields a polymer product which is the exact multiple of monomers. Thus the mechanism is also called addition polymerisation. The compounds containing double bonds undergo chain polymerisation.

Eg: Vinyl compounds.



Where  $y = H$  (Ethylene),  $\text{CH}_3$ , (Propylene),  $\text{Cl}$  (Vinyl chloride),  $\text{C}_6\text{H}_5$  (Styrene),  $\text{CN}$  (Acrylonitrile).

### Characteristics:

- ✓ Monomer contains double bond which makes it bifunctional.
- ✓ The polymerisation takes place by self-addition of monomers through a chain reaction.

- ✓ No by-products like  $\text{H}_2\text{O}$ ,  $\text{CH}_3\text{OH}$  are produced.
- ✓ The polymer has the same chemical composition as that of monomer.
- ✓ The mol.wt. is not the sum of mol. Wt. of the monomers.
- ✓ The mechanism is carried out in three steps, i.e. initiation, propagation and termination.
- ✓ Initiator is required to start the polymerisation; initiators may be heat, light, pressure, catalyst etc.
- ✓ The mechanism is rapid.
- ✓ Linear polymers are formed
- ✓ The conversion of bond to bond takes place during the polymerisation, liberating 20 Kcal/mole of energy      ex: alkenes, vinyl, allyl compounds and dienes.

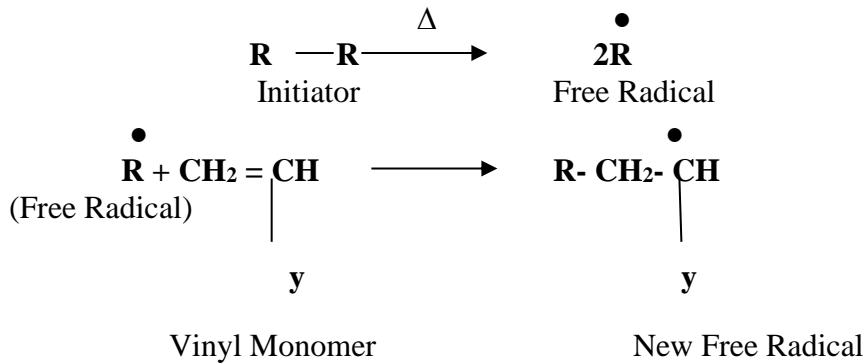
Chain polymerisation mechanism is of 3 different types:

- 1) Free radical chain polymerisation
- 2) Ionic chain polymerisation
- 3) Coordination polymerisation.

**1). Free radical chain polymerisation:** The complete mechanism involves 3 steps.

- (a) Initiation
- (b) Propagation
- (c) Termination

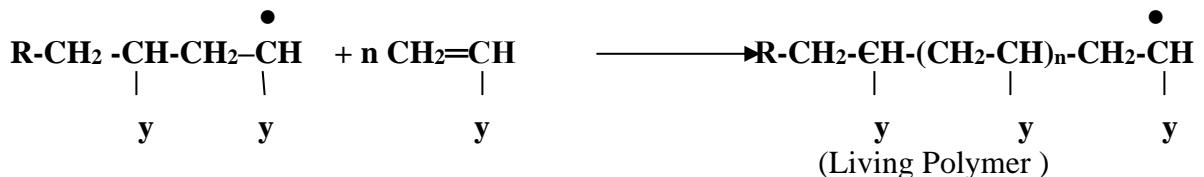
**a).Initiation:** The polymerization is initiated by free radicals generated from initiators such as peroxides. A free radical is an atomic or molecular species having an odd or unpaired electron. They are highly active species (unstable). An initiator on heating undergoes homolytic cleavage and generates free- radicals. It adds to the monomer to produce a new free- radical.



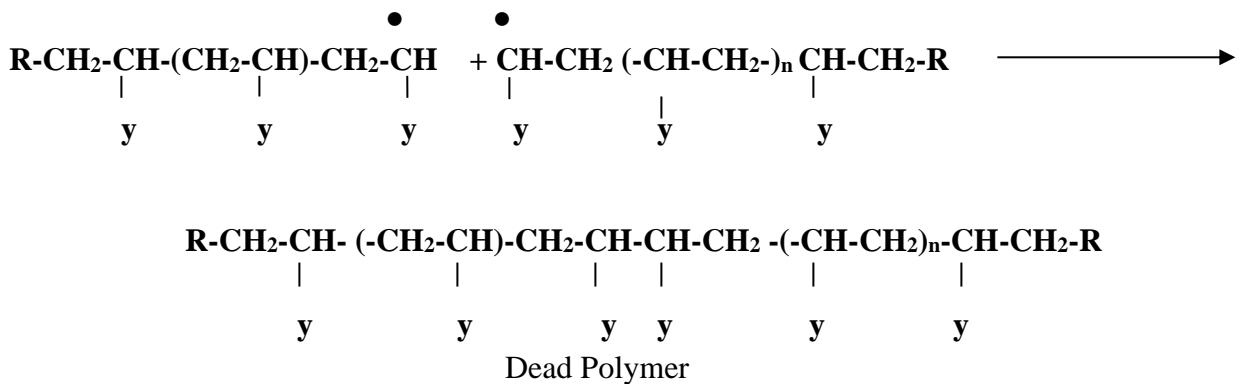
**Eg:** Benzoyl peroxide, hydrogen peroxide are good initiators for free radical chain polymerisation.

**b).Propagation:** In this step, the new free radical attacks another monomer molecule to produce yet another new free radical. Many repetitions of this step leads to polymer chain growth and continues until termination occurs.

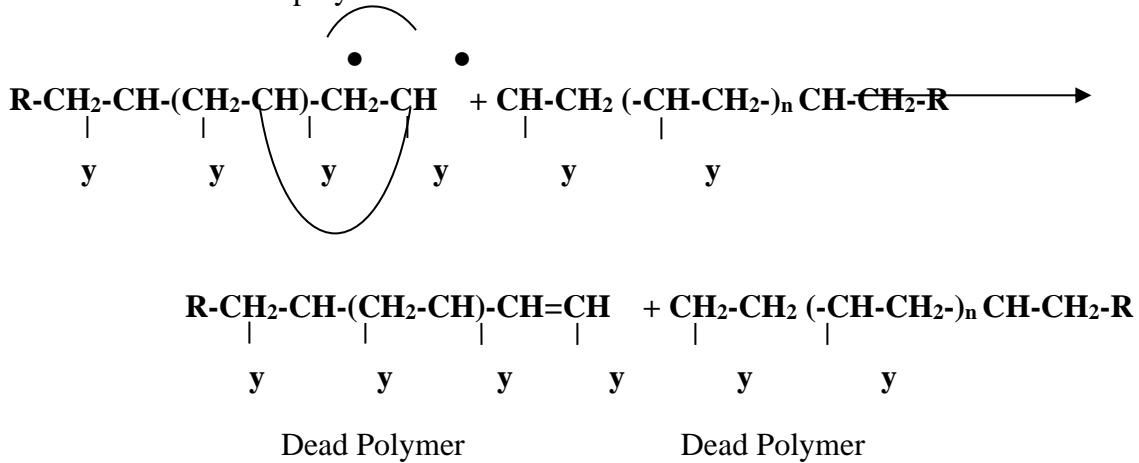




c). **Termination:** Termination of the growing polymer chain is carried by coupling and disproportionation, resulting the dead polymer. In coupling, the collision of two growing chains causes the union of the two chains at their free radical site producing a dead polymer.



In disproportionation, H from the growing chain is transferred to the other growing chain. This results in the formation of two polymer molecules one saturated and other unsaturated.



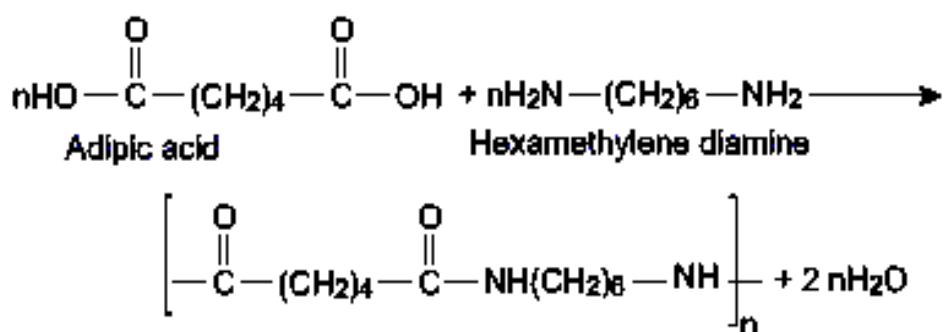
**2. Step polymerisation or condensation polymerisation:** It takes place by condensation reactions of the functional groups of the monomers (by the loss of small groups like H<sub>2</sub>O, HCl, CH<sub>3</sub>OH) hence known as Step polymerisation or condensation polymerisation.

### Characteristics:

- ✓ Monomers contain functional groups like -OH, -COOH, -NH<sub>2</sub>, -RCOOR, Halides etc.
- ✓ it is bifunctional or trifunctional. ( i.e. Monomers must be dibasic acids, diols, diamines or thiols etc.)
- ✓ The polymerisation takes place by slow stepwise condensation reaction of functional groups of the monomer.
- ✓ It is accompanied by the elimination of biproducts like H<sub>2</sub>O, CH<sub>3</sub>OH etc.
- ✓ The mol.wt. is not the sum of mol. Wt. of the monomers.
- ✓ It is not a three step mechanism of initiation, propagation and termination.
- ✓ The reactions are catalysed by catalysts.
- ✓ The reactions are not exothermic.

1 Ex: The polymerisation of diacid with diol produces polyester.

2 Ex: The polymerisation of a diamine with diacid gives Nylon (a polyamide)



Differences between addition and condensation Polymerisation

Condensation Polymerisation	Addition polymerisation
(1) It is also known as step growth polymerisation	(1) It is also known as chain growth polymerization
(2) It takes place in monomers having reactive functional groups	(2) It takes place only in monomers having multiple bonds.

(3) It takes place with elimination of simple molecule like H <sub>2</sub> O,NH <sub>3</sub> ,HCl etc.,	(3) It takes place without elimination of simple molecule.
(4) Repeat units of monomers are different	(4) Repeat units & monomers are same.
(5) The polymer is formed in gradual steps	(5) Reaction is fast and polymer is formed at once.
(6) The molecular mass of polymer increases throughout the reaction	(6) There is very little change in the molecular mass throughout the reaction
(7) Product obtained may be thermosetting/thermoplastic	(7) Product obtained are thermoplastic
(8) E.g.: Bakelite, polyester ,polyamides etc.,	(8) E.g:-Polyethylene, PVC, poly styrene.

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Preparation, properties and engineering applications of PVC, Teflon and Nylon- 6, 6.

## 1. PVC:

Poly Vinyl Chloride is obtained by heating a water emulsion of vinyl chloride in presence of a small amount of benzoyl peroxide or hydrogen peroxide in an auto clave under pressure.

Vinyl chloride, so needed is generally prepared by treating acetylene at 1 to 1.5 atmospheres with hydrogen chloride at 600C to 800C in the presence of metal chloride as catalyst.



## Properties:

- It occurs as a colourless rigid material.
  - It is having high density and low softening point.
  - It is resistant to light, atmospheric oxygen, inorganic acids and alkalis.
  - It is most widely used synthetic plastic.

### **Uses:**

- It is mainly used as cable insulation, leather cloth, packing and toys.
  - It is used for manufacturing of film, sheet and floor covering.
  - PVC pipes are used for carrying corrosive chemicals in petrochemical factories.

## **(2) Teflon (poly tetra fluoro ethylene)**

Teflon is obtained by polymerization of water-emulsion tetrafluoroethylene under pressure in presence of benzoyl peroxide as catalyst

## Polymerisation



benzoyl peroxide / H<sub>2</sub>O      Teflon

## **Properties:-**

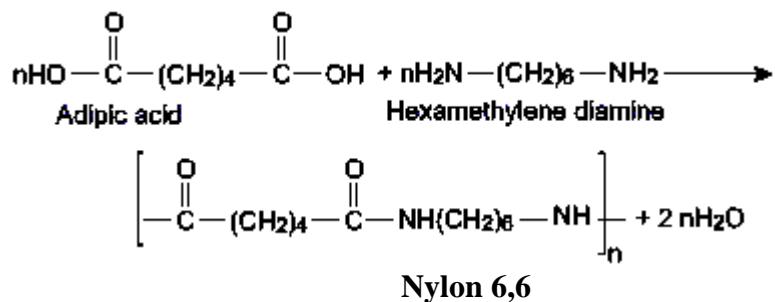
Teflon is also known as Fluon, due to the presence of highly electronegative fluorine atoms. There are strong attractive forces present that are responsible for high toughness & high chemical resistance towards all chemicals except hot alkali metal & hot fluorine.

**Uses:-**It is used in making seals & gaskets, which have to withstand high temperature. It is also used for insulation of electrical items and for making non-sticky surface coating, particularly for cooking utensils. Teflon is also used as insulating material for motors, transformers, cables, wires, fitting etc.

### Polyamide/ nylon:

**Preparation:** Nylon is a polyamide resin, produced by copolymerisation of diamine with diacid. Depending on the number of carbon atoms in diamine and diacid , there are different types of nylons like nylon6:6, nylon 6:10. Where the first number indicates the carbon atoms in diamine and the second number indicates the number of carbon atoms in diacid.

**Nylon-6, 6:** It is prepared by polymerizing Hexamethylene diamine and Adipic acid in 1:1 ratio.



## Properties:

- Nylons possess high strength, hardness and high melting point. The high melting point of the nylons is due to the hydrogen bonding between the hydrogen atom of amide group (-NH) and oxygen the C=O group.
  - Nylons possess high crystallinity, abrasion resistance and good mechanical properties.
  - Nylons are insoluble in common solvents and dissolve only in phenols and formic acid. They possess high temperature; absorb little moisture of ‘drip – dry ‘nature.
  - Nylons possess good chemical resistance and are good electrical insulators.

- Nylons possess good resistance to environmental conditions

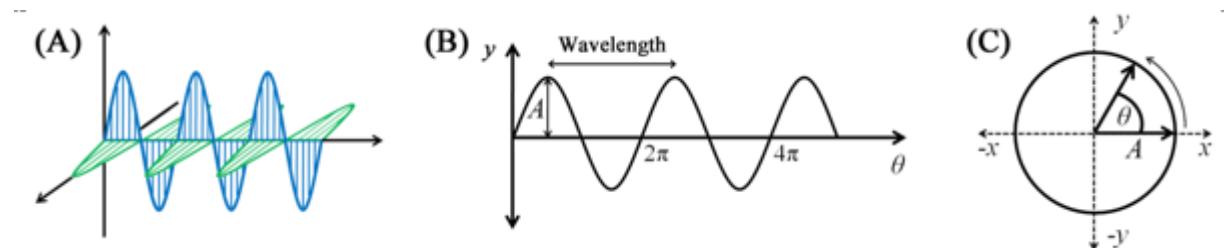
### Engineering Applications:

- The major application is in the Textile industry
- Because of high thermal and abrasion resistance nylons are used in mechanical engineering applications like gears , bearings , machine parts where greater friction is there
- Flexible tubing for conveying petrol etc are made from nylons.
- are used in auto mobile industry and telecommunication industry for making radiator parts and coil Nylons formers respectively.

### Unit-V

#### Spectroscopic techniques and applications

Spectroscopy deals with the study of interaction of electromagnetic radiation with matter. Electromagnetic radiation is a simple harmonic wave of electric and magnetic fields fluctuating orthogonal to each other (Figure 3.1A).



**Figure 3.1: An electromagnetic wave showing orthogonal electric and magnetic components (A); a sine wave (B); and uniform circular motion representation of the sine function (C).**

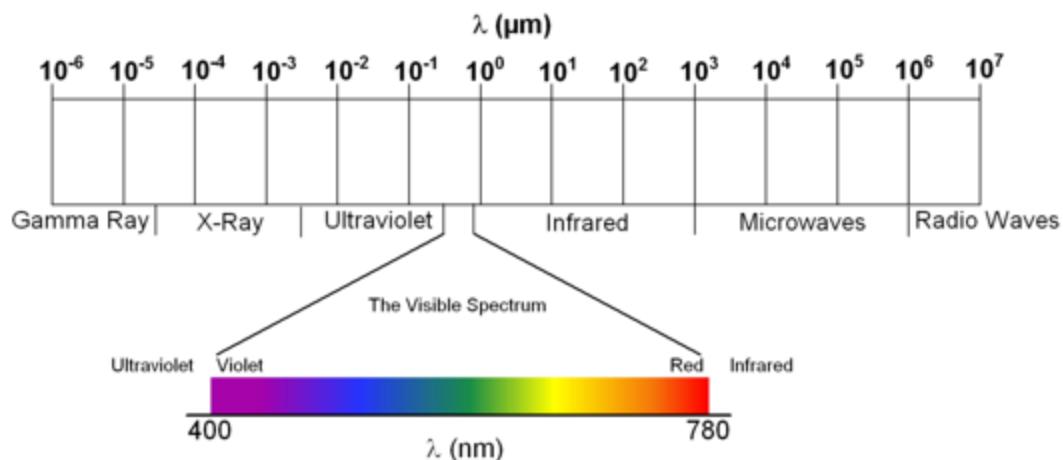
#### Energy of electromagnetic radiation:

Energy of an electromagnetic radiation is given by

$$E = h\nu = \frac{hc}{\lambda} \quad \dots\dots\dots (3.6)$$

where  $h$  is Planck's constant and has a value of  $6.626 \times 10^{-34} \text{ m}^2 \cdot \text{kg} \cdot \text{s}^{-1}$ . Based on the energy, electromagnetic radiation has been divided into different regions. The region of electromagnetic spectrum human beings can see, for example, is called visible region or visible spectrum. The visible region constitutes a very small portion of the electromagnetic spectrum and corresponds to the wavelengths of  $\sim 400 - 780 \text{ nm}$  (Figure 3.2). The energy of the visible spectrum therefore ranges from  $\sim 2.5 \times 10^{-19}$  to  $\sim 5 \times 10^{-19} \text{ Joules}$ . It is not convenient to write such small values of energy; the energies are therefore written in terms of electronvolts (eV). One electronvolt equals

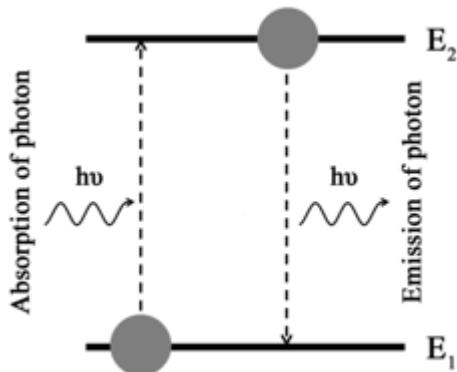
$1.602 \times 10^{-19}$  Joules. Therefore, the energy range of the visible spectrum is  $\sim 1.6 - 3.1$  eV. Spectroscopists, however, prefer to use wavelength ( $\lambda$ ) or frequency ( $v$ ) or wavenumber ( $\nu$ ) instead of energy.



**Figure 3.2 Electromagnetic spectrum**

### Quantization of energy:

As put forward by Max Planck while studying the problem of Blackbody radiation in early 1900s, atoms and molecules can absorb or emit the energy in discrete packets, called quanta (singular: quantum). The quantum for electromagnetic energy is called a photon which has the energy given by equation 3.6. A molecule can possess energies in different forms such as vibrational energy, rotational energy, electronic energy, etc. Introduction to the structure of an atom in a General Chemistry course mentions about the electrons residing in different orbits/orbitals surrounding the nucleus, typically the first exposure to the discrete electronic energy levels of atoms. In much the same way, rotational and vibrational energy levels of molecules are also discrete. A molecule can jump from one energy level to another by absorbing or emitting a photon of energy that separate the two energy levels (Figure 3.3).



**Figure 3.3 Transitions of a molecule between energy levels,  $E_1$  and  $E_2$  by absorbing/emitting the electromagnetic radiation**

### **Electromagnetic spectrum and the atomic/molecular processes:**

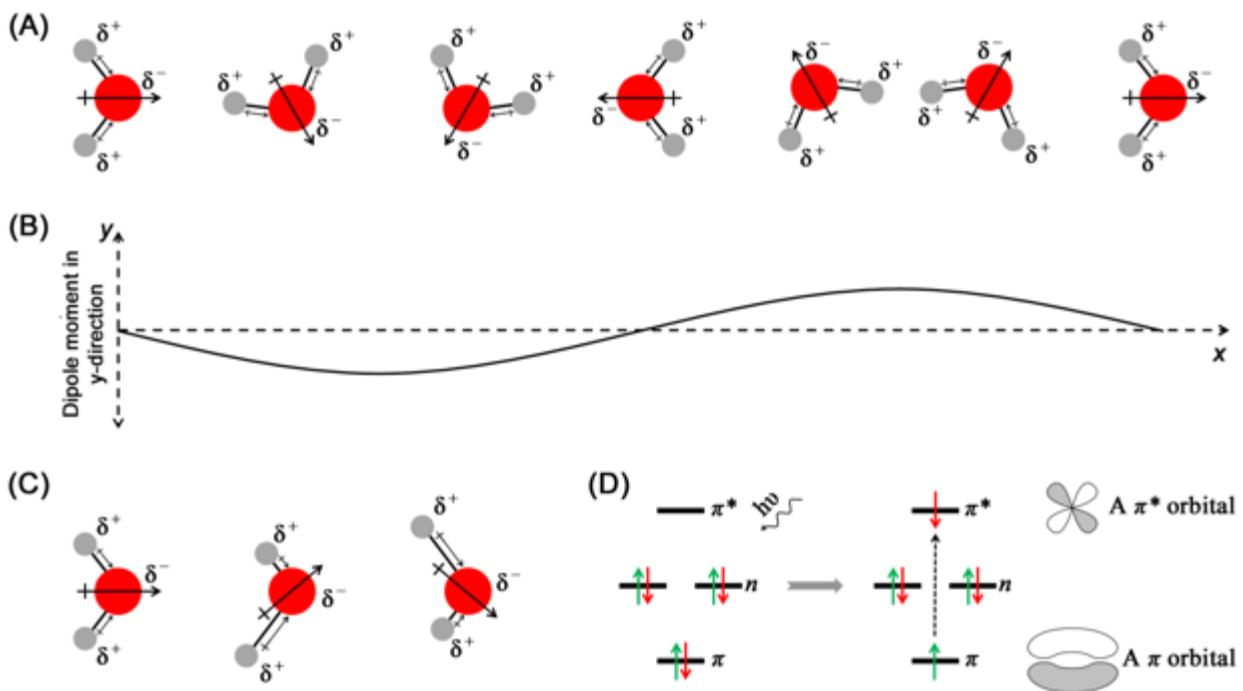
Molecules undergo processes like rotation, vibration, electronic transitions, and nuclear transitions. The energies underlying these processes correspond to different regions in the electromagnetic spectrum (Figure 3.4):

- i. Radiofrequency waves: Radiofrequency region has very low energies that correspond to the energy differences in the nuclear and electron spin states. These frequencies, therefore, find applications in nuclear magnetic resonance and electron paramagnetic resonance spectroscopy.
- ii. Microwaves: Microwaves have energies between those of radiofrequency waves and infrared waves and find applications in rotational spectroscopy and electron paramagnetic resonance spectroscopy.
- iii. Infrared radiation: The energies associated with molecular vibrations fall in the infrared region of electromagnetic spectrum. Infrared spectroscopy is therefore also known as vibrational spectroscopy and is a very useful technique for functional group identification in organic compounds .
- iv. UV/Visible region: UV and visible regions are involved in the electronic transitions in the molecules. The spectroscopic methods using UV or visible light therefore come under 'Electronic spectroscopy'.
- v. X-ray radiation: X-rays are high energy electromagnetic radiation and causes transitions in the internal electrons of the molecules.

### **Mechanisms of interaction of electromagnetic radiation with matter:**

In order to interact with the electromagnetic radiation, the molecules must have some electric or magnetic effect that could be influenced by the electric or magnetic components of the radiation.

- i. In NMR spectroscopy, for example, the nuclear spins have magnetic dipoles aligned with or against a huge magnetic field. Interaction with radiofrequency of appropriate energy results in the change in these dipoles.
- ii. Rotations of a molecule having a net electric dipole moment, such as water will cause changes in the directions of the dipole and therefore in the electrical properties (Figure 3.5A and B). Figure 3.5B shows the changes in the y-component of the dipole moment due to rotation of water molecule.
- iii. Vibrations of molecules can result in changes in electric dipoles that could interact with the electrical component of the electromagnetic radiation (Figure 3.5C).
- iv. Electronic transitions take place from one orbital to another. Owing to the differences in the geometry, size, and the spatial organization of the different orbitals, an electronic transition causes change in the dipole moment of the molecule (Figure 3.5D).



**Figure 3.5** Panel A shows the rotation of a water molecule around its centre of mass. The change in the dipole moment as a result of rotation is plotted in panel B. Panel C shows the change in dipole moment of water due to asymmetric stretching vibrations of O—H bond. Panel D shows an electronic transition from  $\pi$  to  $\pi^*$  orbital and the geometry of the two orbitals.

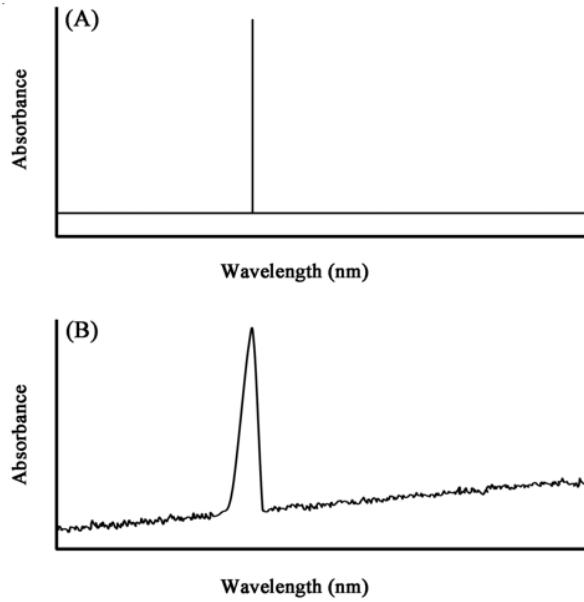
The above examples suggest that a change in either electric or magnetic dipole moment in a molecule is required for the absorption or emission of the electromagnetic radiation.

#### Absorption peaks and line widths:

Absorption of radiation is the first step in any spectroscopic experiment. Absorption spectra are routinely recorded for the electronic, rotational, and vibrational spectroscopy. It is therefore important to see

how an absorption spectrum looks like. As we have already seen, a transition between states takes place if the energy provided by the electromagnetic radiation equals the energy gap between the

two states *i.e.*  $\Delta E = h\nu = \frac{hc}{\lambda}$ . This implies that the molecule precisely absorbs the radiation of wavelength,  $\lambda$  and ideally a sharp absorption line should appear at this wavelength (Figure 3.6A).



**Figure 3.6 An idealized spectrum for a single wavelength transition (A) and an experimentally obtained spectrum (B)**

In practice, however, the absorption lines are not sharp but appear as fairly broad peaks (Figure 3.6B) for the following reasons:

- i. Instrumental factors: The slits that allow the incident light to impinge on the sample and the emerging light to the detector have finite widths. Consider that the transition occurs at wavelength,  $\lambda_t$ . When the wavelength is changed to  $\lambda_t + \Delta\lambda$  or  $\lambda_t - \Delta\lambda$ , the finite slit width allows the radiation of wavelength,  $\lambda$ , to pass through the slits and a finite absorbance is observed at these wavelengths. The absorption peaks are therefore symmetrical to the line at  $\lambda = \lambda_t$ .
- ii. Sample factors: Molecules in a liquid or gaseous sample are in motion and keep colliding with each other. Collisions influence the vibrational and rotational motions of the molecules thereby causing broadening. Two atoms/molecules coming in close proximity will perturb the electronic energies, at least those of the outermost electrons resulting in broadening of electronic spectra. Motion of molecules undergoing transition also causes shift in absorption frequencies, known as Doppler broadening.
- iii. Intrinsic broadening: Intrinsic or natural broadening arises from the Heisenberg's uncertainty principle which states that the shorter the lifetime of a state, the more uncertain is its energy. Molecular transitions have finite lifetimes, therefore their energy is not exact. If  $\Delta t$  is the lifetime of a molecule in an excited state, the uncertainty in the energy of the states is given by:

$$\Delta E \times \Delta t \geq \frac{\hbar}{4\pi} \quad \dots \dots \dots \quad (3.7)$$

$$\Delta E \times \Delta t \geq \frac{\hbar}{2} \quad \dots \dots \dots \quad (3.8)$$

where,  $\hbar = \frac{\hbar}{2\pi}$

## Infrared Spectroscopy

### Introduction

Infrared (IR) region of the electromagnetic spectrum lies between visible and microwave regions and therefore spans the wavelengths from  $0.78 - 250 \mu\text{m}$ . The energies associated with molecular vibrations are smaller than those associated with electronic transitions and fall in the IR region. IR spectroscopy, therefore, is used to probe the vibrations in molecules and is also known as vibrational spectroscopy. Infrared region is usually divided into three regions: near infrared, mid-infrared, and far infrared (Figure 10.1). IR spectroscopists use wavenumbers ( $\bar{v}$ ) to represent the IR spectra and we shall be following the same convention. Mid-IR region ( $\lambda = 2.5 - 25 \mu\text{m}$ ;  $\bar{v} = 4000 - 400 \text{ cm}^{-1}$ ) is the region of interest for studying molecular vibrations.

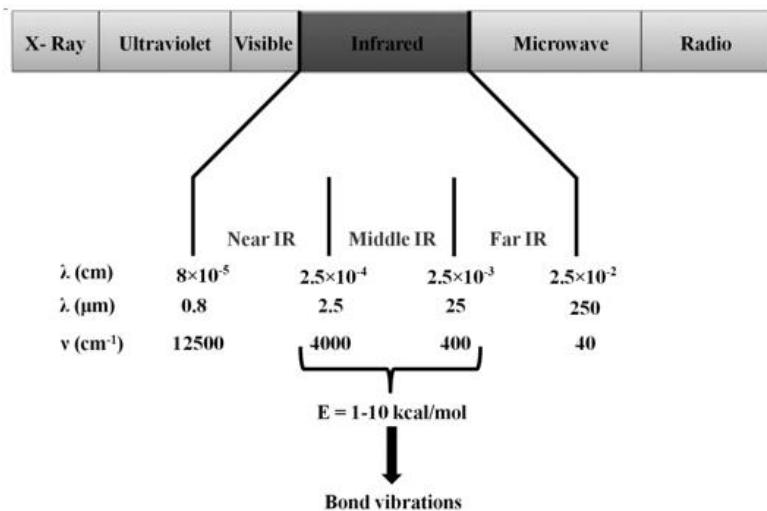
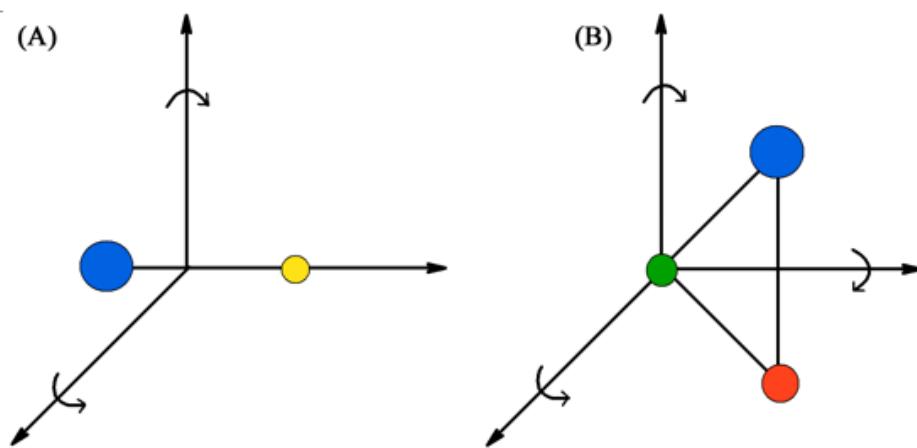


Figure 10.1 Infrared region of the electromagnetic spectrum

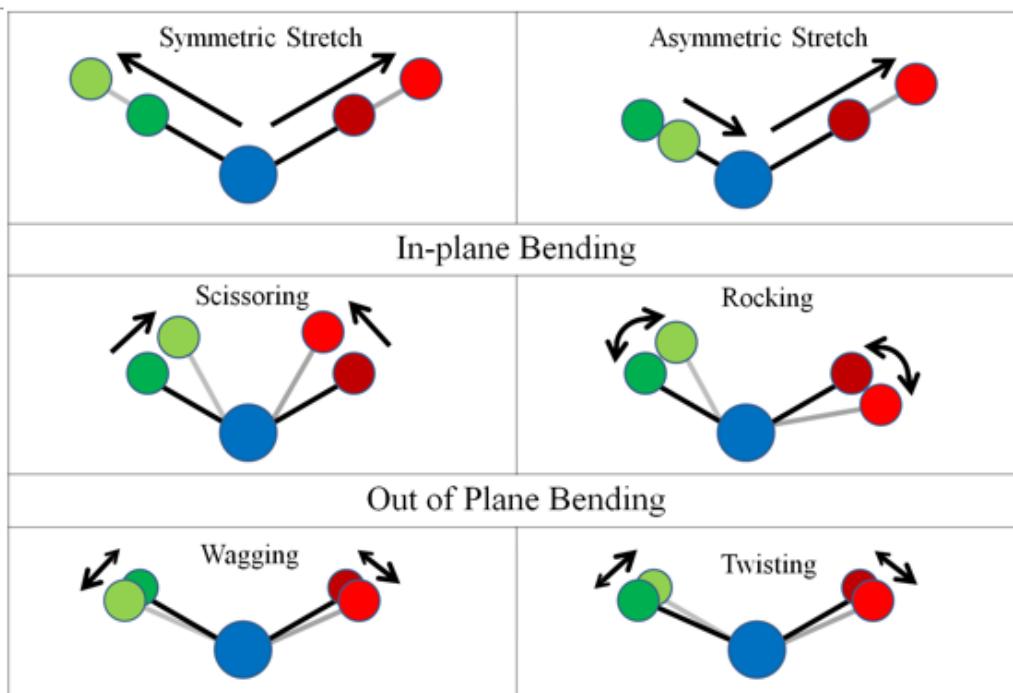
### Degrees of freedom and molecular vibrations

At non-zero temperatures, *i.e.* temperatures above  $0 \text{ K}$ , all the atoms in a molecule are in motion. The molecule itself also is in translational and rotation motion. In a three dimensional space, an atom in isolation has 3 degrees of freedom, corresponding to the motion along the three independent coordinate axes. A molecule composed of  $N$  atoms has a total of  $3N$  degrees of freedom (Figure 10.2).



**Figure 10.2 Degrees of rotational freedom for a diatomic (A) and a triatomic (B) molecule**

For a non-linear molecule, three of these  $3N$  degrees of freedom correspond to translational motion, three correspond to rotational motion while rest  $3N-6$  are the vibrational degrees of freedom. For a linear molecule, there are only two rotational degrees of freedom that correspond to the rotation about the two orthogonal axes perpendicular to the bond (Figure 10.2). A linear molecule, therefore, has  $3N-5$  vibrational degrees of freedom. Let us have a look at the degrees of freedom of a diatomic molecule. A diatomic molecule has a total of  $3 \times 2 = 6$  degrees of freedom. *Three* of these *six* degrees of freedom correspond to translational motion of the molecule; *two* of them define rotational degrees of freedom; while *one* corresponds to the vibration of the atoms along the bond. The  $3N-6$  vibrational degrees of freedom ( $3N-5$  for linear molecules) represent the true/fundamental modes of vibration of a molecule. The different types of vibrations are shown in Figure 10.3.



**Figure 10.3 Stretching and bending vibrations in molecules**

### Hooke's law and frequency of vibration

We have seen that the bonds are not static but vibrating in different ways. A vibrating bond can therefore be considered a spring with its ends tethered to two atoms (Figure 10.4).



**Figure 10.4 Spring analogy of a bond vibration**

If the masses of the atoms are  $m_1$  and  $m_2$ , the frequency of stretching vibration of the diatomic molecule can be given by the Hooke's law:

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad \dots \dots \dots \quad (10.1)$$

where,  $\nu$  is the frequency of vibration,  $k$  is the spring constant, and  $\mu$  is the reduced mass *i.e.*  $\frac{m_1 m_2}{m_1 + m_2}$

Dividing equation 10.1 by  $\lambda$  gives:

$$\frac{\nu}{\lambda} = \frac{1}{2\pi\lambda} \sqrt{\frac{k}{\mu}} \quad \dots \dots \dots \quad (10.2)$$

$$\frac{1}{\lambda} = \frac{1}{2\pi(\lambda\nu)} \sqrt{\frac{k}{\mu}} \quad \dots \dots \dots \quad (10.3)$$

$$\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \quad \dots \dots \dots \quad (10.4)$$

The spring constant,  $k$  is the measure of the bond strength. The stronger the bond, the higher the  $k$ , and consequently the higher is the frequency of vibration. This treatment implies  $\nu$  that the diatomic molecule is a simple harmonic oscillator. The energy of a quantum harmonic oscillator is given by:

$$E = \left(n + \frac{1}{2}\right) h\nu \quad \dots \dots \dots \quad (10.5)$$

where,  $n = 0, 1, 2, \dots$  and  $h$  is the Planck's constant

## Absorption of infrared radiation

A molecular vibration is IR active i.e. it absorbs IR radiation if the vibration results in a change in the dipole moment. A diatomic molecule, that has one mode of vibration, may not absorb an IR radiation if the vibration does not accompany a change in the dipole moment. This is true for all the homonuclear diatomic molecules such as H<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, etc. Vibration of carbon monoxide (C=O), on the other hand, causes a change in dipole moment and is therefore IR active. Vibration of a bond involving two atoms that have large electronegativity difference is usually IR active.

An IR active vibration of a particular frequency absorbs the IR radiation of same frequency. Let us calculate the position of absorption band for carbonyl stretching vibration (frequency =  $5.1 \times 10^{13}$  vibrations/second) in acetone.

$$\bar{v} = \frac{1}{\lambda} = \frac{\nu}{c} \text{ cm}^{-1}$$

$$\bar{v} = \frac{5.1 \times 10^{13} \text{ sec}^{-1}}{3 \times 10^{10} \text{ cm/sec}} = 1700 \text{ cm}^{-1}$$

### Functional group region and fingerprint region

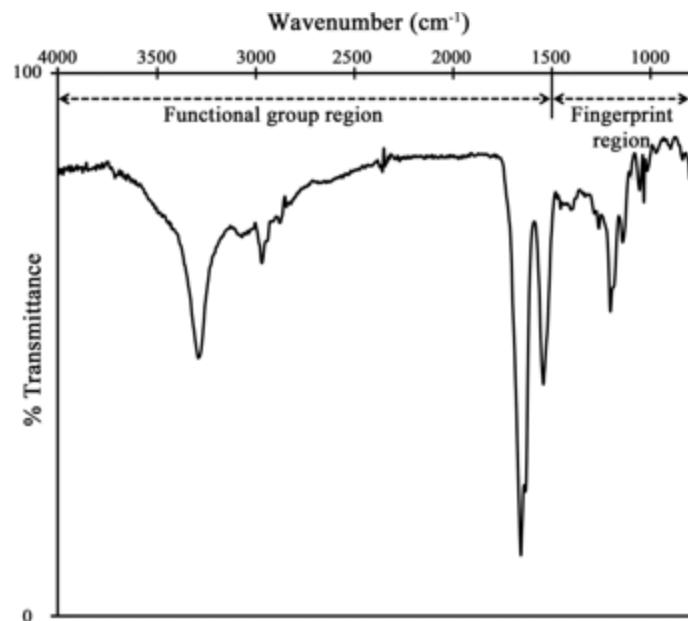
The most common application of IR spectroscopy is perhaps to identify the functional groups. This is possible because different functional groups vibrate at different frequencies allowing their identification. The frequency of vibration, however, depends on additional factors such as delocalization of electrons, H-bonding, and substitutions at the nearby groups. The wavenumbers for some of the bonds are shown in Table 10.1.

**Table 10.1 Typical vibrational frequencies of functional groups**

Bond	Molecule	Wavenumber (cm <sup>-1</sup> )
C–O	Alcohols, ethers, esters, carboxylic acids, etc.	1300 – 1000
C=O	Aldehydes, ketones, esters, carboxylic acids	1750 – 1680
C=O	Amides	1680 – 1630
N–H (Stretching)	Amines and amides	3500 – 3100
–N–H (Bending)	Amines and amides	1640 – 1550
O–H	Alcohols	3650 – 3200
C–N	Amines	1350 – 1000
S–H	Mercaptans	2550

The absorption bands in the 4000 – 1500 cm<sup>-1</sup> region allows identification of functional groups ; this region therefore is also termed the functional group region of the IR spectrum (Figure 10.6). The lower energy portion of the mid-IR region (1500 – 400 cm<sup>-1</sup>) usually contains a very complicated set of peaks arising due to complex vibrations involving several atoms. This region is unique to a particular compound and therefore is known as

the fingerprint region of the IR spectrum. Though it is difficult to assign the vibrational modes to these peaks, these are useful to identify a compound if the spectrum of the compound is already known.



**Figure 10.6. A typical IR spectrum showing functional group and fingerprint regions**

## Applications

- i. *Identification of functional groups:* As has already been discussed, IR spectroscopy allows identification of functional groups. Carbonyl (C=O) is an interesting functional group worth discussing. Carbonyl is a double bond (high spring constant,  $k$ ) with very high polarity. Stretching vibration of carbonyl group causes large changes in the dipole moment consequently resulting in a very intense absorption band. Furthermore, the frequency of carbonyl stretching does not differ significantly for aldehydes, ketone, carboxylic acids, and esters (Table 10.1). The large intensity and relatively unchanged frequency of carbonyl stretching allows easy identification of the carbonyl compounds (It is important to note that carbonyl stretching frequency can be much lower for amides and much higher for anhydrides and acid chlorides).
- ii. *Identification of compounds:* The fingerprint region of the IR spectrum is unique to each compound. It is possible to identify a compound from its IR spectrum if the spectrum for the compound is already known and available for comparison. This is particularly useful in pharmaceutical research and development. A patented drug, if suspected to be synthesized by another pharmaceutical company, can easily be identified by comparing the IR spectra in the fingerprint region.

## Rotational Spectra of diatomics

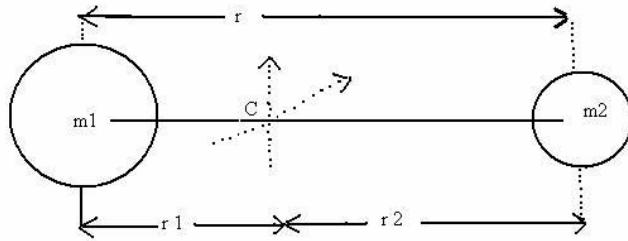


Fig.13.1. A rigid diatomic with masses  $m_1$  and  $m_2$  joined by a thin rod of length  $r = r_1 + r_2$ . The centre of mass is at C.

The center of mass is defined by equating the moments on both segments of the molecular axis.

$$m_1 r_1 = m_2 r_2 \quad (13.1)$$

The moment of inertia is defined by

$$\begin{aligned} I &= m_1 r_1^2 + m_2 r_2^2 \\ &= m_2 r_2 r_1 + m_1 r_1 r_2 \end{aligned} \quad (13.2)$$

$$= r_1 r_2 (m_1 + m_2) \quad (13.3)$$

Since  $m_1 r_1 = m_2 r_2$  and  $m_2 (r_2 - r_1) = (m_1 + m_2) r_1$  Therefore,

$$r_1 = \frac{m_2 r}{m_1 + m_2} \quad r_2 = \frac{m_1 r}{m_1 + m_2} \quad (13.4)$$

Substituting the above equation in (13.3), we get

$$I = \frac{m_1 m_2 r^2}{(m_1 + m_2)} = \mu r^2, \quad \mu = \frac{m_1 m_2}{m_1 + m_2} \quad (13.5)$$

Where  $\mu$ , the reduced mass is given by

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$$

The rotation of a diatomic is equivalent to a “rotation” of a mass  $\mu$  at a distance of  $r$  from the origin C. The kinetic energy of this rotational motion is  $K.E. = L^2/2I$  where  $L$  is the angular momentum,  $I\omega$  where  $\omega$  is the angular (rotational) velocity in radians/sec. The operator for  $L^2$  is the same as the operator  $L^2$  for the angular momentum of hydrogen atom and the solutions of the operator equations  $L^2 Y_{lm} = \bar{l}(l+1) Y_{lm}$ , where  $Y_{lm}$  are the spherical harmonics which have been studied in lecture 3.

The quantized rotational energy levels for this diatomic

Are

$$E_J = \frac{\hbar^2}{8\pi^2 I} J(J+1) \quad (13.7)$$

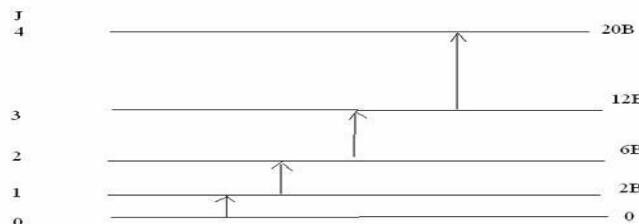
The energy differences between two rotational levels is usually expressed in  $\text{cm}^{-1}$ . The wave number corresponding to a given  $\Delta E$  is given by

$$\nu = \Delta E /hc, \text{ cm}^{-1}$$

The energy levels in  $\text{cm}^{-1}$  are therefore,

$$E_J = B J(J+1) \quad \text{where} \quad B = \frac{\hbar}{8\pi^2 I c} \quad (13.9)$$

The rotational energy levels of a diatomic molecule are shown in Fig. 13.2.



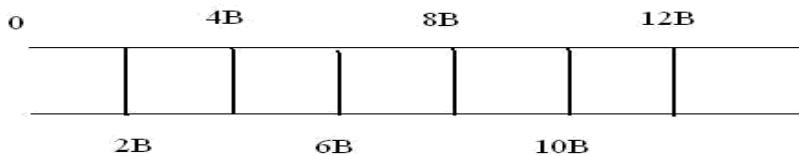
**fig. 13.2 Rotational energy levels of a rigid diatomic molecule and the allowed transitions.**

The selection rule for a rotational transition is,

$$\Delta J = \pm 1 \quad (13.10)$$

In addition to this requirement, the molecule has to possess a dipole moment. As a dipolar molecule rotates, the rotating dipole constitutes the transition dipole operator  $\mu$ . Molecules such as HCl and CO will show rotational spectra while  $H_2$ ,  $Cl_2$  and  $CO_2$  will not. The rotational spectrum will appear as

follows



**Fig. 13.3 Rotational spectrum of a rigid diatomic. Values of B are in  $\text{cm}^{-1}$ . Typical values of B in  $\text{cm}^{-1}$  are 1.92118 (CO), 10.593 (HCl), 20.956 (HF),  $^1\text{H}_2$  (60.864),  $^2\text{H}_2$  (30.442), 1.9987 ( $\text{N}_2$ ).**

From the value of B obtained from the rotational spectra, moments of inertia of molecules I, can be calculated. From the value of I, bond length can be deduced.

**Example 13.1:** Calculate the value of I and r of CO.  $B = 1.92118 \text{ cm}^{-1}$ .

**Solution:**

$$\begin{aligned} I &= h/(8\pi^2 B c) = 6.626 \times 10^{-34}/(8 \times 3.1415^2 \times 1.92118 \times 3 \times 10^{10}) \\ &= 1.45579 \times 10^{-46} \text{ kg m}^2 \end{aligned}$$

Since the value of B is in  $\text{cm}^{-1}$ , the velocity of light c is taken in  $\text{cm/s}$ .  $I = \mu r^2$ . The atomic mass of C  $\equiv 12.0000$  amu, O  $\equiv 15.9994$  amu. 1 amu  $= 1.6604 \times 10^{-27}$  kg. The reduced mass of CO can be calculated to be  $1.13836 \times 10^{-27}$  kg.

$$\text{Therefore } r^2 = I/\mu = 1.45579 \times 10^{-46}/1.13826 \times 10^{-27} \text{ m}^2$$

$$\text{Or } r = 1.131 \text{ \AA}$$

The rotational levels are degenerate. Just as there are three p orbitals for  $l = 1$ , for  $J = 1$ , there are 3 degenerate rotational states. The degeneracy for a given value of J is  $2J + 1$ .

The

Boltzmann factor gets modified due to this degeneracy as follows

(13.  
11)

The implication of this is that the rotational population of the  $J = 1$  level is often more than the population of the  $J = 0$  levels since their degeneracies are 3 and 1 respectively. When molecules rotate with great speeds, they cannot be treated as rigid any more. There are distortions due to centrifugal and other forces. The modification of rotational energies by considering the centrifugal distortion alone is

$$E_J (\text{ in } \text{cm}^{-1}) = B J(J+1) - D J^2(J+1)^2 \quad (13.12)$$

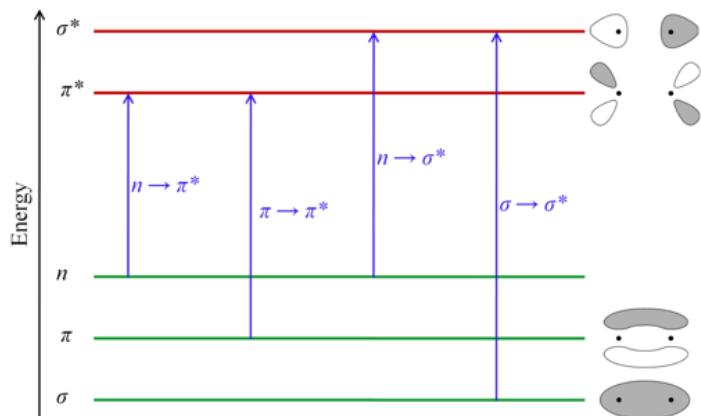
Where the centrifugal distortion constant D is given by

$$D = h^3/(32\pi^4 I^2 r^2 k c) \text{ cm}^{-1} \quad (13.13)$$

The only new term in Eq (13.13) is the force constant k which will be discussed when we study molecular vibrations.

## UV-Visible Absorption Spectroscopy

Absorption of ultraviolet (UV) and visible radiation is one of the most routinely used analytical tools in life sciences research. The simplest application of UV/Visible radiation is to quantify the amount of a substance present in a solution. UV region of electromagnetic radiation encompasses the wavelengths ranging from  $\sim 10$  nm –  $\sim 400$  nm while visible region encompasses the wavelengths from  $\sim 400$  nm –  $\sim 780$  nm. For the sake of convenience in discussing the observations, UV region is loosely divided into near UV (wavelength region nearer to the visible region,  $\lambda \sim 250$  nm – 400 nm), far UV region (wavelength region farther to the visible region,  $\lambda \sim 190$  nm – 250 nm) and vacuum UV region ( $\lambda < 190$  nm). The wavelength ranges defined for these regions are not strict and people use slightly different ranges to define these regions. We shall, however, stick to the wavelengths defined here. As has been discussed in the previous lecture, the absorption of UV and visible light is through the transition of an electron in the molecule from lower to a higher energy molecular orbital. The various electronic transitions observed in organic compound are shown in Figure 4.2.



**Figure 4.2 Schematic diagram showing energy levels of different orbitals and possible absorption transitions**

As shown in figure 4.2,  $\sigma \rightarrow \sigma^*$  transition is a high energy process and therefore lies in the vacuum UV region. Alkanes, wherein only  $\sigma \rightarrow \sigma^*$  transition is possible show absorption bands  $\sim 150$  nm wavelength. Alkenes have  $\pi$  and  $\pi^*$  orbitals and can show several transition; the lowest-energy transition,  $\pi \rightarrow \pi^*$  gives an absorption band  $\sim 170$ - $190$  nm for non-conjugated alkenes (effects of conjugation on electronic transitions are discussed later). The presence of nonbonding electrons in a molecule further expands the number of possible transitions. The entire molecule, however, is not generally involved in the absorption of the radiation in a given wavelength range. In an aliphatic ketone, for example, the absorption band around 185 nm arises due to the  $\pi \rightarrow \pi^*$  transition in the carbonyl group. Atoms that comprise the molecular orbitals involved in the electronic transitions constitute the molecular moiety that is directly involved in the transition. Such a group of atoms is called a **chromophore**. A structural modification in a chromophore is generally accompanied by changes in the absorption properties.

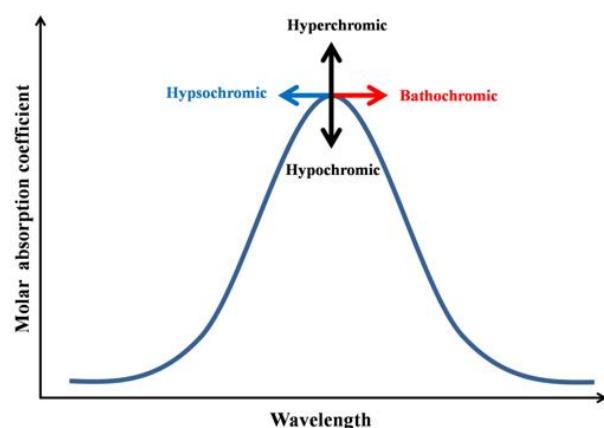
some important terms that are used to refer to the shifts in absorption spectra (Figure 5.2):

*Bathochromic shift* : Shift of the absorption spectrum towards longer wavelength

*Hypsochromic shift* : Shift of the absorption spectrum towards smaller wavelength

*Hyperchromic shift* : An increase in the absorption intensity

*Hypochromic shift* : A decrease in the absorption intensity



**Figure 5.2 Terminology for shifts in absorption spectra**

**Auxochrome:** Auxochromes are the chemical groups that result in a bathochromic shift when attached to a chromophore. The strongest auxochromes like  $-\text{OH}$ ,  $-\text{NH}_2$ ,  $-\text{OR}$ , etc. possess nonbonding electrons. They exhibit bathochromism by extending conjugation through resonance.



The auxochrome modified chromophore is a new chromophore in real sense. The term auxochrome is therefore rarely used these days, and the entire group (basic chromophore + auxochrome) can be considered as a chromophore different from the basic chromophore. Alkyl groups also result in the bathochromic shifts in the absorption spectra of alkenes. Alkyl groups do not have non-bonded electrons, and the effect is brought about by another type of interaction called *hyperconjugation*.

### Nuclear Magnetic Resonance Spectroscopy:

NMR is a physical phenomenon in which nuclei of a given substance under magnetic field absorb and re-emit electromagnetic radiation. This energy is at a particular resonance frequency which depends on the strength of the magnetic field and magnetic properties of the isotope of the atoms.

As nuclei with an odd mass or odd atomic number have nuclear spin (in a similar fashion to the spin of electrons), the spins of nuclei are sufficiently different that NMR experiments can be sensitive for only one particular isotope of one particular element.

The rules for determining the net spin of a nucleus are as follows:

1. If both the number of neutrons and the number of protons are even, then the nucleus has NO spin.
2. If the number of neutrons plus the number of protons is odd, then the nucleus has a half-integer spin (i.e. 1/2, 3/2, 5/2)
3. If the number of neutrons and the number of protons are both odd, then the nucleus has an integer spin (i.e. 1, 2, 3)

Note that the overall spin is important. Quantum mechanics states that a nucleus of spin ' $\frac{1}{2}$ ' has 2/+1 possible orientations, i.e., a nucleus with spin 1/2 will have 2 possible orientations. These orientations are of equal energy in the absence of external magnetic field, but the energy levels split once magnetic field is applied.

The energy separation between the different nuclear spin states lies in the microwave spectral region and hence NMR transitions are excited by frequencies about  $10^8$  Hz and can be varied by applying a magnetic field.

The nucleus has a positive charge and is spinning, resulting in a small magnetic field. As a result, the nucleus possesses a magnetic moment, which is proportional to its spin,  $I$ .

$$\mu = \frac{gI\hbar}{2\pi}$$

The constant  $g$  is gyromagnetic ratio. The energy of a particular energy level is defined as

$$E = \frac{gh}{2\pi} mB$$

where  $B$  is the strength of the magnetic field at the nucleus.

Therefore, the difference in energy levels can be obtained in the form of

$$\Delta E = \frac{gh}{2\pi} B$$

This equation suggests that if the magnetic field  $B$  is increased, then the difference in the energy also increases.

Since a nucleus is a charged particle in motion, it will develop a magnetic field. For instance,  ${}^1H$  and  ${}^{13}C$  have nuclear spins of  $\frac{1}{2}$ . Hence, they would behave in a similar fashion to a simple, tiny bar magnet.

As shown in Figure 35.01, in the absence of magnetic fields, these are oriented randomly. On the other hand, the application of external magnetic field lines up them parallel to the applied field, but either spin aligned or spin opposed.

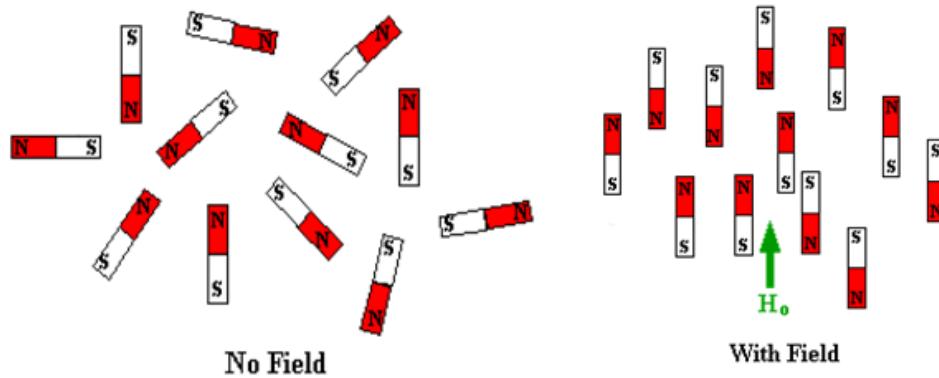


Figure 35.01: Schematic representation of nuclear spins or in the form of tiny magnets under zero and finite magnitude of external applied fields.

As displayed in Figure 35.02, the highly populated state is the lower energy spin aligned situation.

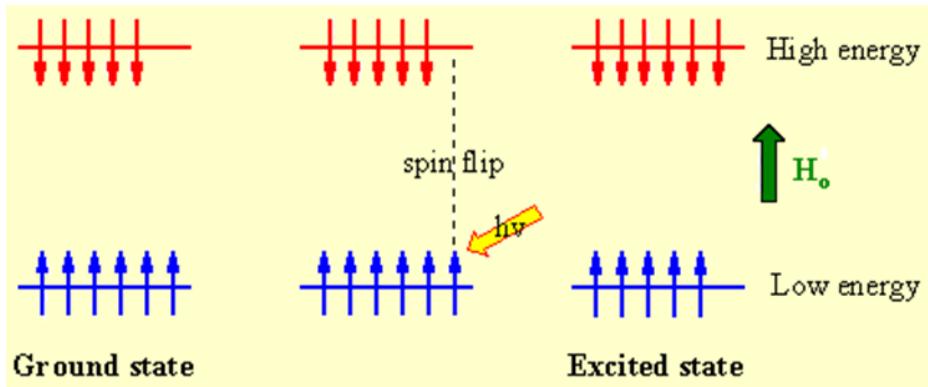


Figure 35.02: Schematic arrangements of spins in ground and excited states.

Upon radiating with microwaves, the alignment of nuclear spins from the low energy aligned state is flipped to the higher energy spin opposed state, resulting in an excited state. As derived earlier, the energy required for making this transition depends on the magnitude of the applied magnetic field, as demonstrated in Figure 35.03.

The two spin states have same energy when the external field is zero, but as the field increases so does the separation of energies of the spin states and therefore so does the frequency required to cause the spin-flip. At a field equal to  $H_0$ , the formula for the energy difference is given.

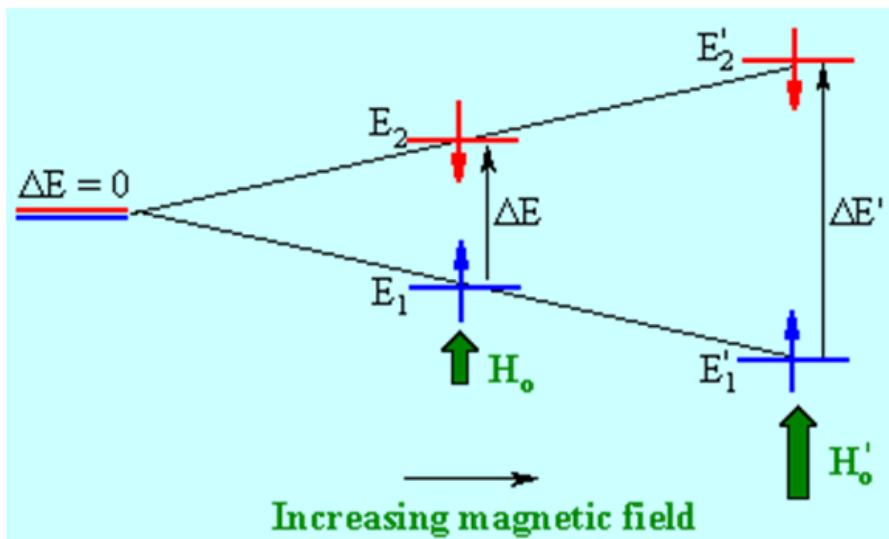


Figure 35.03f: Schematic drawing of variation in energy required for flipping the spins with increasing applied magnetic fields.

Typically, one needs strong magnetic field in the range between 1 to 20 Tesla.

The basic arrangement of NMR spectrometer is shown in Figure 35.04. The sample is positioned in the applied magnetic field using electromagnet and microwaves are used in the radio frequency input circuit to excite the sample and to induce transitions between different nuclear spin states. This induces a radio signal in the output circuit, which generates an output signal.

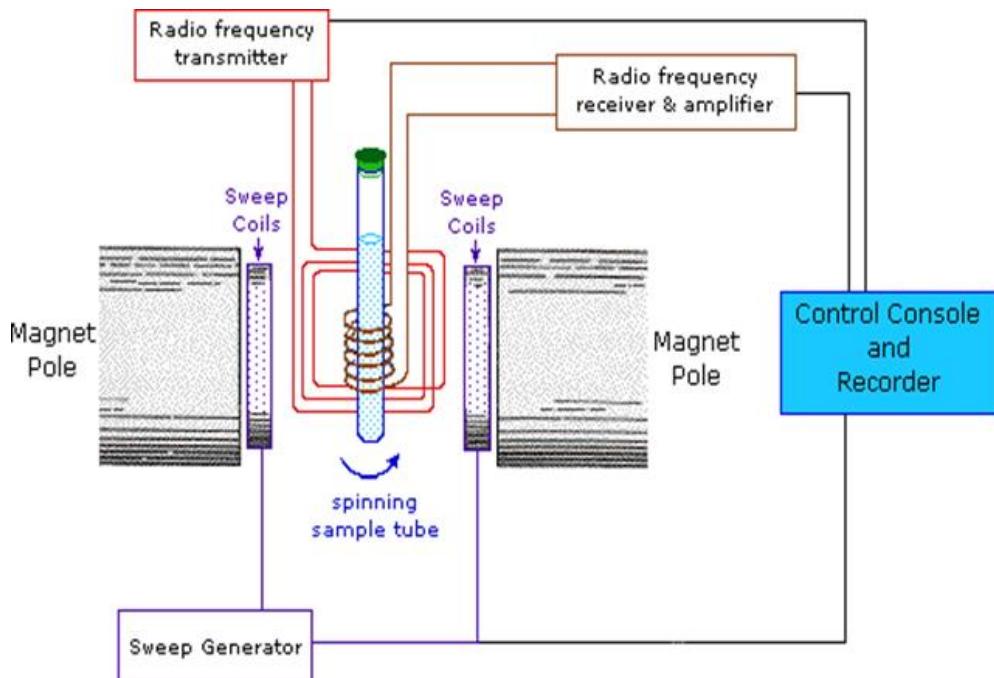


Figure 35.04: Basic arrangement of NMR Spectrometer.

### Nuclear Shielding:

The power of NMR is based on the concept of nuclear shielding. The magnetic field at the nucleus is not equal to the applied magnetic field. This is because, every atom is surrounded by electrons, which orbit the nucleus. When charged particles move in a loop, they create a magnetic field. Hence, the field produced by the movement of electron is felt by the nucleus. Therefore, the field experienced by the nucleus is not same as applied field, known as shielding. Therefore, the change in the energy levels requires a different frequency to excite the spin flip. The shielding allows for structural determination of molecules.

Consider the s-electrons in a molecule as displayed in Figure 35.05. They have spherical symmetry and circulate in the applied field, producing a magnetic field which opposes the applied field. This means that the applied field strength must be increased in order for the nucleus to absorb at its transition frequency. This up-field shift is also termed diamagnetic shift.

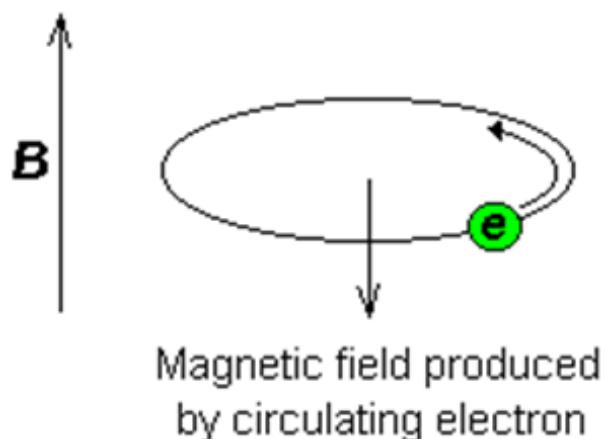


Figure 35.05: Schematic of nuclear shielding.

Similarly, electrons in p-orbitals having no spherical symmetry produce comparatively large magnetic fields at the nucleus giving a low-field shift and termed as a paramagnetic shift.

### Chemical Shift:

- 1) NMR spectrum is a plot of the ratio of the frequency applied against absorption.
- 2) A signal in the spectrum is referred to as a resonance.
- 3) The frequency of a signal is known as its chemical shift.

**The chemical shift is defined as**

$$\text{chemical shift, } \delta = \frac{\nu_{\text{signal}} - \nu_{\text{reference}}}{\text{spectrometer frequency}} \times 10^6$$

The shielding of the nucleus allows for chemically inequivalent environments to be determined by Fourier Transforming the NMR signal, which results in a spectrum.

- In general, the spectrum consists of a set of peaks in which each peak corresponds to a distinct chemical environment.
- The area underneath the peak is directly proportional to the number of nuclei in that chemical environment.
- The x-axis of an NMR spectrum is given in parts per million (ppm).

### NMR Spectrum:

The 60 MHz proton NMR spectrum of pure methanol as shown in Figure 35.06 exhibits two signals located at 3.35 and 4.80 ppm. The higher-field methyl signal (magenta) being three times as strong as OH signal (orange) at a lower field.

Cooling the methanol to  $-45^{\circ}\text{C}$ , the larger higher-field signal changes to a doublet ( $J = 5.2 \text{ Hz}$ ) having the same chemical shift. The smaller signal moves downfield to 5.5 ppm and splits into a quartet ( $J = 5.2 \text{ Hz}$ ). However, the relative intensities of signals remain unchanged.

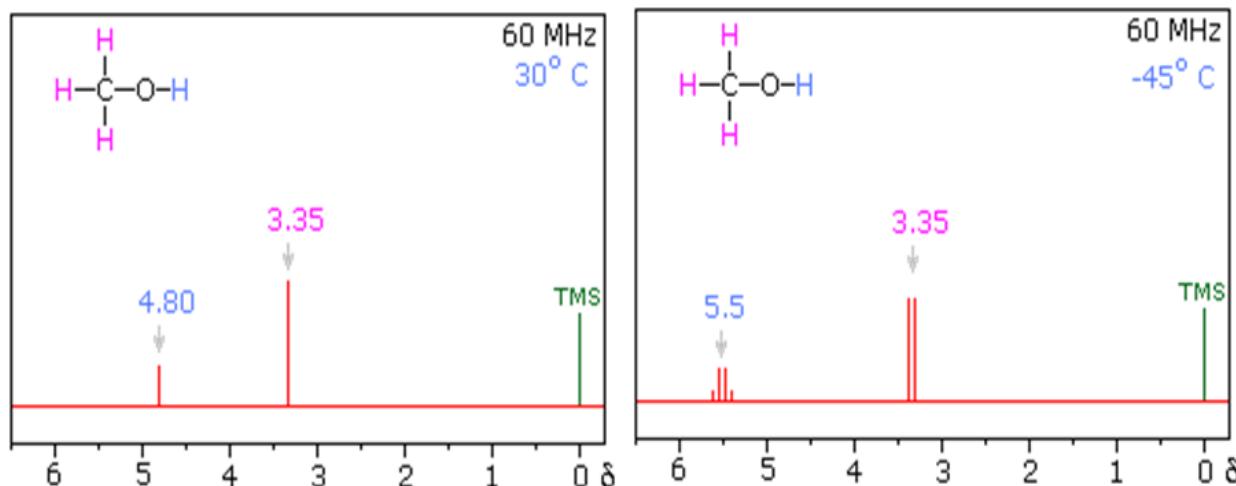


Figure 35.06:: NMR Spectra of pure methanol at  $30^{\circ}\text{C}$  (left) and  $-45^{\circ}\text{C}$  [1].

### Chemical Shift:

It is convenient to describe the relative positions of the resonances in an NMR spectrum. For instance, as shown in Figure 35.07, a peak at a chemical shift,  $\delta$ , of 10 ppm is said to be downfield or deshielded with respect to a peak at 5 ppm. Otherwise, the peak at 5 ppm is upfield or shielded with respect to the peak at 10 ppm.

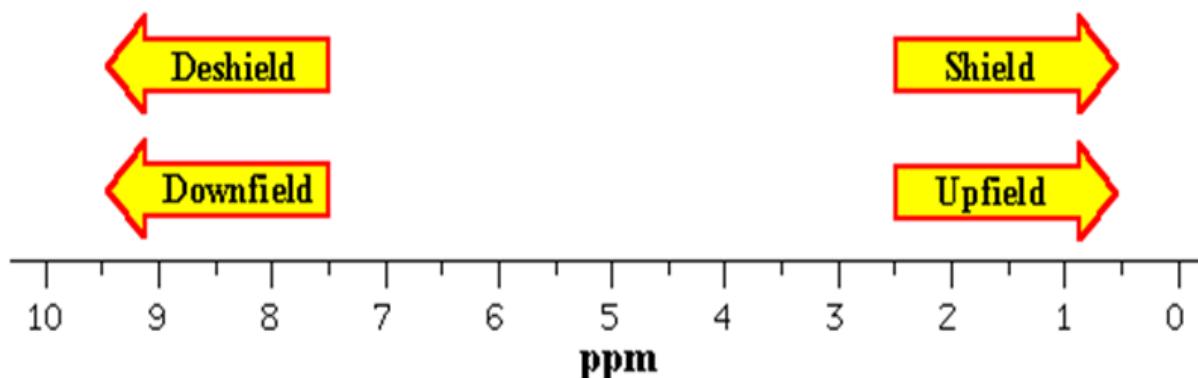


Figure 35.07: Schematic representation of de-shielded and shielded in NMR spectrum.

Taking the example shown in Figure 35.06, we can conclude that the peak at 4.8 is downfield or deshielded with respect to peak at 3.35 or the peak at 3.35 is upfield or shielded to peak at 4.8 ppm.

#### NMR Spectrum:

Figure 35.08 displays another NMR spectrum of  $\text{CH}_3\text{Br}$ . Since  $\text{CH}_3\text{Br}$  contains only a single type of hydrogen atom, only a single peak at 2.7 ppm was observed.

The position is slightly de-shielded due to the presence of the Br.

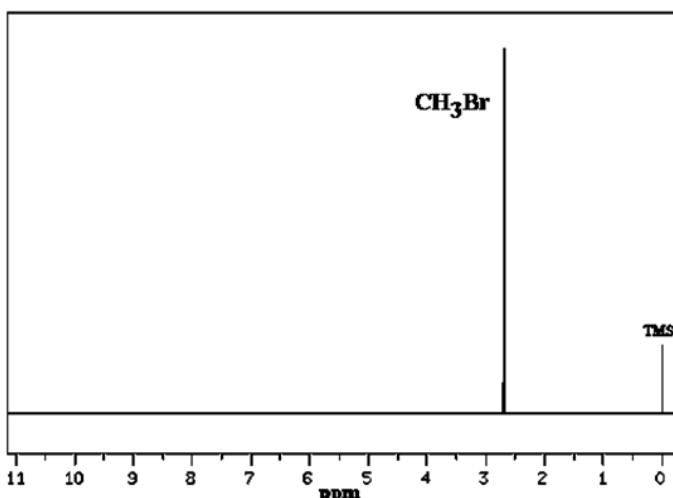


Figure 35.08: NMR Spectrum of methyl bromide

#### 14. Additional topics

None

## 15. Model Question paper

Code No: 18CH1101

AR18

Geethanjali College of Engineering and Technology (Autonomous), Hyderabad  
I.B.Tech (ECE/EEE) I Semester (Regular) End Examinations, December 2018

Time: 3 hours

### Engineering Chemistry

Answer ALL Questions  
Part-A (10 x 2 = 20)

Max. Marks: 70

1. a)  $e_g$  orbitals have greater splitting energy in octahedral complexes. Give reason.  
b) Tetrahedral complexes are high spin complexes. Why?  
c) Hardness water is expressed in terms of  $\text{CaCO}_3$  equivalents. Why?  
d) Mention any four specifications of potable water.  
e) Define reference electrode.  
f) How metals are chosen in cathodic protection to protect the base metal?  
g) State Anti-Markownikoff's rule.  
h) List any two pharmaceutical applications of Aspirin.  
i) Define chemical shift.  
j) Mention any two applications of IR spectra.

Part-B (5 x 10 = 50)

2. How ABMO and MO orbitals are formed by LCAO method? Draw molecular orbital energy level diagram of  $\text{F}_2$  and  $\text{N}_2$ .

(OR)

3. a) Why magnetic properties of  $\text{Fe}^{+3}$  are different when it forms complexes with  $\text{H}_2\text{O}$  and  $\text{CN}^-$  ligands?  
b) Combining atomic orbitals must have same or nearly same energy. Justify. (4)

4. a) What is breakpoint chlorination? State its significance.  
b) Why calgon conditioning is better than Phosphate conditioning? (4)

(OR)

5. What is the principle of EDTA method? Describe estimation of hardness of water by EDTA method.

6. a) Describe how pH of a solution is determined using glass electrode.  
b) Mention any five factors effecting corrosion. (5)

(OR)

7. a) Construct Li ion battery and describe working principle.  
b) Explain electrolyte plating. (5)

8. a) Explain  $\text{S}_{\text{N}}^1$  reaction.  
b) Explain reduction of carbonyl compounds using  $\text{LiAlH}_4$ . (5)

(OR)

9. a) Write preparation of PVC and Teflon. Mention properties and two engineering applications for each.  
b) Explain oxidation of alcohols using  $\text{KMnO}_4$ . (5)

10. a) Why HCl is IR active? Explain.  
b) Write selection rules and four applications of Electronic spectroscopy. (5)

(OR)

11. a) Explain stretching and bending vibrations observed in IR spectra.  
b) Explain magnetic resonance imaging. (5)

*V*

Code No: 18CH1201

Geethanjali College of Engineering and Technology, Hyderabad (Autonomous)  
I B. Tech (CSE/ME/CE) II Semester II Mid-Term Examinations, April, 2019

## ENGINEERING CHEMISTRY

Time: 100 Min

Max. Marks: 15

Note: Answer All Questions. (3 x 5 = 15)

- |     |  |      |     |      |
|-----|--|------|-----|------|
| 1 a | Metal covered by a water drop undergoes corrosion whereas the metal at the peripheral (borders) of the water drop does not. Justify.           | [2M] | CO3 | BTL4 |
| b   | Explain the mechanism of electrochemical corrosion.  | [3M] | CO3 | BTL2 |
|     | (OR)   |      |     |      |
| 2 a | Explain the process of electroless plating of Nickel.  | [2M] | CO3 | BTL2 |
| b   | Describe sacrificial anodic method of protection of metals.  | [3M] | CO3 | BTL2 |
| 3 a | Explain the free radical mechanism of addition polymerization.   | [3M] | CO4 | BTL2 |
| b   | Reduction of carbonyl compound using $\text{NaBH}_4$ is slower than reduction of carbonyl compound using $\text{LiAlH}_4$ . Justify.           | [2M] | CO4 | BTL4 |
|     | (OR)   |      |     |      |
| 4 a | Explain the mechanism of $\text{S}_{\text{N}}^1$ reaction.   | [3M] | CO4 | BTL2 |
| b   | Explain the Saytzeff's rule with an appropriate example.   | [2M] | CO4 | BTL2 |
| 5 a | $\text{CO}_2$ exhibits four types of fundamental vibrations. One anticipates four peaks in the IR spectra but only two were observed. Justify. | [3M] | CO5 | BTL4 |
| b   | $\text{O}_2$ and $\text{F}_2$ are IR inactive whereas $\text{HCl}$ and $\text{HCN}$ are IR active. Explain.                                    | [2M] | CO5 | BTL2 |
|     | (OR)   |      |     |      |
| 6 a | Mention any four applications of UV-VIS spectroscopy.  | [3M] | CO5 | BTL2 |
| b   | Justify the use of tetramethylsilane as the most commonly used reference compound while recording NMR spectrum.                                | [2M] | CO5 | BTL4 |

**Set 2****Code No: 18CH1101****Geethanjali College of Engineering and Technology, Hyderabad (Autonomous)**  
**I B.Tech.(ECE/EEE) I Semester I Mid-Term Examinations, Oct 2019****ENGINEERING CHEMISTRY****Time: 100 Min****Max. Marks: 15****Note: Answer All Questions.****(3 x 5 = 15)**

- 1 a Write the various factors affecting the crystal field splitting energy in complex compounds. [3M] CO1 BTL2  
b Calculate CFSE for the following complexes. [2M] CO1 BTL4  
i)  $[\text{Cu}(\text{F})_6]^{4-}$  (High spin) ii)  $[\text{Co}(\text{CN})_6]^{3+}$  (Low spin).  
**(OR)**
- 2 a State postulates of molecular orbital theory. [2M] CO1 BTL1  
b Interpret bond order with the help of molecular energy level diagram of  $\text{O}_2$  molecule. [3M] CO1 BTL3
- 3 a Explain construction and working of Ion exchange method with appropriate reactions and diagram. [3M] CO2 BTL3  
b Mention the advantages and disadvantages of the above method and explain the regeneration process of exhausted ion exchange resin.  
**(OR)** [2M] CO2 BTL2
- 4 a Describe the treatment of brackish water using reverse osmosis method with a labeled diagram. [3M] CO2 BTL4  
b Calculate the temporary and permanent hardness in degree French of water sample collected in Medchal district. The analysis of water is  $\text{Ca}(\text{HCO}_3)_2 = 16.2 \text{ ppm}$ ,  $\text{Mg}(\text{HCO}_3)_2 = 14.6 \text{ ppm}$ ,  $\text{CaSO}_4 = 13.6 \text{ ppm}$ ,  $\text{MgSO}_4 = 12 \text{ ppm}$ ,  $\text{MgCl}_2 = 9.2 \text{ ppm}$ .  
**(OR)** [2M] CO3 BTL1
- 5 a Define single electrode and standard electrode potentials. [2M] CO3 BTL1  
b Explain the construction and working of calomel electrode. [3M] CO3 BTL4
- 6 a Differentiate primary and secondary cells with examples. [2M] CO3 BTL4  
b Explain the construction and working of Lead acid storage battery. [3M] CO3 BTL2

★  
Code No: 18CH1201

Geethanjali College of Engineering and Technology, Hyderabad (Autonomous)  
I B.Tech. (CSE/ME/CE/IT) II Semester, I Mid-Term Examinations, February 2020

**ENGINEERING CHEMISTRY**

**Time: 100 Min**

**Note: Answer All Questions.**

**Max. Marks: 15**

$(3 \times 5 = 15)$

[2M] CO1 BTL2  
[3M] CO1 BTL3

- 1 a Explain the postulates of Molecular Orbital Theory.  
b Interpret the bond order with the help of molecular energy level diagram of  $F_2$  and predict the magnetic behavior.

**(OR)**

- 2 a Among  $F^-$ ,  $H_2O$ ,  $CN^-$ , oxalate pick the strongest ligand and justify your answer.  
b Draw crystal field energy level diagram and calculate crystal field stabilization energy of the following complexes.  
(i)  $[Co(F)_6]^{3-}$  (High spin)      (ii)  $[Co(NH_3)_6]^{3+}$  (Low spin)  
(iii)  $[Ni(CN)_6]^{4-}$  (Low spin)

[2M] CO1 BTL2  
[3M] CO1 BTL3

- 3 a Explain the steps involved in the treatment of river water to potable water for domestic purposes.  
b A sample of hard water on analysis in Medchal district found to contain 13.6 mg/l of calcium sulphate, 7.3 mg/l of magnesium bicarbonate, 12 mg/l of magnesium sulphate and 9.5 mg/l of magnesium chloride. Calculate total, permanent and temporary hardness of water.

[3M] CO2 BTL2  
[2M] CO2 BTL2

**(OR)**

- 4 a Describe the process of softening of water by Ion Exchange method with diagram.  
b Mention advantages and disadvantages of the above method.

[4M] CO2 BTL2  
[1M] CO2 BTL2

- 5 a Explain the construction and working of Calomel electrode.  
b A Copper electrode ( $E^0 = 0.34V$ ) was combined with an Aluminium electrode ( $E^0 = -1.66V$ ) to form a cell. Write half-cell reactions and calculate the cell potential.

[2M] CO3 BTL2  
[3M] CO3 BTL3

**(OR)**

- 6 a Distinguish between primary and secondary cells with examples.  
b Explain the construction, working and reactions involved during charging and discharging of Lead acid storage battery.

[2M] CO3 BTL2  
[3M] CO3 BTL2



3 hours

**Engineering Chemistry**

Answer All Questions

**PART-A**       $10 \times 2 = 20M$ 

Max. Marks: 70

- Differentiate the atomic and molecular orbitals.  
 Explain Crystal field stabilization energy.  
 What is reverse Osmosis? Give its significance.  
 A sample of water contains:  $Mg(HCO_3)_2 = 73\text{mg/l}$ ,  $CaCl_2 = 222\text{ mg/l}$ , hardness in degree clark.  
 Write on pitting corrosion.  
 Calculate the emf of the given cell at  $25^\circ C$ ,  $Zn/Zn^{+2}(0.06M) // Cu^{+2}(0.028M)/Cu$ .  
 $E^0(Zn^{+2}/Zn) = -0.76V$ ,  $E^0(Cu^{+2}/Cu) = 0.34V$ .

- Define and differentiate enantiomers and diastereomers.  
 Define Electrophilic addition reactions. Give any two examples.  
 What is  $\lambda_{max}$ ? Explain its importance.  
 Define chemical shift in NMR spectroscopy.

**PART-B**       $5 \times 10 = 50M$ 

Explain the postulates of molecular orbital theory.

5

With the help of molecular energy level diagram, calculate bond order and predict the magnetic properties of Oxygen and Fluorine molecules.

5

**OR**

Explain salient features of Crystal field Theory.

5

Explain the crystal field splitting in octahedral and tetrahedral complexes with diagram

5

What do you understand by disinfection of water? Explain it with reference to Chlorination and Ozonization.

5

Define hardness of water. Explain the determination of hardness of water by complexometric method using EDTA.

5

**OR**

A standard hard water sample is prepared by dissolving 1 gm of Calcium carbonate in 1 litre of distilled water. 25 ml of this sample has consumed 20 ml of EDTA on titration. 25ml of a hard water sample has consumed 18 ml of EDTA solution on titration. The hard water is boiled, cooled, filtered, and 25 ml of this is titrated against EDTA which consumed 13 ml. Calculate the temporary, permanent and total hardness of the water sample.

5

Describe ion exchange method for softening of hard water with the help of a diagram. What are the advantages of this method over other methods?

5

Define electrochemical series. Explain its applications with suitable examples.

5

Explain Galvanic and waterline corrosion with a neat diagram.

5

**OR**

What are reference electrodes? Write the construction of Calomel electrode with a neat diagram.

5

Explain the process metal coating for the protection of metals with reference to Galvanizing and Tinning.

5

Explain the Markonikov's rule with suitable example. Why this rule is failed during the addition of HBr in the presence of peroxide?

5

Write the preparation, properties and applications of Teflon and Nylon 6.6.

5

**OR**

Explain the synthesis and pharmaceutical applications of Aspirin.

5

Explain the mechanism of  $SN^2$  reactions.

5

Explain the principle, selection rules and applications of rotational spectroscopy.

5

Explain any five applications of Infra-red spectroscopy.

5

**OR**

Explain various modes of electronic transitions when a molecule absorbs in UV-Visible region.

5

Explain the principle involved in NMR spectroscopy.

5

Name: \_\_\_\_\_

Roll No. \_\_\_\_\_

**Geethanjali College of Engineering and Technology, Hyderabad (Autonomous)**  
**I B.Tech. II Semester I Mid-Term Examinations, February, 2020**  
**ENGINEERING CHEMISTRY**  
**OBJECTIVE QUESTION PAPER**

**Time: 20 Min.****Max. Marks: 10****Answer all questions. All questions carry equal marks.**

Cos	CO 1	CO 2	CO 3
No. of questions	8	8	4
Marks	4	4	2

**I. Choose the correct answer:**

1. Among the following, which is paramagnetic [ ]  
 a) N<sub>2</sub>      b) O<sub>2</sub>      c) F<sub>2</sub>      d) H<sub>2</sub>
2. Bond order for N<sub>2</sub> molecule is [ ]  
 a) 3      b) 2      c) 1      d) 4
3. Among the following, identify which is e<sub>g</sub> orbital [ ]  
 a) d<sub>xy</sub>      b) d<sub>yz</sub>      c) d<sub>zx</sub>      d) d<sub>xz-yz</sub>
4. In LCAO, bonding molecular orbitals are formed by [ ]  
 a) constructive overlapping      b) destructive overlapping  
 c) differ in phase      d) none of these
5. In EDTA titration, the colour of the end point is [ ]  
 a) red      b) blue      c) pink      d) yellow
6. Temporary hardness of water can be removed by [ ]  
 a) filtration      b) screening      c) boiling      d) sedimentation
7. One part of CaCO<sub>3</sub> equivalent hardness per 10<sup>5</sup> parts of water is called as [ ]  
 a) degree Clark      b) ppm      c) degree French      d) mg/L
8. Semi permeable membrane is used in [ ]  
 a) ion exchange      b) zeolite      c) lime soda      d) reverse osmosis
9. The cell whose reactions are reversible is called [ ]  
 a) Fuel cell      b) primary cell      c) secondary cell      d) all of these
10. The standard EMF of a galvanic cell can be calculated from [ ]  
 a) the size of the electrode      b) the P<sup>H</sup> of the solution  
 c) the amount of metal in the anode      d) the E<sup>0</sup> values of the half cells

Code: 18CH1201

AR18

Geethanjali College of Engineering and Technology (Autonomous), Hyderabad  
I B.Tech (CE/ME/CSE) II Semester (Regular) End Examinations, May 2019

## Engineering Chemistry

Time: 3 hours

Max. Marks: 70

Answer All Questions

### PART-A

10 X 2M = 20M

1. a. Write crystal field splitting pattern for octahedral complexes.  
b. Why finger print region is more significant in IR spectroscopy?  
~~c. "Ni(CO)<sub>4</sub> is a diamagnetic complex whereas NiCl<sub>4</sub> is paramagnetic". Explain.~~  
d. What is the significance of breakpoint chlorination in the treatment of municipal water?  
e. Write the reaction involved in phosphate conditioning.  
~~f. Write equation involved in the oxidation of secondary alcohols using KMnO<sub>4</sub>.~~  
g. Why the Teflon is highly chemical resistant?  
~~h. Write selection rules of electronic spectroscopy.~~  
i. What is Electro chemical series?  
j. Define single and standard electrode potentials.

### PART-B

5 X 10M = 50M

2. a. Explain the postulates of molecular orbital theory. 4M  
b. With the help of molecular energy level diagram, calculate bond order and predict magnetic behavior of O<sub>2</sub> and N<sub>2</sub>. 6M

OR

3. a. Discuss various factors that influence crystal field stabilization energy in complex compounds. 6M  
b. Calculate crystal field stabilization energy for the following compounds. 4M  
i). [NiCl<sub>4</sub>]<sup>2-</sup> ii). [Fe(CN)<sub>6</sub>]<sup>3-</sup>
4. a. Describe ion exchange method for softening of hard water with the help of a diagram. 4M  
b. A sample of water on analysis contains 8.4 mg/l of magnesium bicarbonate, 12.0 mg/l of magnesium sulphate, 8.1 mg/l of calcium bicarbonate, 11 mg/l of calcium chloride and 13.6 mg/l of calcium sulphate. Calculate the total, permanent and temporary hardness of the sample and also express the result in degree Clark and degree French. 6M

OR

5. a. Describe how brackish water can be desalinated by reverse osmosis method with a diagram. 5M  
b. Give an account of disinfection of municipal water. 5M

6. a. Explain the construction and working of calomel electrode. 5M  
b. Write Nernst equation. Explain the significance of terms involved in it. Mention its applications. 5M

OR

7. a. How steel is protected from corrosion by sacrificial anodic method? 4M  
b. Describe the process of galvanizing with neat diagram. 6M

## **16. Question Bank**

### **UNIT -I:**

1. “Why is the atomic orbital of oxygen is higher in energy than the atomic orbital of nitrogen”  
Explain in terms of Molecular orbital theory with neat diagram.
2. Explain distribution of electrons as stated in LCAO with pictorial representation.
3. Explain the crystal field splitting in octahedral complex  $[\text{Co}(\text{NH}_3)_6]^{3+}$ , with neat diagram.
4. Explain the crystal field splitting in tetrahedral complex  $[\text{Co}(\text{NH}_3)_6]^{3+}$ , with neat diagram.

### **UNIT -II:**

1. How hard water can be converted to soft water? Classify them.
2. Outline various steps involved in the treatment of potable water.
3. Explain the process of Reverse osmosis and its significance.
4. The water emanating from cation exchanger, is it acidic or basic?
5. Convert ppm into mg/L and degree French.

### **UNIT -III:**

1. Define standard electrode potential and explain the construction and applications of calomel electrode and glass electrode.
2. Explain the various factors which affect on rate of corrosion.
3. Explain waterline, pitting and galvanic corrosion.

### **UNIT-IV**

1. Explain  $\text{SN}^1$  and  $\text{SN}^2$  mechanism with an example for each.
2. Explain Markownikoff's and anti Markownikoff's addition products in addition of HBr to propene.
3. Write the mechanism involved in addition of Grignard reagent to carbonyl compounds.
4. What is Saytzeff rule? Explain E1 and E2 mechanism involved in dehydro halogenation of alkylhalides.
5. Write the steps involved in Free radical polymerization.
6. Discuss various steps involved in the synthesis of Paracetamol and Aspirin.
7. Write Preparation, properties and four engineering applications of PVC, Teflon and Nylon- 6, 6.

### **UNIT-V**

1. Discuss the selection rules and types of electronic transitions for electronic spectra of molecules.
2. What is spin-spin coupling? Explain the splitting pattern with suitable examples.
3. Explain why the absorption bands in UV-visible spectra are very broad.
4. Explain the principle of NMR spectroscopy.
5. Explain the principle of IR spectroscopy and the types of stretching and bending vibrations with suitable examples.

## **SHORT QUESTIONS**

### **UNIT I**

1. Define atomic and molecular orbitals.
  2. "Molecular orbitals are formed by the combination of atomic orbitals."
- Explain with a neat diagram.
3. What are bonding, nonbonding and anti-bonding orbitals?
  4. Compare high spin and low spin complexes.
  5. Define crystal field stabilization energy (CFSE).
  6. "Combining atomic orbitals must have same or nearly same energy" Justify

### **UNIT -II:**

1. Write various units of hardness of water. Why do we express hardness of water in terms of calcium carbonate equivalents?
2. Define colloidal conditioning.
3. A sample of hard water contains 120mg/l of hardness.  
Express the hardness of water in degree French and degree Clarke.
4. Write specifications of potable water.
5. Define break point chlorination.

### **UNIT III:**

1. Define electrochemical series and its applications.
2. Write the half cell and net cell reactions of the following cell at  $25^{\circ}\text{C}$   
 $\text{Zn}/\text{Zn}^{+2}(1\text{M})/\text//\text{Cu}^{+2}(1\text{M})/\text{Cu}$
3. Find the EMF of the cell given  $E^0_{\text{Zn}/\text{Zn}^{+2}} = -0.76\text{V}$  and  $E^0_{\text{Cu}^{+2}/\text{Cu}} = 0.34\text{V}$
4. Differentiate between primary and secondary cells.
5. Temperature increases rate of corrosion increases. Give reason.
6. What is the basic principle of cathodic protection method?

### **UNIT IV**

1. Write the mechanism involved in the oxidation of alcohols using  $\text{KMnO}_4$  and chromic acid.
2. Explain the mechanism of reduction of carbonyl compounds using  $\text{LiAlH}_4$  &  $\text{NaBH}_4$ .
3. Discuss various steps involved in the synthesis of Paracetamol and Aspirin.
4. Write Structure and five pharmaceutical applications of Paracetamol and Aspirin.
5. How are polymers classified?
6. Write addition and condensation polymerization by taking one example for each.
7. Differentiate between addition and condensation polymerization.

### **UNIT V**

1. How many fundamental vibrational frequencies can be observed in the infrared absorption spectrum of  $\text{CO}_2$ ?
2. What is the selection rule for the microwave absorption spectra?
3. Which of the following set of molecules  $\text{O}_2$ ,  $\text{HF}$ ,  $\text{CCl}_4$ ,  $\text{H}_2\text{O}$  &  $\text{CO}$  would exhibit a microwave spectrum?
4. How many signals would you expect in the NMR spectrum of ethanol .
5. What is the necessary condition for a molecule to absorb infrared radiation ?

## **17. Assignment Questions**

### **UNIT-I Molecular structure and Theories of Bonding**

1. Mention the postulates of Molecular orbital theory and draw the molecular orbital energy level diagram of  $N_2$ .
2. Explain the crystal field splitting in octahedral complex  $[CO(NH_3)_6]^{3+}$ , with neat diagram.
3. Explain the crystal field splitting in tetrahedral complex  $[CO(NH_3)_6]^{3+}$ , with neat diagram.
4. Explain the magnetic properties of octahedral complexes.
5. Calculate CFSE for the following complexes  
 $[CO(NH_3)_6]^{3+}$ ,  $[CO(CN)_6]^{3-}$ ,  $[CO(F)_6]^{3-}$ ,  $[Fe(H_2O)_6]^{2+}$ ,  $[CO(H_2O)_6]^{3+}$ ,  
 $[Cr(NH_3)_6]^{3+}$ ,  $[Mn(H_2O)_6]^{3+}$ ,  $[Ni(NH_3)_6]^{2+}$ ,  $[Cu(NH_3)_6]^+$

### **UNIT-II Water and its treatment**

1. Explain Ion- exchange process with a neat labeled diagram.
2. Outline various steps involved in the treatment of potable water.
3. Explain Calgon and phosphate conditioning.
4. With the help of a neat diagram describe the reverse osmosis process.
5. Calculate the temporary and permanent hardness in degree French of water.  
Sample collected in Medchal district. The analysis of water is as follows.  
 $Ca(HCO_3)_2 = 16.2$  ppm,  $Mg(HCO_3)_2 = 14.6$  ppm,  $CaSO_4 = 13.6$  ppm,  
 $MgSO_4 = 12$ ,  $MgCl_2 = 9.2$  ppm.

### **UNIT-III Electrochemistry and corrosion**

1. What is reference electrode? Explain how pH is determined using quinhydrone electrode.
2. What are batteries?
3. Define corrosion. Explain the mechanism of wet or electro chemical corrosion.
4. i) How do the following factors influence the rate of corrosion?  
a) Position in galvanic series b) Nature of Surface film  
ii) Explain electroless plating of Nickel.
5. How a metal can be protected by sacrificial anodic and impressed current cathodic method.

## **UNIT-IV Reaction Mechanisms and molecules of industrial importance**

1. Write the mechanism involved in the oxidation of alcohols using  $\text{KMnO}_4$  and chromic acid. Why tertiary alcohols do not get oxidized?
2. Explain  $\text{SN}^1$  and  $\text{SN}^2$  mechanism with an example for each.
3. What is Saytzeff rule? Explain E1 and E2 mechanism involved in dehydro halogenation of alkylhalides.
4. Explain Markownikoff's and anti Markownikoff's addition products in addition of HBr to propene.
5. Explain the mechanism of reduction of carbonyl compounds using  $\text{LiAlH}_4$  &  $\text{NaBH}_4$ .

## **UNIT- V Spectroscopic techniques and applications**

1. What is meant by the term absorption spectroscopy?
2. Which of the following set of molecules  $\text{H}_2$ ,  $\text{HCl}$ ,  $\text{NH}_3$  &  $\text{CO}_2$  would exhibit a IR spectrum?
3. Write applications for UV-Vis spectroscopy.
4. What is finger print region region?
5. What is meant by chemical shift?

## **ASSIGNMENT QUESTIONS MAPPED TO COURSE OUTCOMES AND BLT**

Q No:	BLT1	BLT2	BLT3	BLT4	BLT5
1 CO1			✓		
2 CO1		✓			
3 CO1		✓			
4 CO1		✓			
5 CO1		✓			
6 CO2		✓			
7 CO2	✓				
8 CO2		✓			
9 CO2		✓			
10 CO2		✓			
11 CO3		✓			

12 CO3	✓				
13 CO3		✓			
14 CO3			✓		
15 CO3		✓			
16 CO4			✓		
17 CO4			✓		
18 CO4			✓		
19 CO4			✓		
20 CO4	✓				
21 CO5	✓				
22 CO5		✓			
23 CO5	✓				
24 CO5	✓				
25 CO5		✓			

## 18. Unit wise Objective questions

### UNIT -I:

1. The metal in a complex acts as \_\_\_\_\_.
2. The groups satisfying the secondary valencies of a cation in a complex are called \_\_\_\_\_.
3. In complexes ligands are linked to central metal by \_\_\_\_\_ bond.
4. In the formation of complex, the transition metal ion \_\_\_\_\_ electron pair.
5. Coordination number of Cobalt in  $[Co(NH_3)NO_2]Cl_2$  \_\_\_\_\_.
6. Complexes with bidentate ligands are called \_\_\_\_\_.
7. The outer complexes are generally formed by \_\_\_\_\_ ligands.
8. Spin only formula \_\_\_\_\_ BM.
9. The energy of molecular orbital can be calculated by \_\_\_\_\_ equation.
10. Bonding orbitals are \_\_\_\_\_ in energy than anti-bonding orbitals.

## **UNIT -II:**

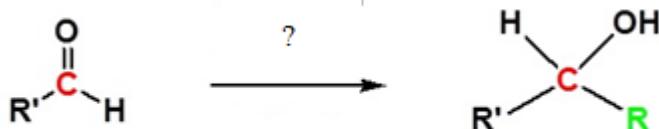
1. The \_\_\_\_\_ of calcium and magnesium are decomposed by boiling the water.
2. Carbonates and bicarbonates of calcium and magnesium causes \_\_\_\_\_
3. EDTA forms \_\_\_\_\_ with calcium and magnesium ions
4. One ppm of hardness is equal to \_\_\_\_ degreeFrench.
5. Water coming out of hydrogen cation exchanger is highly \_\_\_\_\_
6. EDTA is \_\_\_\_\_
7. Chemical name given to Calgon is \_\_\_\_\_
8. Sulphates and chlorides of calcium and magnesium causes \_\_\_\_\_
9. If the pH value of the solution is made 10 and a dye, known as \_\_\_\_\_
10. One ppm of hardness is equal to \_\_\_\_\_<sup>0</sup>Cl

## **UNIT -III:**

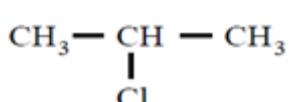
1. The Nernst equation for a general reduction reaction is \_\_\_\_\_
2. The relative corrosion tendencies of the metals and alloys can be known by using \_\_\_\_\_
3. The potential of calomel electrode depends on the concentration of \_\_\_\_\_
4. Quinhydrone is 1:1 Molar compound of \_\_\_\_\_ and \_\_\_\_\_
5. Pb-Acid storage cell is an example of \_\_\_\_\_
6. The greater the \_\_\_\_\_ between the two metals in the actual contact, the faster will be the corrosion
7. The active part of the metal becomes \_\_\_\_\_ and it gets corroded
8. \_\_\_\_\_ is a method of protecting metals and alloys from corrosion by making them completely cathodic.
9. The coating of the metal surface is done by using zinc is called \_\_\_\_\_
10. In the \_\_\_\_\_ chemically more active metals are given higher place.

## **UNIT IV**

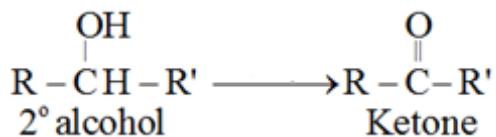
1. Write the reagent involved in the following reaction



2. Identify 'α' carbon , 'β' carbon and hydrogen in the following compound



3. In alkyl halides, dehydrohalogenation follows \_\_\_\_\_ order.
4. The following reaction may be carried out using \_\_\_\_\_ reagents.



5. In E<sub>1</sub> mechanism, the intermediate involves the formation of \_\_\_\_\_.
6. Grignard reagent is \_\_\_\_\_.
7. Structure of Aspirin is \_\_\_\_\_.
8. Inversion takes place in \_\_\_\_\_ mechanism.
9. \_\_\_\_\_ is a good initiator for free radical polymerization.
10. Example for an addition polymer is \_\_\_\_\_.

## UNIT V

1. Greater the de - shielding of protons \_\_\_\_\_ will be the value of  $\delta$ .
2. \_\_\_\_\_ is generally employed as an internal standard in NMR spectroscopy.
3. The difference in the absorption position of the proton with respect to TMS signal is called \_\_\_\_\_
4. The region below 1500 cm<sup>-1</sup> is called \_\_\_\_\_ region.
5. The region of electromagnetic spectrum for nuclear magnetic resonance is \_\_\_\_\_
6. H<sup>1</sup>, C<sup>13</sup>, F<sup>19</sup>, P<sup>31</sup> have nuclear spin equal to \_\_\_\_\_
7. Linear molecules have \_\_\_\_\_ vibrational degrees of freedom whereas non-linear molecules have \_\_\_\_\_ vibrational degrees of freedom.
8. The range of infra -red radiations is \_\_\_\_\_
9. Shifting of absorption to a longer wavelength is called \_\_\_\_\_
10. Electronic spectra is obtained due to the absorption of radiation in the \_\_\_\_\_ regions.

**20. Known gaps :** Standard Hydrogen electrode

**21. Discussion topics:** None

**22. References, Journals, Websites and E-links if any:**

- 1 . Engineering Chemistry by P.C.Jain & M.Jain; Dhanpat Rai Publishing Company (P) Ltd., New Delhi.
2. University Chemistry, by B.H. Mahan
3. Inorganic Chemistry by J.D.Lee

**Websites:**

<http://www.chemweb.com/>  
<http://chemfinder.cambridgesoft.com/>  
[www.vlcc.chem](http://www.vlcc.chem)  
[www.indiana.edu/~chemlib/](http://www.indiana.edu/~chemlib/)  
[www.polysort.com/](http://www.polysort.com/)

**23. Quality Measurement Sheets:**

- a. Course End Survey
- b. Teaching Evaluation

**24. Students List:**

**25. Group-wise Students List for Discussion Topics:**

<b>S. No.</b>	<b>Discussion Topics</b>	<b>Regular/ Additional</b>	<b>Teaching aids used OHP/ PPT/BB</b>	<b>Date</b>	<b>Remarks</b>
<b>1</b>	Salient features of CFT	Regular	<b>PPT/OHP</b>		
<b>2</b>	Importance of green chemistry	Additional	<b>PPT/OHP</b>		
<b>3</b>	Financial loss because of corrosion in railways.	Additional	<b>BB</b>		
<b>4</b>	Significance of NMR in medicine.	Additional	<b>PPT/OHP</b>		
<b>5</b>	Significance of chemistry in Polymer industry.	Regular	<b>PPT/OHP</b>		