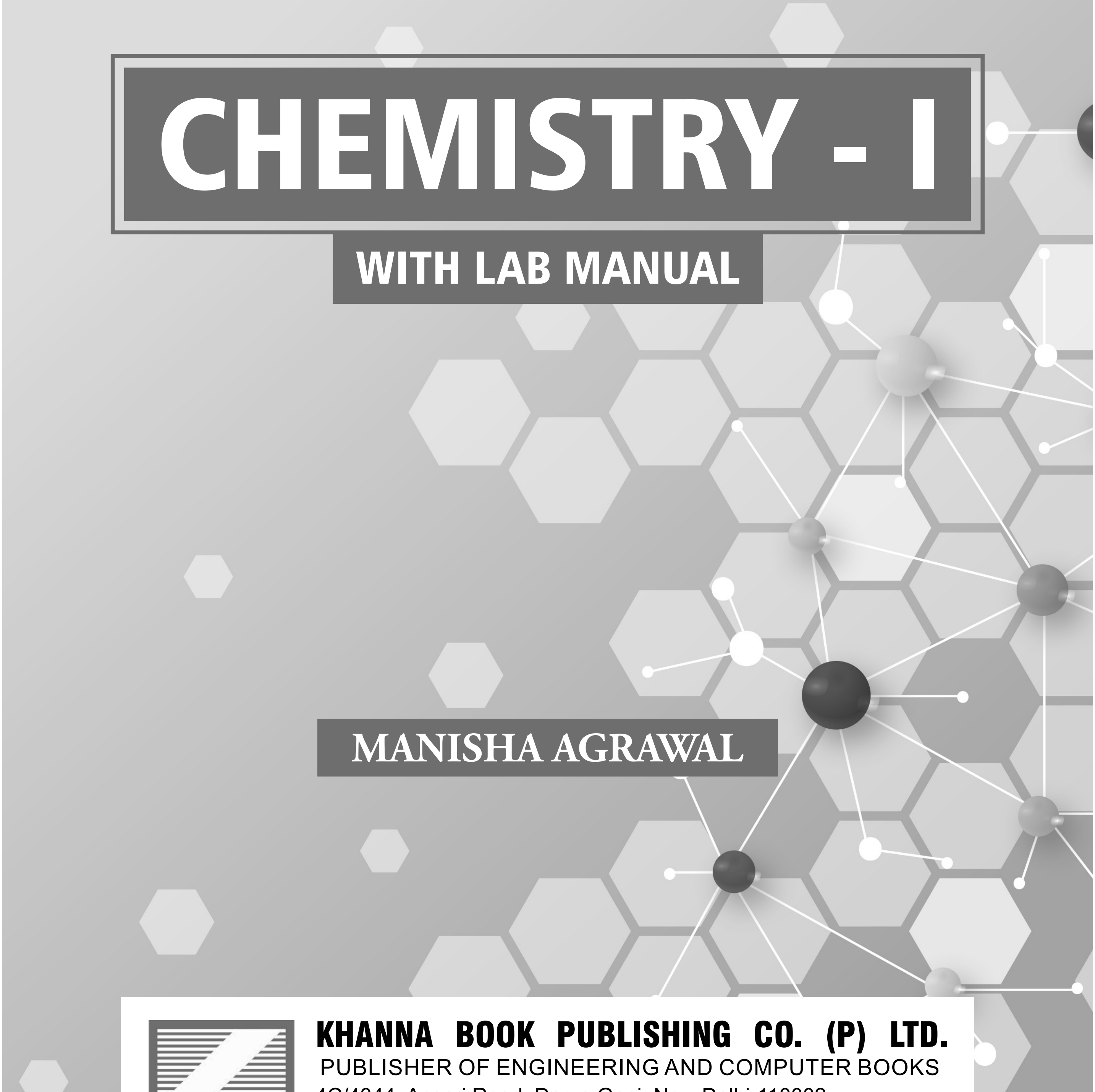
CHEMISTRY - I

WITH LAB MANUAL



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FOREWORD

Engineering has played a very significant role in the progress and expansion of mankind and society for centuries. Engineering ideas that originated in the Indian subcontinent have had a thoughtful impact on the world.

All India Council for Technical Education (AICTE) had always been at the forefront of assisting Technical students in every possible manner since its inception in 1987. The goal of AICTE has been to promote quality Technical Education and thereby take the industry to a greater heights and ultimately turn our dear motherland India into a Modern Developed Nation. It will not be inept to mention here that Engineers are the backbone of the modern society - better the engineers, better the industry, and better the industry, better the country.

NEP 2020 envisages education in regional languages to all, thereby ensuring that each and every student becomes capable and competent enough and is in a position to contribute towards the national growth and development.

One of the spheres where AICTE had been relentlessly working from last few years was to provide high-quality moderately priced books of International standard prepared in various regional languages to all it's Engineering students. These books are not only prepared keeping in mind it's easy language, real life examples, rich contents and but also the industry needs in this everyday changing world. These books are as per AICTE Model Curriculum of Engineering & Technology – 2018.

Eminent Professors from all over India with great knowledge and experience have written these books for the benefit of academic fraternity. AICTE is confident that these books with their rich contents will help technical students master the subjects with greater ease and quality.

AICTE appreciates the hard work of the original authors, coordinators and the translators for their endeavour in making these Engineering subjects more lucid.

(Anil D. Sahasrabudhe)

Acknowledgement

The author grateful to AICTE for their meticulous planning and execution to publish the technical book for Engineering and Technology students.

I sincerely acknowledge the valuable contributions of the reviewer of the book Prof. Vimal Rarh, for making it students' friendly and giving a better shape in an artistic manner.

This book is an outcome of various suggestions of AICTE members, experts and authors who shared their opinion and thoughts to further develop the engineering education in our country.

It is also with great honour that I state that this book is aligned to the AICTE Model Curriculum and in line with the guidelines of National Education Policy (NEP) -2020. Towards promoting education in regional languages, this book is being translated in scheduled Indian regional languages.

Acknowledgements are due to the contributors and different workers in this field whose published books, review articles, papers, photographs, footnotes, references and other valuable information enriched us at the time of writing the book.

Finally, I like to express my sincere thanks to the publishing house, M/s. Khanna Book Publishing Company Private Limited, New Delhi, whose entire team was always ready to cooperate on all the aspects of publishing to make it a wonderful experience.

Manisha Agrawal

Preface

Subject Chemistry teaches useful skills and knowledge. It plays an important and useful role in everyday life, towards the development and growth of a number of industries. Such as the food we eat, the air we breathe, the various cleansing agents we use, even human emotions are sometimes a result of chemical reactions within our body.

The text book on **"Chemistry-I"** (Theory and Lab) is designed to cater the needs of young minds of 21st century. The theoretical concepts and practical utility of these are blended in all the topics of the content with relevant examples. Book is strictly aligned with AICTE model curriculum incorporating student centric and self-learning activities as per New National Education Policy. Salient features of this model curriculum have been designed in such a way that it encourages innovation and research. A total number of credits have been reduced and many new courses have been incorporated in consultation with industry experts. The Curriculum has been designed where the students can understand the industry requirements and have hands-on experience. The students will develop a problem - solving approach and will be able to meet the challenges of the future.

To fulfil the aims and objectives of the above, this book is written for undergraduate students of Engineering. The Book contains seven Units. Flow of each unit begins with rationale, pre-requisites and unit outcomes. 'Interesting facts', 'E- resources', 'Use of ICT', 'Case studies and Projects' are mentioned after every topic. Which provides a window to students to realize the importance and efforts behind those particular topics. After completion of the topics summary of the units is briefed. Descriptive and objective questions are included in the exercise with feedback of correct options in each Unit. The additional reading information of a particular topic is shared in the section "know more", to encourage the teachers and students to get the additional information.

The separate reference section is cited at the end of all chapters. Book ends with the appendices, attainments & gap analysis, suggestive outlines to report experiments and Rubrics for assessments.

I hope this book will be advantageous for the students to enhance their skills and knowledge. Although every care has been taken to avoid misprints and mistakes, yet it is difficult to claim perfection. I will be grateful to the readers if any errors are pointed out. Suggestions, corrections, and feedbacks for further improvement of the book will be thankfully acknowledged.

Manisha Agrawal

Outcome Based Education

For the implementation of an outcome based education the first requirement is to develop an outcome based curriculum and incorporate an outcome based assessment in the education system. By going through outcome based assessments evaluators will be able to evaluate whether the students have achieved the outlined standard, specific and measurable outcomes. With the proper incorporation of outcome based education there will be a definite commitment to achieve a minimum standard for all learners without giving up at any level. At the end of the programme running with the aid of outcome based education, a students will be able to arrive at the following outcomes:

PO-1: **Engineering knowledge:** Apply the knowledge of mathematics, science, engineering fundamentals, and an engineering specialization to the solution of 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, natural 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.

Course Outcomes

After completion of the course the students will be able to:

CO-1: Analyse microscopic chemistry in terms of atomic and molecular orbitals and intermolecular forces.

CO-2: Rationalise bulk properties and processes using thermodynamic considerations.

CO-3: Distinguish the ranges of the electromagnetic spectrum used for exciting different molecularenergy levels in various spectroscopic techniques

CO-4: Rationalise periodic properties such as ionization potential, electronegativity, oxidation statesand electronegativity.

CO-5: List major chemical reactions that are used in the synthesis of molecules.

Mapping of Course Outcomes with Program Outcomes

Course Outcome	**Expected Mapping with Programme Outcomes** (1- Weak Correlation; 2- Medium correlation; 3- Strong Correlation)											
	PO-1	**PO-2**	**PO-3**	**PO-4**	**PO-5**	**PO-6**	**PO-7**	**PO-8**	**PO-9**	**PO-10**	**PO-11**	**PO-12**
CO-1	3	1		2								
CO-2	3		2	2					2			
CO-3	3	2			1	2	1		2			
CO-4	3	3	1			2					1	
CO-5	3	2	2		1	3						1

Abbreviations and Symbols

Symbols	Details
ψ	Wave-function
H	Hamiltonian operator
σ	σ- bonding orbital
σ^*	σ-antibonding orbital
π	π - bonding orbital
π^*	π - antibonding orbital
Δ_o	Energy for octahedral complex
Δ_t	Energy for tetrahedral complex
μ	Magnetic moment
τ	Tau
δ	Delta
λ	Lambda

List of Figures

Unit 1: Atomic and Molecular Structure

Unit 2: Spectroscopic Techniques and Applications

Unit 3: Intermolecular Forces and Potential Energy Surfaces

Unit 4: Use of Free Energy in Chemical Equilibria

Unit 5: Periodic Properties

Unit 6: Stereochemistry

Unit 7: Organic Reactions and Synthesis of a Drug Molecule

List of Tables

Unit 1: Atomic And Molecular Structure

Unit 2: Spectroscopic Techniques and Applications

Unit 3: Intermolecular Forces and Potential Energy Surfaces

Unit 5: Periodic Properties

Unit 7: Organic Reactions and Synthesis of a Drug Molecule

Guidelines for Teachers

To implement Outcome Based Education (OBE) knowledge level and skill set of the students should be enhanced. Teachers should take a major responsibility for the proper implementation of OBE. Some of the responsibilities (not limited to) for the teachers in OBE system may be as follows:

- Within reasonable constraint, they should manipulate time to the best advantage of all students.
- They should assess the students only upon certain defined criterion without considering any other potential ineligibility to discriminate them.
- They should try to grow the learning abilities of the students to a certain level before they leave the institute.
- They should try to ensure that all the students are equipped with the quality knowledge as well as competence after they finish their education.
- They should always encourage the students to develop their ultimate performance capabilities.
- They should facilitate and encourage group work and team work to consolidate newer approach.
- They should follow Blooms taxonomy in every part of the assessment.

Bloom's Taxonomy

Level	Teacher should Check	Student should be able to	Possible Mode of Assessment
Creating	Students ability to create	Design or Create	Mini project
Evaluating	Students ability to Justify	Argue or Defend	Assignment
Analysing	Students ability to distinguish	Differentiate or Distinguish	Project/Lab Methodology
Applying	Students ability to use information	Operate or Demonstrate	Technical Presentation/ Demonstration
Understanding	Students ability to explain the ideas	Explain or Classify	Presentation/Seminar
Remembering	Students ability to recall (or remember)	Define or Recall	Quiz

Guidelines for Students

Students should take equal responsibility for implementing the OBE. Some of the responsibilities (not limited to) for the students in OBE system are as follows:

- Students should be well aware of each UO before the start of a unit in each and every course.
- Students should be well aware of each CO before the start of the course.
- Students should be well aware of each PO before the start of the programme.
- Students should think critically and reasonably with proper reflection and action.
- Learning of the students should be connected and integrated with practical and real life consequences.
- Students should be well aware of their competency at every level of OBE.

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1

Atomic and Molecular Structure

UNIT SPECIFIC

This unit discusses the topics: Schrodinger equation, Particle in a box. Forms of the hydrogen atom wave functions and the plots. Molecular orbitals of diatomic and multicentre orbitals. Equations and energy level diagrams for atomic and molecular orbitals. Pi-molecular orbitals of butadiene, aromaticity, CFT, Band structure and doping of solids.

RATIONALE

Engineers have to deal with all kinds of matter and their properties. The understanding of properties of different kind of matter arises from the microscopic understanding. This unit will provide the insight on various theories to understand the microscopic behaviours of different types of matter so, one should know the Quantum mechanical model of atom and MOT. The MOT can also be extended to explain the extra-stability of aromatic compounds like benzene. While dealing with solids Crystal Field Theory to predict the properties of inorganic solids like complexes; On other hand one may require the knowledge of Band Theory to deal with properties of metals and metalloids.

PRE-REQUISITES

Chemistry: Structure of Atom, Periodic Table, Nomenclature of Organic compounds
Maths: Basic Algebra and Trigonometric Functions
Physics: Electric charges and interactions

LEARNING OUTCOMES

After this Unit, students must be able to—

U1-O1: Apply Schrodinger equation through conceptual interpretation of quantum chemistry

U1-O2: Construct energy level diagrams for diatomic molecules and interpret their properties using Molecular Orbital Theory.

U1-O3: Identify aromaticity of organic compounds from their structure and correlate with MO Theory.

U1-O4: Differentiate shapes of transition metal ions and predict their magnetic properties.

U1-O5: Analyse different semi-conductors with the help of band theory and doping.

MAPPING OF UNIT WISE LEARNING OUTCOMES WITH THE COURSE OUTCOMES

Outcome	EXPECTED MAPPING WITH COURSE OUTCOMES (1- Weak Correlation; 2- Medium correlation; 3- Strong Correlation)				
	CO-1	CO-2	CO-3	CO-4	CO-5
U1-O1	3		2		
U1-O2			3		
U1-O3			2		1
U1-O4	2				
U1-O5	1		2		

1.1 INTRODUCTION TO QUANTUM MECHANICS

Quantum Mechanics is one of the most remarkable discoveries of the contemporary sciences developed over the last century. The term "**Quantum Mechanics**" was coined by Max Born in 1924.

A chemist's intention to learn quantum mechanics is to be able to understand the Structure, Bonding and Reactivity of/in/between chemical entities be it an atom or a molecule, which is defined by the behavior of electrons (microscopic matter).

1.1.1 What is Quantum Mechanics?

The term "**Quantum Mechanics**" is made up of two words **QUANTUM** + **MECHANICS**. The term "**Mechanics**" refers to the science of motion of the body. The other word is "**Quantum**" which is Latin word for "amount" and in modern conventions is used to represent smallest possible discrete unit of any physical property.

Quantum Mechanics replaces Classical Mechanics at the atomic or subatomic levels (electrons and nuclei in atoms and molecules). It gives the laws of motion of microscopic objects (the way classical mechanics gives for macroscopic objects). So, we can say that Quantum Mechanics is the theoretical science of microscopic matter.

1.1.2 Origin of Quantum Mechanics

Till the end of 19th century, Classical or Newtonian Mechanics was considered to be the only right and undisputed theoretical science. But soon some new experimental phenomena were observed which could not be explained by Classical Mechanics. This includes Black Body Radiation, Photo-electric Effect, Compton Effect, Atomic Spectrum, Heat capacity of solids and so on. Because of paucity of space and time, a detailed discussion about each experimental phenomenon is out of scope of this article. In all, the correct interpretations of the above mentioned experimental phenomena gave two important conclusions:

1. Energy is quantized or one can say that it can be transferred only in discrete packets called quanta.
2. Light (or radiation) exhibits particle like behaviour.

These two new concepts were the basis for origin of the field of quantum mechanics. Classical mechanics failed to explain the above- mentioned experimental phenomena as Classical mechanics considered an electromagnetic radiation solely a wave phenomenon.

But now it seems that radiation shows a dual nature. In some cases, it behaves like a wave (reflection, refraction, diffraction, etc.) and sometimes it manifests itself as a particle, the photon (A photon is a single quantum of electromagnetic energy or, one can say photons are quanta [plural of quantum] of electromagnetic energy which means that the energy is quantized and can only be transferred in discrete units (or packets) of size hν.), with energy E = *h*ν (photoelectric effect, Compton effect, etc.). Neither picture is wrong.

In 1924, Louis De Broglie suggested some logic to this situation. Broglie said that nature manifests itself in two forms – matter and radiation. And if radiation has dual behavior, then by virtue of symmetry, matter should also have dual behavior. Broglie suggested that particles have wave-like properties characterized by a wavelength as,

$$\lambda = \frac{h}{p}$$

where λ is the wavelength (wave nature) and p is the momentum of the particle ($p = mv$, particle nature). The wave nature of matter was first confirmed by Davisson and Germer experiment. This established **WAVE-PARTICLE DUALITY** in matter**.**

A direct consequence of wave-particle duality of matter as well as radiation led to **Heisenberg Uncertainty Principle**. This principle states that the position and momentum of a particle cannot be simultaneously measured with arbitrarily high precision.

$$\Delta x.\ \Delta p_x \geq \frac{h}{4\pi}$$

If we look around, we face no difficulty in locating large macroscopic matter and determining their velocities at the same time. However, this is not so for microscopic matter. An object becomes visible when a photon of light after colliding with the object enters the human eye. To measure the position of particle within a certain range of uncertainty, Δx, we must use a light of wavelength λ smaller than the uncertainty range. But from de Broglie's relation, we know that shorter the wavelength, larger will be the momentum of the photon. So, when, the light strikes the particle, it would give up some or all of its momentum to the particle. Consequently, the momentum of the particle would become uncertain, Δp_x. Thus, the more precisely we determine a particle's position, the more we disturb its motion (momentum). This is the basis of Heisenberg uncertainty principle.

With Heisenberg uncertainty principle came in the concept of ORBITAL. Bohr's atomic model was one model which was widely appreciated but was later replaced by quantum theory of atom. Bohr postulated that the electrons in an atom revolves round the nucleus in fixed circular paths called ORBITS. This concept of orbit is not valid as per Heisenberg uncertainty principle because the trajectory of a particle can only be defined if its position and momentum are known simultaneously with precision. An important consequence of the Heisenberg uncertainty principle is that one cannot determine the path of a moving microscopic particle. Bohr's concept of ORBIT failed and got replaced by ORBITAL. In terms of uncertainty principle, one can only predict the probability or relative chances of locating an electron in a particular region of space round the nucleus *i.e.* , one can only predict where an electron is most likely to be found.

1.1.3 Fundamentals of Quantum Mechanics

The dual behavior of matter and uncertainty principle gave birth to Quantum Mechanics. These ideas inspired Schrödinger and Heisenberg and they independently formulated quantum mechanics in 1925 (Schrödinger – Wave mechanics and Heisenberg – Matrix mechanics), to study the behavior of microscopic matter. At first sight, the two approaches appeared different but, later Dirac and Newman showed that in essence the two formulations are mathematically equivalent. Here, we will be discussing the basis of the Schrödinger quantum theory.

Schrödinger Quantum Mechanics: Schrödinger proposed quantum theory to explain the behavior of microscopic particles taking into account the wave nature of particles as suggested by de Broglie. The Schrödinger quantum theory revolves around a partial differential equation now popularly known as the Schrödinger equation which describes the behavior of microscopic particles by means of a function called the wave-function ψ.

There are two forms of Schrödinger equation: time-dependent and time-independent The wave-function is a function of particle's position and time, $\psi(x, y, z, t)$, in the time-dependent Schrödinger equation, whereas it is a function of position only, $\psi(x, y, z)$, in the time-independent Schrödinger equation. The discussions are restricted to Schrödinger's time-independent quantum mechanics.

The time independent Schrödinger equation is of the form,

$$\hat{H}\psi = E\psi$$

where the Hamiltonian $\hat{H}$ operator acts on the wave-function ψ and the result is proportional to the same wave-function ψ (stationary state) and the proportionality constant, E, which is the energy of the state ψ.

Wave-function ψ (also called state function or eigen function) is the store house of information. The heart of Schrödinger equation is "Wave-function" which contains all the information about the system it describes.

Interestingly, wave-function itself does not have any explicit meaning. Max Born gave correct statistical interpretation of the wave-function for which he was awarded Nobel Prize in 1954. According to Born, ψ has no physical significance. It is merely a mathematical function of the coordinates of the system. He called ψ as **PROBABILITY AMPLITUDE** and ψ^2 or $\psi\cdot\psi^*$, the **PROBABILITY DENSITY** of the system (which is of significance). of a system is the measure of probability density at that point (probability of finding a particle in a given space).

In context of atoms, an atomic orbital (ψ) is a three dimensional region around the nucleus within which the probability of finding an electron with a certain energy is maximum.

There is no limit to the number of solutions of the Schrödinger equation. However, a number of conditions are required for a physical realistic solution of wave-function. So, an acceptable wave-function is the one which is

- Single valued
- Continuous and doubly differentiable
- Finite
- Satisfy Boundary condition
- Normalized

The wave-functions which satisfy the above conditions are called WELL BEHAVED Wave-functions.

1.1.4 Quantum Mechanical Study for Particle in a One-dimensional Box – MODEL SYSTEM

Let us suppose that a particle of mass m is enclosed in a one dimensional box (so that we know its position lies within the boundaries of the box), let's say along x axis and is restricted to move in a region of space from $x = 0$ to $x = L$ and that its potential energy (P.E.) within the box is constant and taken as equal to zero for the sake of convenience.

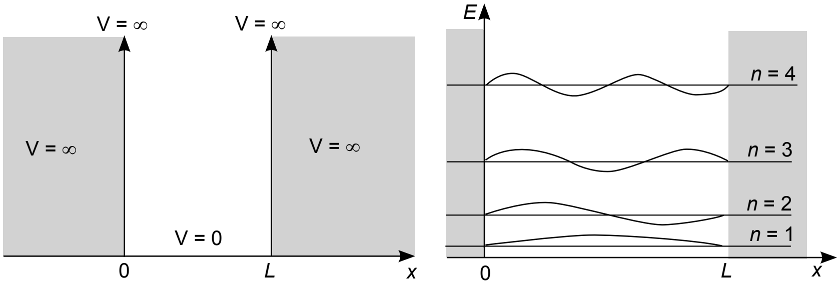


Fig. 1.1: A particle in a one-dimensional box with P.E. = 0 inside the box and P.E. = ∞ on the walls of the box and outside the box.

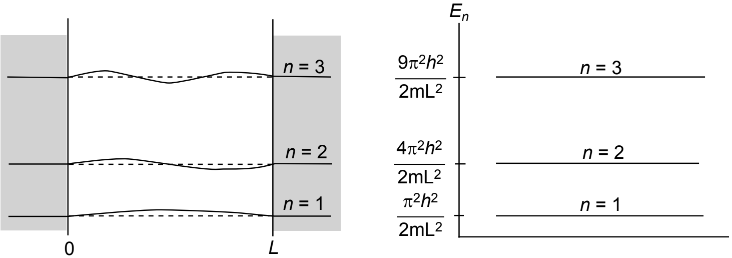
$$\text{Schrödinger Equation} = \frac{-h^2}{8\pi^2 \text{m}} \cdot \frac{d^2}{dx^2}\,\psi(x) = E\psi(x)$$

$$\psi(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi}{L}x\right)$$

The above equation gives the normalized wave-function for particle in a one dimensional box.

$$E = \frac{n^2h^2}{8\text{mL}^2} \text{ where } n = 1, 2, 3 \text{ ... but } n \neq 0$$

The allowed values of energy given by equation are called the **energy levels** of the system. One also notices over here that the energy of a particle in a one dimensional box is quantized. The least energy that the particle may possess is called the **zero point energy**, or the **ground state energy E_0**. Note that, if **n = 0**, the wave function vanishes everywhere and we lose our particle. For the particle in the box, the least energy value or ground state energy is defined for n = 1, so that $E_0 = \frac{h^2}{8\text{mL}^2}$.



(a) (b)

Fig. 1.2: A plot of ψ*n(x)*ψ*n(x)* for the first four wavefunctions.

Extending this model to a 3-dimensional box gives the equation as **Schrödinger equation for a particle in a three dimensional box**:

$$-\left(\frac{h^2}{8\pi^2 m}\nabla^2\right)\psi = E\psi$$

$$-\left(\frac{h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\right)\psi = E\psi$$

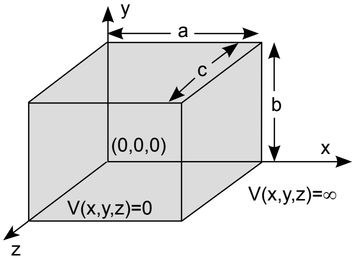


Fig. 1.3: Particle in a 3D box with three lengths: *a, b* and *c*

$$E = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2}+\frac{n_y^2}{b^2}+\frac{n_z^2}{c^2}\right)$$

$$\psi(x, y, z) = \sqrt{\frac{2}{a}}\sin\left(\frac{n_x \pi x}{a}\right)\sqrt{\frac{2}{b}}\sin\left(\frac{n_y \pi y}{b}\right)\sqrt{\frac{2}{c}}\sin\left(\frac{n_z \pi z}{c}\right)$$

This treatment is extended to conjugated polyenes to understand quantum mechanically the systems.

1.1.5 Quantum Mechanics and Atomic Structure

The simplest chemical system which has been investigated quantum mechanically is hydrogen atom (two body problem–one electron and one nucleus). The Hamiltonian for this system contains three terms – kinetic energy term for electron, kinetic energy term for nucleus and electron–nucleus attraction potential energy. The Schrödinger equation for this system is of the form,

$$\left[-\frac{h^2}{8\pi^2}\frac{1}{\mu}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi-\frac{ze^2}{4\pi\varepsilon_0 r}\psi\right] = E\psi \quad \text{where } \mu = \frac{1}{m_e}+\frac{1}{m_n}$$

This Schrödinger equation cannot be separated as the potential energy term does not allow the solution in Cartesian co-ordinates. Therefore, this Schrödinger equation in Cartesian co-ordinates for hydrogen atom is converted into spherical polar co-ordinates (r, θ, φ) because of spherical symmetry of atom and we get,

$$\left(\left[\left\{\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{sin\,\theta}\frac{\partial}{\partial\theta}\left(sin\,\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right\}\right]+\frac{8\pi^2\mu r^2}{h^2}\left[E_{ele}-V\right]\right)\psi_{r\theta\varphi} = 0$$

The wave-function for this system is found to depend on r, θ and φ; and is therefore taken as product of radial and angular parts.

$$\psi_{r\theta\varphi} = R(r)\cdot\Theta(\theta)\cdot\Phi(\varphi)$$

The radial function $R(r)$ gives information about the electron density at different distances from the nucleus whereas the angular function ($Y = \Theta(\theta)\cdot\Phi(\varphi)$) gives the shapes of orbitals and its orientation in space. The most rewarding outcomes of the solution of Schrödinger equation for the atom, is the occurrence of a set of integers (called Quantum Numbers) every time a wave equation is solved with boundary conditions applied. The quantum numbers obtained from solution hydrogen atom Schrödinger equation are n (Principal quantum number; $n = 1, 2, 3..$);, l (Azimuthal quantum number; $l = 0, \ldots.\ n - 1$) and m (Magnetic quantum number; $m = -l, \ldots., 0 \ldots.., +l$).

However, the Schrödinger equation cannot be solved exactly for a multi-electron system due to the presence of electron-electron repulsion terms in the Hamiltonian. The fundamental difficulty arises due to the fact that each electron repels every other electron so that the motion of each electron is dependent on the motion of all the others. However, solutions of reasonable accuracy can be obtained using approximate methods. The total wave-function for a multi-electron atom can be constructed from atomic orbital having different energies. These atomic orbitals are a function of the co-ordinates of a single electron and their angular part has the same form as the hydrogen atom (depends on l

and m). However, their radial part (depends on n, l and nuclear charge Z) is different, which also takes into account the mutual repulsions between the electrons. In all, the quantum mechanical solution of hydrogen atom lays the foundation of Atomic Structure. The quantum numbers so defined help to designate the electron present in an orbital. The distribution of electrons of an atom in its various orbitals gives the electronic configuration.

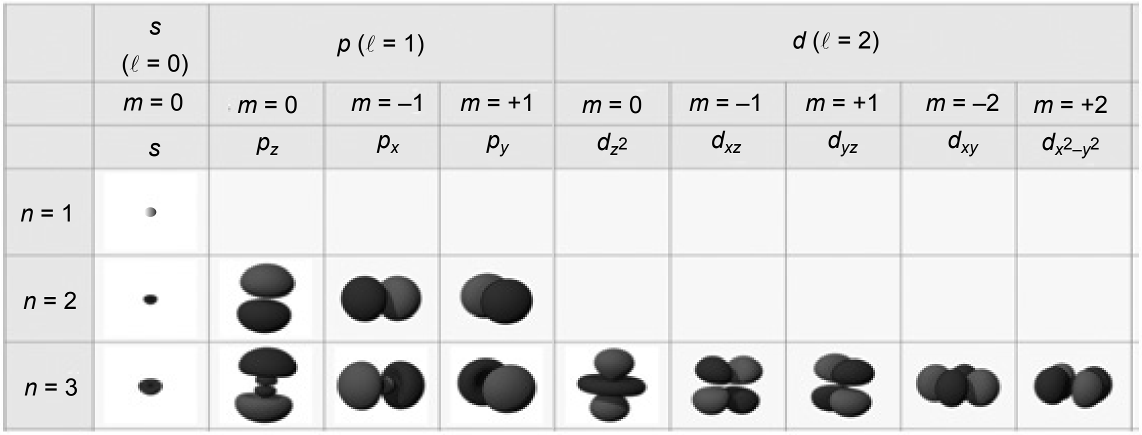
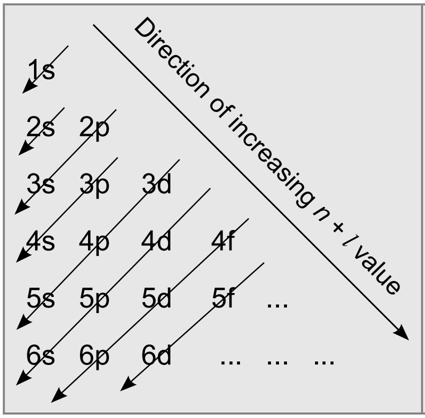


Fig. 1.4: Shapes of orbitals and sub-orbitals derived from quantum numbers

One can fill-up the electrons in various elements using the Aufbau's rule.

Aufbau rule, states that in the ground state of an atom or ion, electrons fill atomic orbitals of the lowest available energy levels before occupying higher levels.



Thus orbitals are filled in the order of increasing energy, using two general rules to help predict electronic configurations:

1. Electrons are assigned to orbitals in order of increasing value of ($n+\ell$).
2. For subshells with the same value of ($n+\ell$), electrons are assigned first to the subshell with lower n.

Fig. 1.5: Filling of electrons as per Aufbau's rule

So now you can construct and visualize just any atom!

Once you know how many and which types of electrons are there in which orbitals and sub-orbitals, you can visualize any elements' quantum mechanical model of any atom; obviously the small and dense nucleus at the centre!

1.1.6 Historical Time-Lines

Table 1.1: Historical Time-Lines

Year	Scientist	Contribution
1600's	Huygens and Newton	The idea of dual nature of matter roots back to 1600's when two competing theories of light were proposed by Huygens (who proposed light consists of waves) and Newton (who proposed light consists of particles).
1900	Max Planck	Referred as "date of birth of quantum mechanics", as on this particular date, Max Planck gave the equation to explain Black Body radiation at the meeting of German Physical Society.
1909	Geoffrey ingram Taylor	Demonstrated that interference patterns of light were generated even when the light energy introduced consisted of only one photon (signifying wave-particle duality)
1911	Lord Rutherford	Proposed nuclear theory of atomic structure
1913	Niels Bohr	Gave Bohr's Model, according to which, electron of an atom moves in close circular path called orbits. Each orbit is associated with a definite amount of energy. Electrons moving in orbits neither absorb or emit energy. This Bohr model could explain successfully the hydrogenatom spectrum. However, it could not explain fine structure and atomic spectrum of atoms having morethan one electron.
1923	Louis de Broglie	A Nobel laureate in 1929, extended wave- particle duality to particles, that electrons in motion are associated with waves.
1925	Werner Heisenberg	He was awarded the Nobel Prize for Physics in 1932 "for the creation of Quantum mechanics". He formulated the matrix mechanics and also the uncertainty principle
1926	Erwin Schrodinger	Founder of Quantum mechanics. He mathematically evolved the wave equation, famously known as Schrodinger equation. He was awarded Nobel Prize in 1933.

Use of ICT

- https://en.wikipedia.org/wiki/Atomic_orbital
- https://chem.libretexts.org/Ancillary_Materials/Laboratory_Experiments/Dry_Lab_Experiments/Simulation%3A_Probabilistic_Interpretation_of_Atomic_Orbitals_(Dry_Lab)

Interesting Facts

- **GPS or Global Positioning System**: Is a network of satellites that has made finding locations and directions quite easy. Each satellite in the GPS constellation includes an ensemble of atomic clocks and these atomic clocks use the principles of quantum theory to measure time.
- **Fluorescent Light:** The light which you are getting from the tubes or those curly bulbs is a result of a quantum phenomenon only. In fluorescent lighting, a small amount of mercury vapour is excited into the plasma.

1.2 QUANTUM MECHANICS AND CHEMICAL BONDING

A chemical bond may be defined as the force that holds the atoms together in a molecule. The chemical bonding in molecules is explained quantum mechanically via two popular theories viz., Valence Bond Theory (VBT) and Molecular Orbital Theory (MOT). Both these approaches assume a guess/approximate wave-function but the physical interpretation is different. Valence Bond Theory considers bond formation by overlapping of valence electrons in atomic orbitals and gives the concept of hybridization. Whereas, Molecular Orbital Theory describes bonding in terms of the combination and arrangement of atomic orbitals to form molecular orbitals that are associated with the molecule as a whole.

This way the quantum mechanical treatment has been extended via more appropriate approximations to conjugated molecules (a popular approach to study the structures of conjugated molecules is via Hückel Molecular Orbital Theory), complexes and even polymers. The results/trends obtained from quantum mechanical approximations of various multi-electron atoms and molecules are in good agreement with the experimental results and it is for this reason, the quantum mechanical wave-function interpretations have found acceptability.

1.2.1 Molecular Orbital Theory

Valence Bond Theory fails to answer certain questions like why He_2 molecule does not exist and why O_2 is paramagnetic? Therefore in 1932 F. Hund and R.S. Mulliken came up with theory known as Molecular Orbital Theory.

According to Molecular Orbital Theory individual atoms combine to form molecular orbitals, as the electrons of an atom are present in various atomic orbitals and are associatedwith several nuclei.

Homonuclear Diatomics: Molecules consisting of two identical atoms **Ex**–H_2, N_2, O_2, F_2.

Heteronuclear Diatomics: Molecules consisting of two non-identical atoms **Ex**–CO,NO, HF, LiF.

1.2.2 Salient features of VBT and MOT

Features of VBT

1. A central metal ion provide number of vacant s,p & d orbital to ligands to form coordinate bond.
2. Number of vacant orbitals provided by central metal ion will equal to its coordination number.

Features of MOTs

1. The atomic orbitals merge with each other to form the molecular orbital.
2. The electrons of the molecules fill the new energy states of the molecular orbitals, similar to filling up of the energy states of the atomic orbitals.

1.2.3 Linear Combination of Atomic Orbitals (LCAO)

As per this method the formation of orbitals is because of Linear Combination (addition or subtraction) **of atomic orbitals which combine to form molecule**. Consider two atoms A and B which have atomic orbitals described by the wave functions Ψ_A and Ψ_B .If electron cloud of these two atoms overlap, then the wave function for the molecule can be obtained by a **linear combination of the atomic orbitals** Ψ_A and Ψ_B *i.e.* **by subtraction or addition of wave functions of atomic orbitals**

$$\Psi_{MO} = \Psi_A \pm \Psi_B \qquad \text{... (1.6)}$$

The above equation forms two molecular orbitals.

Table 1.2: Bonding and Antibonding Molecular Orbitals

Bonding Molecular Orbitals	Anti-Bonding Molecular Orbitals
It forms when addition of wave function takes place.	It forms when molecular orbital is formed by subtraction of wave function takes place,
Equation for Bonding Molecular Orbital is $\Psi_{MO} = \Psi_A + \Psi_B$.	Equation for **Antibonding Molecular Orbitals** is $\Psi_{MO} = \Psi_A - \Psi_B$.
They have lower energy than atomic orbitals involved.	They have higher energy than atomic orbitals.
It is similar to **constructive interference** occurring in phase because of which electron probability density increases resulting in formation of bonding orbital.	It is similar to **destructive interference** occurring out of phase resulting in formation of antibonding orbitals.
Bonding Molecular orbital formed by addition of overlapping of two s orbitals shown in figure below.	Molecular Orbital formed by subtraction of overlapping of two s orbitals shown in figure below.
It **is represented by** σ.	**It is represented by** σ*

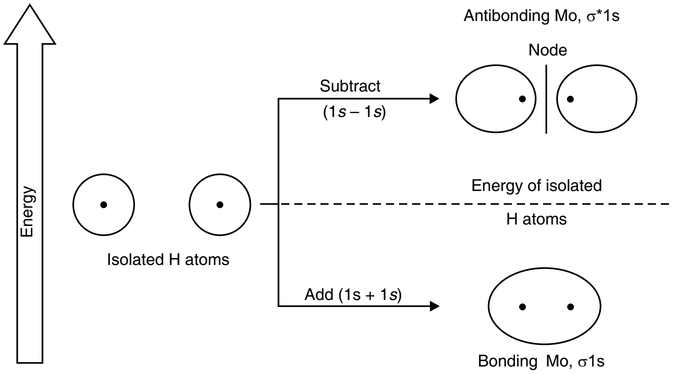


Fig. 1.6: Formation of Bonding and Anti-Bonding Orbital

Therefore, combination of two atomic orbitals results in formation of bonding molecular orbital with (BMO) whereas other is anti-bonding molecular orbital (ABMO).BMO has lower energy and hence greater stability than ABMO.

Molecular orbital diagrams

Filling of Electrons

Now let's learn how to construct a MO diagram by applying **three basic rules.**

- The **Aufbau principle** states that orbitals are filled starting with the lowest energy levels.
- The **Pauli exclusion principle** states that the maximum number of electrons occupying an orbitalis two, with opposite spins.
- **Hund's rule** states that when there are several MO's with equal energy, the electrons occupy the MO's one at a time before two electrons occupy the same MO.

1.2.4 Energy Level Diagram

The factors upon which relative energies of molecular orbitals depend are:

(*i*) Energies of the Atomic orbitals combining to form Molecular Orbitals.

(*ii*) The extent of overlapping between the atomic orbitals. The greater the overlap, the more the bonding orbital is lowered and the anti-bonding orbital is raised in energy relative to AOs

1*s* Atomic Orbitals (AOs) of two atoms form two Molecular Orbitals (MOs) designated as σ1*s* and σ*1*s*. The 2*s* and 2*p* orbitals (eight AOs of two atoms) form four bonding MOs and four anti-bonding MOs as:

Bonding MOs: $\sigma\ 2s$, $\sigma\ 2pz$, $\pi\ 2p_x$, $\pi\ 2p_y$

Anti-Bonding MOσ: $\sigma\ {}^*2s$, $\sigma\ {}^*2p_z$, $\pi\ {}^*2p_x$, $\pi\ {}^*2p_y$

Using Spectroscopy, the energy levels of these molecular orbitals are determined experimentally. The order of increasing energy of molecular orbitals obtained by combination of 1*s*, 2*s* and 2*p* orbitals of two atoms is →

$$\underrightarrow{\sigma 1s,\ \sigma^*1s,\ \sigma 2s,\ \sigma^*2s,\ \sigma 2p_z,\ \pi 2p_x = \pi 2p_y,\ \pi^*2p_x = \pi^*2p_y,\ \sigma^*2p_z}$$

(Energy Increases from left to right)

But experimental evidence for some diatomic molecules have shown that the above sequence of energy levels of MOs is not correct for all the molecules. For example, homonuclear diatomic molecules of second row elements like Li_2, Be_2, B_2, C_2, N_2 , the σ2pz MOs is higher in energy than π 2*px* and π 2*py* MOs

For these atoms, the order is: → $\sigma 1s$, $\sigma^* 1s$, $\sigma 2s$, $\sigma^* 2s$, $[\pi\ 2px = \pi\ 2py]$, $\sigma 2pz$ $[\pi^* 2px = \pi^* 2py]$, $\sigma^* 2pz$

Example 1. Hydrogen molecule–H_2

Atomic number = 1

Electronic configuration–$1s^1$

Order of energy for MO–σ1s, σ*1s

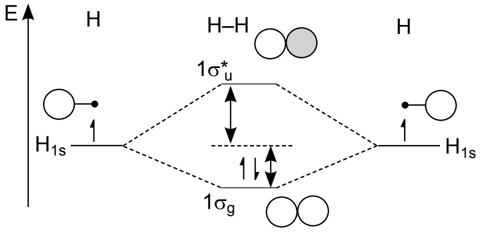


Fig. 1.7: Molecular Orbital diagram for hydrogen molecule

Table 1.3 Order of energy for N_2 and O_2 molecules

N_2 and lower molecules	**O_2 and higher molecules**
Atomic Number of nitrogen = 7 Electronic configuration– **$1s^2$, $2s^2$, $2p^3$** **Order of energy for MO –** σs, σ^*1s, $\sigma 2s$, σ^*2s, $[\pi 2p_x = \pi 2p_y]$, $\sigma 2px$ $[\pi^*2p_x = \pi^*2p_y]$, σ^*2p_z	Atomic number of oxygen atom = 8 Electronic configuration– **$1s^2$, $2s^2$, $2p^4$** **Order of energy for MO** $\sigma 1s$, σ^*1s, $\sigma\ 2s$, σ^*2s, $\sigma 2p_z$, $[\pi 2p_x = \pi 2p_y]$, $[\pi^*2p_x = \pi^*2p_y]$, σ^*2p_z

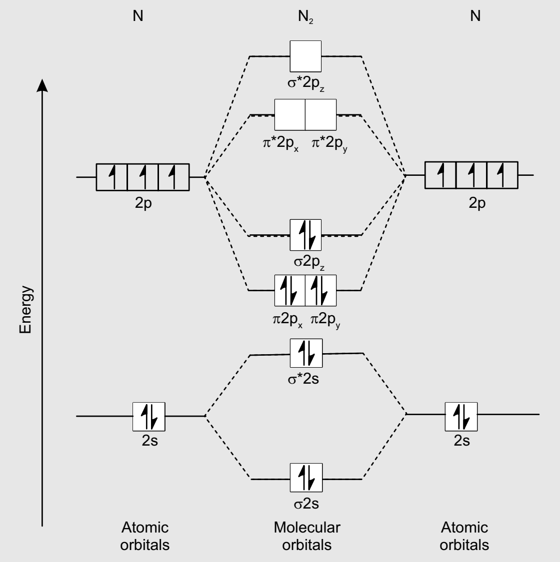


Fig. 1.8: Order of Energy for N_2 and lower molecules

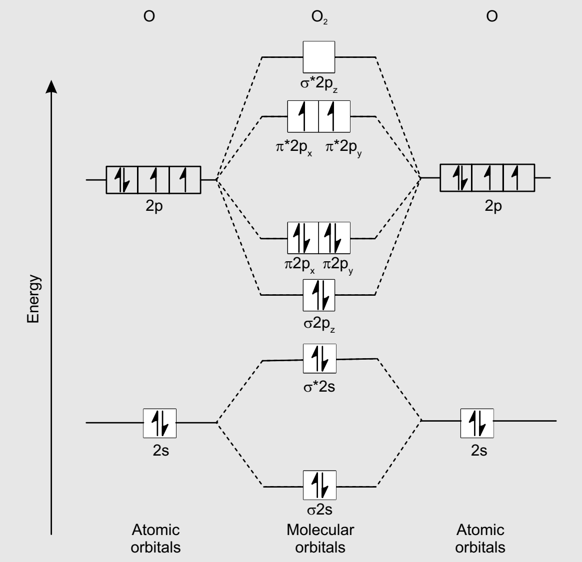


Fig. 1.9: Order of Energy for O_2 and Higher molecules

Explanation

With Nitrogen, we see the two molecular orbitals mixing and the energy repulsion. This is the reasoning for the rearrangement from a more familiar diagram. Notice how the σ from the 2*p* behaves more non-bonding like due to mixing, same with the 2s σ. This also causes a large jump in energy in the 2*p* σ* orbital. **The bond order of diatomic nitrogen is three, and it is a diamagnetic molecule.**

Oxygen, has a similar setup to H_2, but now we consider 2*s* and 2*p* orbitals. When creating the molecular orbitals from the *p*-orbitals, notice the three atomic orbitals split into three molecular orbitals, a singly degenerate σ and a doubly degenerate π orbital. **The bond order of diatomic oxygen is two and Oxygen is an example of a paramagnetic diatomic molecule,**

1.2.5 Bond Order

It may be defined as the half of difference between the number of electrons present in the bonding orbitals and the antibonding orbitals that is,

$$\textbf{Bond order (B.O.)} = \frac{\textbf{(No. of electrons in BMO – No. of electrons in ABMO)}}{\textbf{2}} \qquad \dots (1.7)$$

Those with positive bond order are considered stable molecule while those with negative bond order or zero bond order are unstable molecule.

Solved Example – Calculate bond order of diatomic molecules Nitrogen and Oxygen.

Solution – Formula used for Calculation of bond order

$$\textbf{Bond order (B.O.)} = \frac{\textbf{(No. of electrons in BMO – No. of electrons in ABMO)}}{\textbf{2}}$$

For diatomic Nitrogen molecule

Using Figure 1.9 –

Bond order of N_2 = (6–0) / 2

Bond order of N_2 = 3

Means triple bond (N≡N) will exist between two atoms of Nitrogen to form one molecule of Nitrogen, N_2.

For diatomic Oxygen molecule

Using Figure 1.10–

Bond order of O_2 = (6 –2) / 2

Bond order of O_2 = 2

Means double bond (O=O) will exist between two atoms of Oxygen to form one molecule of Oxygen, O_2

1.2.6 Analysis done by Bond Order

1. **Stability:** If value of bond order is positive, it indicates a stable molecule and if the value is negative or zero, it means that the molecule is unstable.
2. **Bond Dissociation Energy:** The stability of a molecule is measured by its bond dissociation energy. But the bond dissociation energy is directly proportional to the bond order. Greater the bond order, greater is the bond dissociation energy.
3. **Bond Length:** Bond order is inversely proportional to the bond length. The higher the bond order value, smaller is the bond length. For example, the bond length in nitrogen molecule is shorter than in oxygen molecule.
4. **Magnetic Character:** If all the electrons in the molecule of a substance are paired, the substance is diamagnetic (repelled by the magnetic field). On the other hand, if there are unpaired electrons in the molecule, the substance is paramagnetic (attracted by the magnetic field).

1.3 MAGNETIC BEHAVIOUR

If all the molecular orbitals in species are spin paired, the substance is diamagnetic. But if one or more molecular orbitals are singly occupied, it is paramagnetic.

Example: The magnetic property of diatomic Nitrogen is a diamagnetic molecule where as Oxygen is an example of a paramagnetic molecule.

Diatomic Molecule Nitrogen-

p bonding molecular orbital of Nitrogen contains 6 electrons. p^* antibonding orbital have empty orbital means no electrons. All 6 electrons present in *p* orbitals are in paired state, due to absence of unpaired electron it behaves like as diamagnetic molecule.

1.3.1 Diatomic Molecule Oxygen

p-bonding molecular orbital of Oxygen contains 6 electrons. p^* antibonding orbital have two unpaired electrons means p_x^* and p_y^* anti bonding orbitals are half filled with electrons. Due to presence of unpaired electron it behaves like as paramagnetic molecule.

1.4 π – MOLECULAR ORBITALS OF BUTADIENE

The π -molecular orbitals of butadiene is a result of combining the π -molecular orbitals of two ethene molecules. This shows the effect of conjugation. The overall energy of the two bonding butadiene molecular orbitals is lower than that of the two molecular orbitals for ethene. This means that butadiene is thermodynamically more stable than we might expect if its structure were just two isolated double bonds.

1.4.1 HOMO and LUMO

The filled MO highest in energy is called the Highest Occupied Molecular Orbital or HOMO and the empty MO just above it is then the Lowest Unoccupied Molecular Orbital or LUMO. The electrons in the bonding MO's are called bonding electrons and any electrons in the antibonding orbital would be called antibonding electrons.

Explanation

- The HOMO for butadiene is higher in energy relative to the HOMO for ethene. This means butadiene should be more reactive than ethene towards nucleophiles.
- The LUMO for butadiene is lower in energy than the LUMO for ethene. Consequently, butadiene would be expected to be more reactive towards nucleophiles than ethane.
- So whilst butadiene is more stable than two isolated double bonds, it is also more reactive.
- # Together, these are the frontier orbitals of the alkylation, and they control the chemistry of the species.
- Nucleophiles will interact with the LUMO, and electrophiles with the HOMO, creating new pairs of MOs.

Finally, here are the MOs for a system built from four *p*-orbitals: butadiene, $CH_2 = CH - CH = CH_2$.

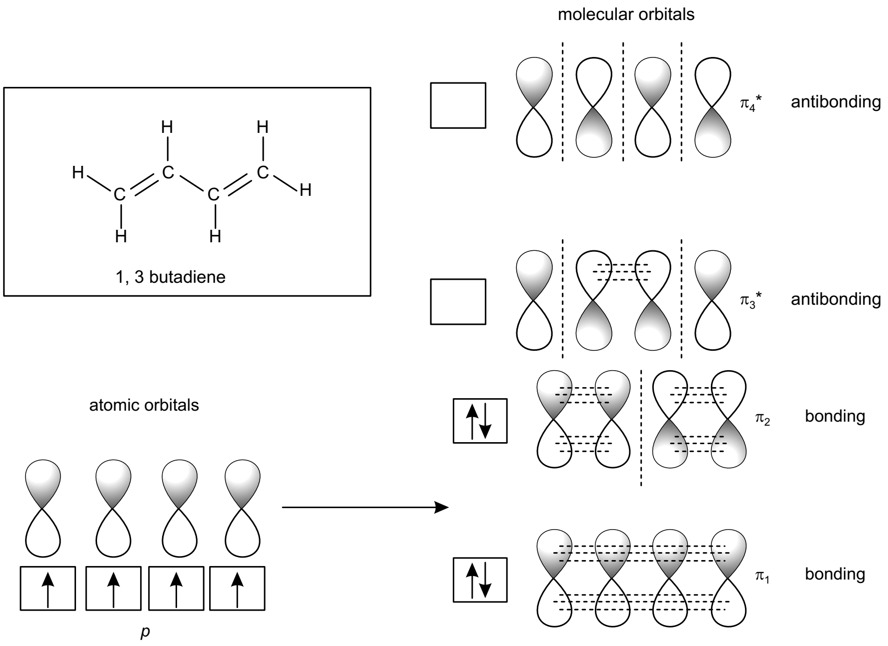


Fig. 1.10: Bonding and antibonding orbitals in 1,3-butadiene molecule

The lowest energy molecular orbital, π_1, has only constructive interaction and zero nodes. Higher in energy, but still lower than the isolated *p*-orbitals, the π_2-orbital has one node but two constructive interactions, thus it is still a bonding orbital overall. Looking at the two antibonding orbitals, π_3^* has two nodes and one constructive interaction, while π_4^* has three nodes and zero constructive interactions.

Butadiene has four *p*-electrons. Two go in the lowest MO, and two in the next. All electrons thus occupy orbitals lower in energy than individual *p*-orbitals, and thus the molecule is stabilized by the interaction of the two double bonds.

1.5 π – MOLECULAR ORBITALS OF BENZENE AND AROMATICITY

MO theory explains why aromatic compounds like benzene are quite stable. Let us first understand how to make out from the structure of a given organic compound whether it is aromatic or not.

Aromaticity

Benzene and other organic compounds display certain characteristic property that differentiate them from aliphatic compounds. These characteristic properties constitute which is called aromatic character or aromaticity.

1.6 HUCKEL'S RULE : CRITERIA FOR AROMATICITY

On the basis of Quantum mechanics E. Huckel in 1931 proposed a new law related to aromaticity which is called Huckel's rule, "A cyclic conjugated compound will be aromatic, if its ring contains $(4n + 2)\pi$ electrons", where n = whole number.

When deciding if a compound is aromatic, go through the following checklist. If the compound does notmeet all the following criteria, it is likely not aromatic in nature.

1. The molecule is cyclic (a ring of atoms)
2. The molecule is planar (all atoms in the molecule lie in the same plane)
3. The molecule is fully conjugated, *i.e.* has continuously delocalized π electrons (*p*-orbitals at every atom in the ring)
4. The molecule has $(4n + 2)$ π electrons (where n is a whole number).

To apply the $(4n + 2)\pi$ rule,

1. First count the number of π electrons in the molecule.
2. Then, set this number equal to $(4n + 2)$ and solve for n.
3. It is a whole number (1, 2, 3,...), the rule has been met.

For example, benzene has six π electrons: 4

$$n + 2 = 6\,\pi$$
$$4n = 4$$
$$n = 1$$

For benzene, we find that $n = 1$, which is a positive integer, so the rule is met.

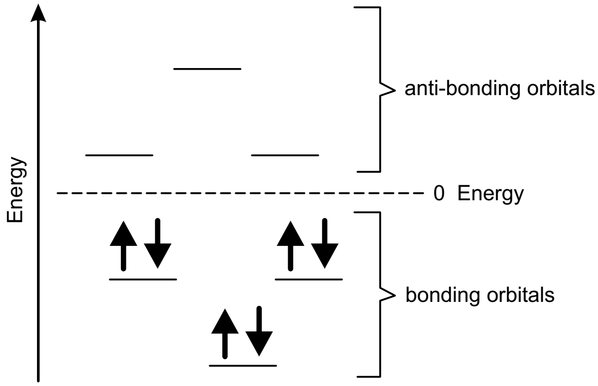
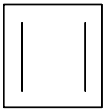


Fig. 1.11: MOT diagram for benzene

According to MO theory, antibonding orbitals of higher energy level are vacant in benzene as no electron is there. The pi electrons of benzene occupy three molecular orbitals, all of which are lower in energy and make benzene molecule very stable.

Aromatic	Aliphatic	Anti-Aromatic
• cyclic, planar, and have continuous delocalization of pi electrons. • (4n + 2) π electrons	• Are either not cyclic, or not planar or do not have continuous delocalization of pi electrons • (No need to count pi electrons)	• cyclic, planar, and have continuous delocalization of pi electrons. • (4n) π electrons

Increasing stability →



Cyclobutadiene has 4 pi electrons
(There are 2 double bonds in the right each double bond is counted as 2 pi electrons)

$4n + 2 = 4$
Find n:

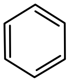
$4n + 2 = 4$
$4n = 4 - 2$
$4n = 2$
$n = ½$

An aromatic compound follows Huckel's rule if n in equal to zero or a positive whole number.

Cyclobutadiere is not aromatic Because n is not a whole number

Fig. 1.12: Explanation of anti-aromaticity in Cyclobutadiene

Benzene



Since benzene has 6 pi electrons:

$4n + 2 = 6$
Find in:

$4n + 2 = 6$
$4n = 6 - 2$
$4n = 4$
$n = 1$ ←

An aromatic compound follows Huckel's rule if n is equal to zero or a positive whole number.

Benzene is aromatic

Fig. 1.13: Explanation of aromaticity in Benzene

Thus MOT explains the extra stability of benzene and other aromatic compounds.

VIDEO RESOURCES

Chemistry & Quantum Chemical Methods

CFT & VBT

Interesting Facts

- Aromatic compounds play important roles in biochemistry and in industry. Most important aromatic compound is benzene.
- As benzene tends to be a by product of various combustion cycles, you are exposed to a small amount of it every time you go outside. Sources include cigarette smoke, gas stations, car exhausts, and other industrial emissions.
- Many products inside your home also contain benzene to some degree. Glues, paints, furniture wax and detergents regularly have benzene as an ingredient.
- Very low levels of benzene have been detected in foodstuffs like fruit, vegetables, nuts, dairy products, eggs, and fish. However, this tends to be pretty safe. Somewhat higher levels have been found in some processed foods.
- Long-term exposure to benzene can lead to blood-related cancers like Leukemia. It can enter the body either through direct absorption via the skin, through inhalation, or consumption.

1.7 CRYSTAL FIELD THEORY

CFT was proposed by the physicist Hans Bethe in 1929. Subsequent modifications were proposed by J.H. Van Vleck in 1935 to allow for some co-valency in the interactions. Crystal Field Theory was developed to describe important properties of complexes (magnetism, absorption spectra, oxidation states, coordination).

1.7.1 Basic Concept

In Crystal Field Theory, it is assumed that the ions are simple point charges (a simplification). When applied to alkali metal ions containing a symmetric sphere of charge, calculations of bond energies are generally quite successful. The approach taken uses classical potential energy equations that take into account the attractive and repulsive interactions between charged particles (that is, Coulomb's Law interactions).

$$E \propto \frac{q_1 q_2}{r^2} \qquad \text{...(1.8)}$$

Where,

E = bond energy between the charges

q_1 and q_2 = charges of the interacting ions

r = separating distance

1.7.2 Postulates of CFT

- Ligand used in the complex formation are either negative ions *e.g.*, F^-, Cl^-, Br^-, CN^-, etc. or neutral molecule consisting dipole *e.g.* NH_3, H_2O etc.
- Complex is a group of central metal ion and ligand surrounding the central metal ion.
- At the time of formation of complex by metal ion and ligands, ligands as point charge move towards the metal ions with their negative charge facing the metal ion.
- Attraction between the central metal ion and ligands in the form of point charges is perfectly electrostatic. Overlapping does not take place between orbitals. Hence, the bond formed is purely ionic.
- Energy of d-orbitals of the metal ion increases when ligands move towards central metal ions.

- Increase in the energy of d- orbitals is not uniform. Energy of orbitals which are found direct in the way of ligand increases to a greater extent as compared to the energy of the orbitals.
- Nature of ligand, nature of metal ions and number of ligands affect the approaching way of ligands.
- Metal ion orbitals get splitted in the set of different energy due to non-uniform increase in the energy of orbitals of metal ion. This splitting of energy depends on the geometry of the complex which may be octahedral or tetrahedral or square planar.

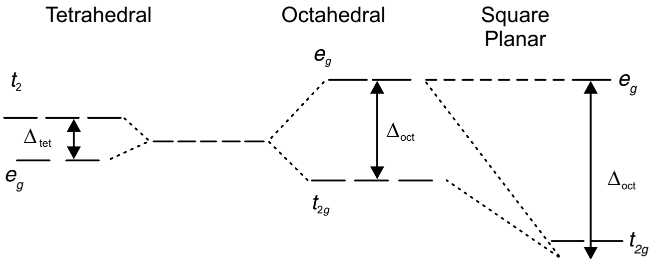


Fig. 1.14: CFT of central metal ion in different geometries of the complex

When the splitting of the *d*-orbital of metal ions occurs, it gets divided into two parts referred as e_g and t_{2g} as shown in the figure.

When examining a single transition metal ion, the five d-orbitals have the same energy. When ligands approach the metal ion, some experience more opposition from the d-orbital electrons than others based on the geometric structure of the molecule. Since ligands approach from different directions, notall d-orbitals interact directly. These interactions, however, create a splitting due to the electrostatic environment. Orientation of orbitals have two types related to their axis.

Axial orientation – In this orientation the lobes of orbitals lies along the axis are d_{z^2} and $d_{x^2-y^2}$ orbitals. According to group theory this group of orbital is called e_g group and these orbital are called e_g orbital.

Non axial orientation – In this orientation the lobes of orbitals are found between the axis. d_{xy}, d_{xz}, and d_{yz}. According to the group theory this group of orbital is called t_{2g} group and these orbital are called t_{2g} orbitals. Angular dependence functions of *d*-orbitals t_{2g} and e_g.

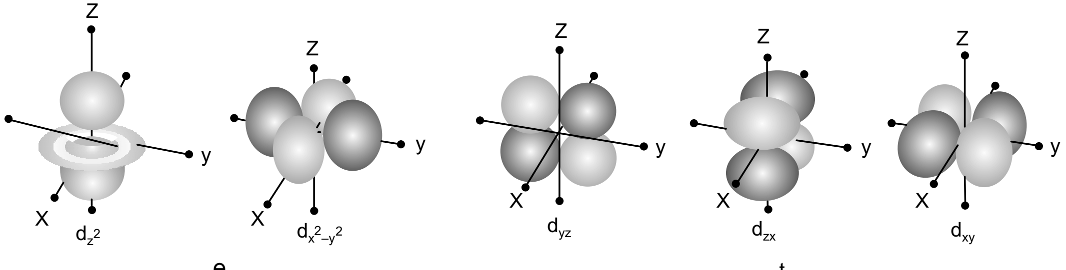


Fig. 1.15: Angular dependence functions of d-orbitals t_{2g} and e_g

1.7.3 Orbital Splitting

The five d-orbitals are given the symbols d_{xy}, d_{zx}, d_{yz}, $d_{x^2-y^2}$ and d_{z^2}. In a complex they are all differently aligned relative to the incoming charge. Depending on the geometry of the complex, some of the *d*-orbitals will point directly towards the ligands, while some will point between them. The orbitals pointing at the ligands will be less stable and higher in energy. Now all the *d*-orbitals are no longer equivalent, giving rise to the phenomenon of orbital splitting, and the difference in energy between the more and less repelled orbitals is called the crystal field splitting parameter.

1.7.4 This splitting is affected by the following factors

- The nature of the ligands. The stronger the ligand, the greater is the splitting.
- Oxidation state of the central metal ion. A higher oxidation state leads to larger splitting.
- Size of d orbitals (*i.e.* , transition series).
- Geometry of the complex.

The electrons can go into either a high spin or low spin arrangement depending on the magnitude of the crystal field splitting energy.

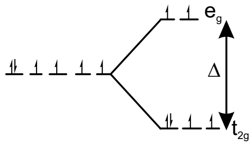
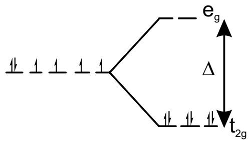
High spin	Low spin
	

Fig. 1.16: Splitting of *d* orbital in high and low spin

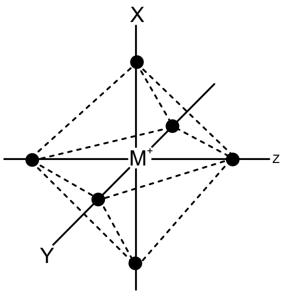
Strong and weak field ligands – The spectrochemical series ranks ligands according the energy difference Δ_0 between the t_{2g} and e_g orbitals in their octahedral complexes. This energy difference is measured in the spectral transition between these levels, which often lies in the visible part of the spectrum and is responsible for the colors of complexes with partially filled d-orbitals. Ligands that produce a large splitting are called strong field ligands, and those that produce a small splitting are called weak field ligands.

An abbreviated spectrochemical series is:

Weak field $I^- < Br^- < Cl^- < NO_3^- < F^- < OH^- < H_2O <$ Pyridine $< NH_3 < NO_2^- < CN^- < CO$ Strong field

1.7.5 Octahedral Complexes

The octahedral arrangement of six ligands surrounding the central metal ion is as shown in the below figure.



In an octahedral complex, the metal ion is at the centre and the ligands are at the six corners. In the figure, the directions x, y and z pointed to the three adjacent corners of the octahedran. The lobes of the e_g orbitals ($d_{x^2-y^2}$ and d_{z^2}) pointed along the *x*, *y* and *z* axis while the lobes of the t_g orbitals (d_{xy}, d_{zx} and d_{yz}) pointed in between the axes. As a result, the approach of six ligands along the *x*, *y*, *z*, –*x*, –*y* and –z directions will increase the energy of $d_{x^2-y^2}$ and d_{z^2} orbitals (which point towards the ligands) much more than that it increases the energy of d_{xy}, d_{zx} and d_{yz} orbitals (which point in between the metal-legand bond axis).

Thus, under the influence of an octahedral field, the d orbitals split into triply degenerate orbitals with less energy and another as doubly degenerate orbitals with higher energy. The main energy level between these two sets of orbitals is taken as zero, which is called bari centre. The splitting between these two orbitals is called crystal field splitting. The magnitude of stabilization will be 0.4 Δ_0 and the magnitude of destabilization will be 0.6 Δ_0.

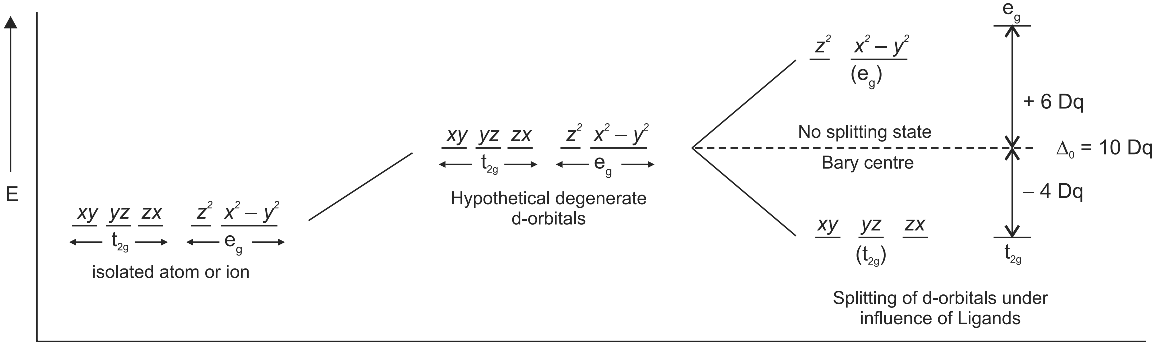
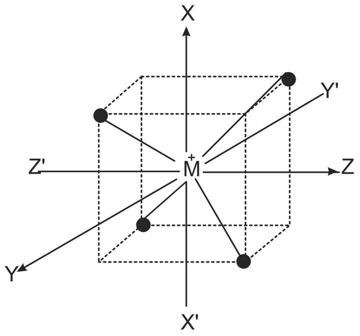


Fig. 1.17: The magnitude of splitting stabilization in Octahedral complex

The magnitude of the splitting of the t_{2g} and e_g orbitals changes from one octahedral complex to another. It depends on the identity of the metal ion, the charge on this ion, and the nature of the ligands coordinated to the metal ion.

1.7.6 Tetrahedral Complex



The tetrahedral arrangement of four ligands surrounding the metal ions is as shown in the figure.

A regular tetrahedron is a cube. One atom is at the centre of the cube and four of the eight corners of the cube are occupied by ligands. The directions x, y and z point to the face centres. The $d_{x^2-y^2}$ and d_{z^2} orbitals point along the x, y and z directions and d_{xy}, d_{zx} and d_{yz} orbitals point in between x, y and z directions.

The direction of approach of ligands does not coincide exactly with either the e_g or t_{2g} orbitals. The t_{2g} orbitals are pointing close to the direction in which the e_g orbitals are lying in between the ligands. As a result, the energy of t_{2g} orbitals increases compared to the energy of e_g orbitals. Thus, d-orbitals again split into two sets- triply degenerate t_{2g} of higher energy and doubly degenerate e_g-orbitals of lower energy. That is, t-orbitals are raised by 0.4 Δ_t in energy and the e_g-orbitals are stabilized by 0.6 Δ_t in energy.

The energy difference between the two sets of orbitals (Δ_t) will be about half the magnitude of that in an octahedral complex (Δ_0).

The *d*-orbitals will thus split as shown below:

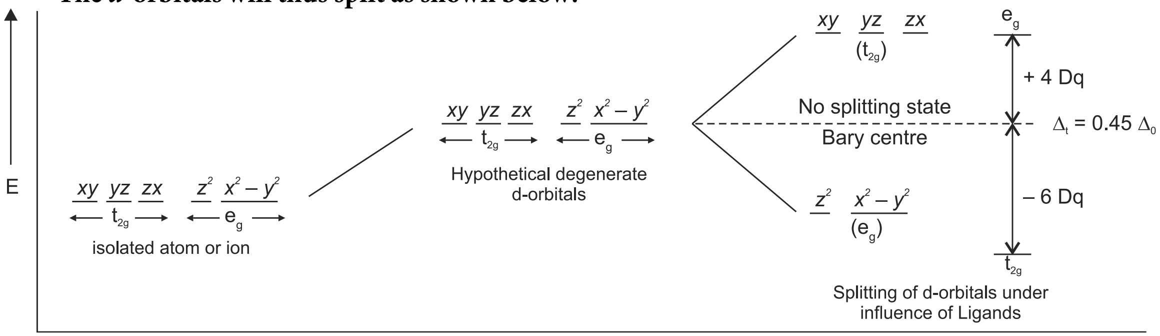


Fig. 1.18: The magnitude of splitting stabilization in tetrahedral complex

1.8 CRYSTAL FIELD STABILIZATION ENERGY

The crystal field stabilization energy (CFSE) is the stability that results from placing a transition metal ion in the crystal field generated by a set of ligands. It arises due to the fact that when the *d*-orbitals are split in a ligand field (as described above), some of them become lower in energy than before with respect to a spherical field known as the bari centre in which all five d-orbitals are degenerate. For example, in an octahedral case, the t_{2g} set becomes lower in energy than the orbitals in the bari centre. Owing to the splitting of the d orbitals in a complex, the system gains an extra stability due to the rearrangement of the d electrons filling in the d levels of lower energy. The consequent gain in bonding energy is known as crystal field stabilization energy (CFSE).

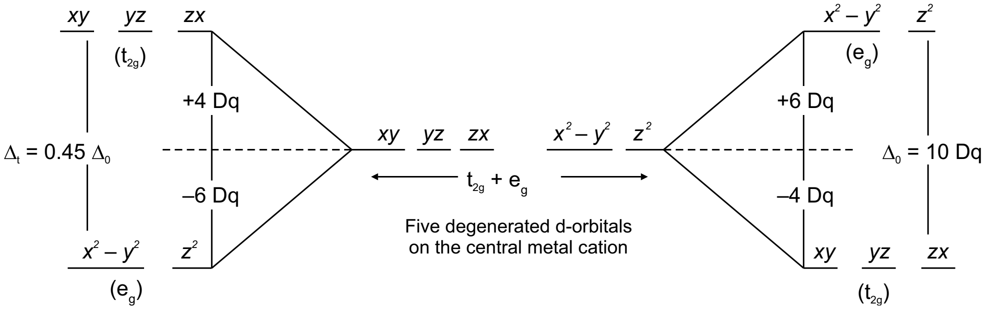


Fig. 1.19: The CFSE in octahedral and tetrahedral complex

If the splitting of the *d*-orbitals in an octahedral field is Δ_{oct}, the three t_{2g} orbitals are stabilized relative to the bari centre by 2/5 Δ_{oct}, and the e_g orbitals are destabilized by 3/5 Δ_o.

For an octahedral complex, CFSE:

$$\text{CSFE} = -\,0.4 \times n(t_{2g}) + 0.6 \times n(e_g)\ \Delta_0$$

Where, $n(t_{2g})$ and $n(e_g)$ are the no. of electrons occupying the respective levels.

For a tetrahedral complex, CFSE:

$$\text{CSFE} = 0.4 \times n\ (t_{2g}) - 0.6 \times n\ (e_g)\ \Delta_t$$

The tetrahedral crystal field stabilization energy is calculated the same way as the octahedral crystal field stabilization energy.

The magnitude of the tetrahedral splitting energy is only 4/9 of the octahedral splitting energy, or $\Delta_t = 4/9\ \Delta_0$.

Summary of rules for high and low spin complexes

- **3d complexes:** Can be high or low spin, depending on the ligand (d^4, d^5, d^6, d^7)
- **4d and 5d complexes:** Always low spin, because Δ is large
- Maximum CFSE is for d^3 and d^8 cases (e.g., Cr^{3+}, Ni^{2+}) with weak field ligands (H_2O, O, F^-,...) and for d^3– d^6 with strong field ligands (Fe^{2+}, Ru^{2+}, Os^{2+}, Co^{3+}, Rh^{3+}, Ir^{3+},...)

Coordination Compound

1.9 MAGNETISM OF TRANSITION METAL COMPLEXES

Magnetic Properties:

According to Bohr's model, the motion of electron is of two types–

1. **Orbital motion –** Electron revolves round the nucleus at a definite angle in an atom. It generates magnetic field or magnetic moment. It is called orbital magnetic moment or orbital moment of electron.
2. **Spin motion –** Electron revolves on its axis continuously, due to this spin motion is called spin magnetic moment or spin moment.

An atom behaves as a small magnet due to these two moments. Magnetic properties of substances are due to these moments.

Fully, empty and partially filled d orbital of transition metal shows various magnetic properties. A range of magnetic properties can be expected, depending on the oxidation state, electronic configuration and coordination number of the central metal. The unpaired electrons in $(n - 1)$ d-orbitals are responsible for the magnetic properties.

1.9.1 Characteristics for Magnetism

- Unpaired electrons exist when the complex has an odd number of electrons or because electron pairing is destabilized.
- The more unpaired electrons, the stronger the magnetic property.
- Tetrahedral complexes have weaker splitting because none of the ligands lie within the plane of the orbitals.
- Square planar compounds are always low-spin and therefore are weakly magnetic.

  In bi-and polymetallic complexes, the electrons may couple through the ligands, resulting in aweak magnet, or they may enhance each other.

1. **Diamagnetism:** When any substance is placed in an external magnetic field, there is an induced circulation of electronsproducing a net magnetic moment aligned in opposition to the applied field. This is the diamagnetic effect and it arises from paired electrons within a sample, since all compounds contain some paired electrons,diamagnetism is a universal property of matter. If a substance has only paired electrons, this effect willdominate, the material will be classified as diamagnetic, and it will be slightly repelled by a magnetic field.
2. **Paramagnetism:** It is produced by unpaired electrons in a sample. The spins and orbital motions of these electrons give rise to permanent molecular magnetic moments that tend to align themselves with an applied field. Because it is much larger than the diamagnetic effect, the paramagnetic effect cancels any repulsions between anapplied field and paired electrons in a sample, Thus even substances having only one unpaired electronper molecule will show a net attraction into a magnetic field. The paramagnetic effect is observed onlyin the presence of an external field.

   Paramagnetism is due to motion and spin of electron. Contribution of orbital moment is negligible.Para magnetism depends on temperature and decreases with increase in temperature.

Paramagnetic substances are attracted in magnetic field. If number of unpaired electrons is n, magnetic moment,

$$\mu = \sqrt{n(n+2)} \qquad \text{...(1.9)}$$

Number of unpaired electrons is calculated by magnetic measurement. Cuprous ion with d^{10} configuration forms diamagnetic salts. Cupric salts are paramagnetic. It means it has d^9 configuration for Cu^{2+} *i.e.* one unpaired electron.

Solved Examples

Calculate magnetic moment and magnetic property of (*a*) Cr^{2+} ion (*b*) Zn^{2+} ion

Solution-

(***a***) ***For Cr^{2+} ion***

Formula used $\mu = \sqrt{n(n+2)}$

Outer electronic configuration = $3d^4$

Number of unpaired electrons = 4

Magnetic moment

$$\mu = \sqrt{4\ (4 + 2)} = 4.89$$

Due to presence of unpaired electron Cr^{2+} ion will be paramagnetic in nature

(***b***) **For Zn^{2+} ion**

Formula used $\mu = \sqrt{n(n+2)}$

Outer electronic configuration = $3d^{10}$

Number of unpaired electrons = 0

Magnetic moment

$$\mu = \sqrt{0\ (2 + 2)} = 0$$

Due to absence of unpaired electron Zn^{2+} ion will be Diamagnetic in nature

Interesting Facts

- The diamagnetic levitation technique has been utilized in biological studies, which mainly deal with its effects on animals, plants, embryos, and cells.
- Paramagnetic materials / Magnets are used to make a tight seal on the doors to refrigerators and freezers, power speakers in stereos, earphones, and televisions.
- These materials are used to store data in computers, and are important in scanning machines called MRIs (magnetic resonance imagers), which doctors use to look inside people's bodies.

Extension of MO Theory to polymers or metals gives rise to Band Theory of Polymers/Metals.

1.10 BAND STRUCTURE OF SOLIDS AND THE ROLE OF DOPING ON BAND STRUCTURE

According to the Bohr atomic model, in an isolated atom the energy of any of its electrons is decided by the orbit in which it revolves. But when the atoms come together to form a solid they are close to each other.Each electron will have a different energy level are called energy bands. These are of two types:

1. **Valence band** – The energy band which includes the energy levels of the valence electrons is called the valence band.
2. **Conduction band** – The energy band above the valence band is called the conduction band. Normally the conduction band is empty.

Solids may be classified in three types on the basis of their electrical property conductors, insulators and semiconductors.

A. **Conductors** – In conductors, there is no band gap between their valence and conduction bands,since they overlap. There is a continuous availability of electrons in these closely spaced orbitals. Through these materials electricity can pass. Examples – Metals.

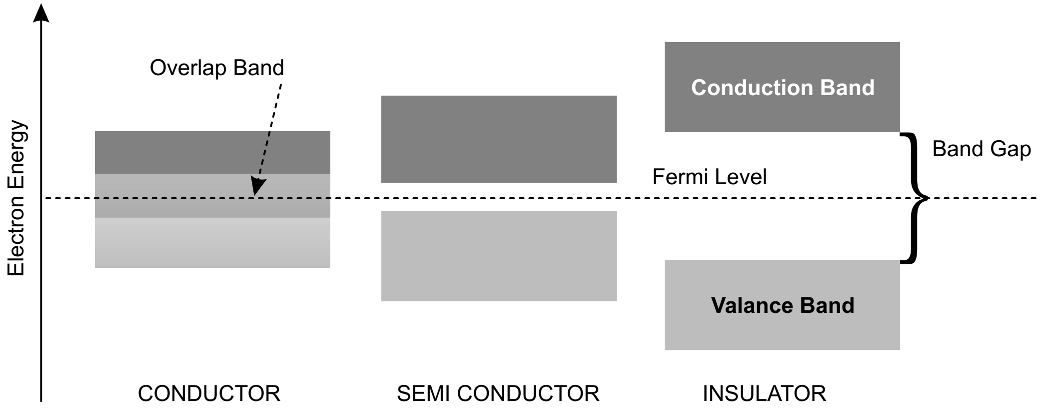
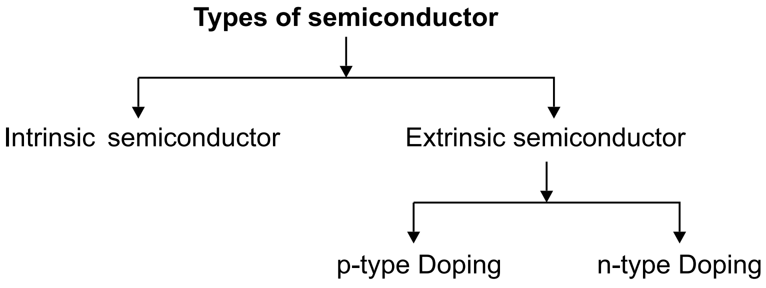


Fig. 1.20: Conductors, Insulators and Semiconductors

B. **Insulators** – In insulators, the band gap between the valence band the conduction band is so largethat electrons cannot make the energy jump from the valence band to the conduction band. Through these materials electricity cannot pass. Example – wood, non metals, plastics.

C. **Semiconductors** – Semiconductors have a small energy gap between the valence band and the conduction band. Electrons can make the jump up to the conduction band, but not with the same ease as they do in conductors. Semiconductors are those materials whose electrical conductivity is between conductors and insulators. Examples – silicon and germanium.



Semiconductors are classified into two types:

(*i*) **Intrinsic Semiconductors:** An intrinsic semiconductor is a semiconductor in its pure state. For every electron that jumps into the conduction band, the missing electron will generate a hole that can move freely in the valence band. Thenumber of holes will equal the number of electrons that have jumped.

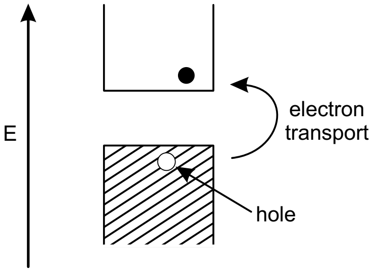


Fig. 1.21: Intrinsic Semiconductors

(*ii*) **Extrinsic Semiconductors:** In extrinsic semiconductors, the band gap is controlled by purposefully adding small impurities to the material. This process is called doping. Doping, or adding impurities to the lattice can change the electrical conductivity of the lattice and therefore vary the efficiency of the semiconductor. In extrinsicsemiconductors, the number of holes will not equal the number of electrons jumped. There are two different kinds of extrinsic semiconductors, *p*-type (positive charge doped) and *n*-type (negative charge doped).

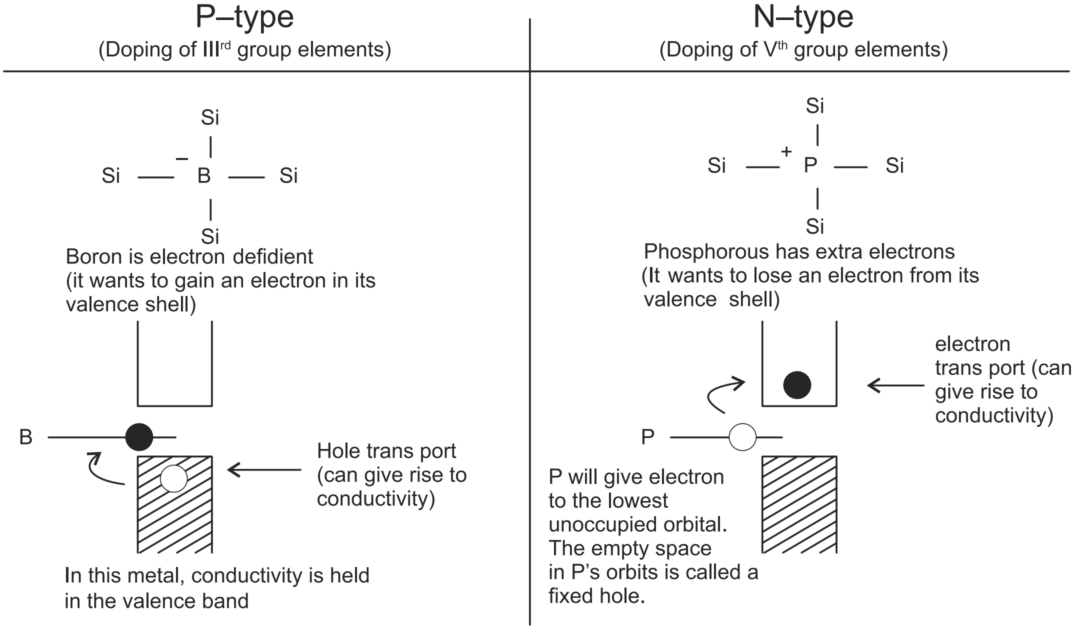


Fig. 1.22: Extrinsic Semiconductors

1.10.1 Doping

Doping means the introduction of impurities into a semiconductor crystal to the defined modification of conductivity.

Doping may be performed two types

n–Type doping

If tetravalent semiconductor Silicon or Germanium doped with penta valent elements (Phosphorous, Arsenic) it is called n-type doping.

n–Type

The 5-valent dopant has an outer electron more than the silicon atoms. Four outer electrons combinewith ever one silicon atom, while the fifth electron is free to move and serves as charge carrier. This freeelectron requires much less energy to be lifted from the valence band into the conduction band, than the electrons which cause the intrinsic conductivity of silicon. The dopant, which emits an electron, is known as an electron donor.

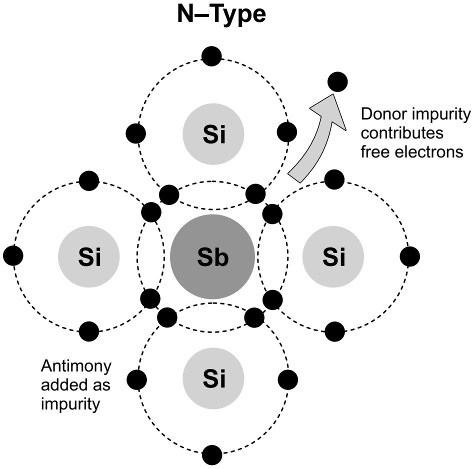


Fig. 1.23: n–type doping

The dopants are positively charged by the loss of negative charge carriers and are built into the lattice, only the negative electrons can move. Doped semimetals whose conductivity is based on free (negative) electrons are n-type or n-doped. Due to the higher number of free electrons those are alsonamed as majority charge carriers, while free mobile holes are named as the minority charge carriers.

p–Type doping

If tetravalent semiconductor Silicon or Germanium is doped with trivalent elements (Boron, Aluminium) it is called p-type doping.

p–Type

The 3-valent dopants can catch an additional outer electron,thus leaving a hole in the valence band of silicon atoms. Therefore the electrons in the valence band become mobile. The holes move in the opposite direction to the movement of the electrons. The necessary energy to lift an electron into the energy level of Indium as a dopant, is only 1% of the energy which is needed to raise a valence electron of silicon into the conduction band.

With the inclusion of an electron, the dopant is negatively charged, such dopants are called acceptors. Due to positive holes these semiconductors are called *p*-conductive or *p*-doped. Analog to *n*-doped semiconductors, the holes are the majority charge carriers, free electrons are the minority charge carriers. *n*-and *p*-doped semiconductors behave approximately equal in relation to the current flow. With Increasing amount of dopants, the number of charge carriers increases in the semiconductor crystal.

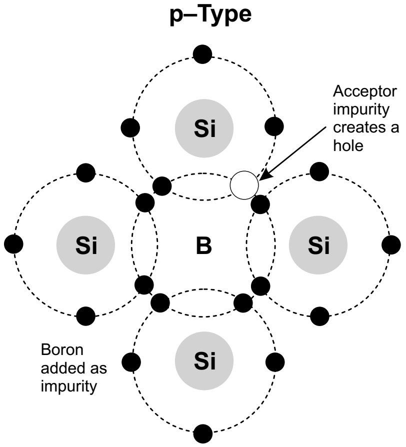


Fig. 1.24: p - type doping

Interesting Facts

- Diode is a combination of n-type and p-type semiconductors extensively used as a rectifier. npn and pnp type of transistors are used to detect or amplify radio or audio signals.
- We are using semiconductors in day today life mobile phones, smartphones, digital cameras, televisions, washing machines, refrigerators and LED bulbs etc.
- In future, the following can be used in place of silicon to make semi-conductors:
  - **Graphene:** A monoatomic sheet of carbon atoms with a very regular lattice is being studied with the goal to replace silicon.
  - **Gallium Nitride:** New material Gallium Nitride (GaN) has the potential to replace silicon. Gallium Nitride can sustain higher voltages than silicon and the current can flow faster through it.
  - **Black phosphorus:** a new semiconductor material made from black phosphorus may be a candidate to replace silicon in future tech.

Video Resources

Band Theory of Metals and Insulators

Fundamentals of semiconductor devices

Semiconductor Device Modeling

SUMMARY

1. **Schrodinger Wave equation** –
   - For One dimension : $\frac{d^2\Psi}{dx^2}+\frac{8\pi^2 m}{h^2}(E - P.E)\Psi = 0$
   - For Three dimensions: $\frac{d^2\Psi}{dx^2}+\frac{d^2\Psi}{dy^2}+\frac{d^2\Psi}{dz^2}+\frac{8\pi^2 m}{h^2}(E - P.E)\Psi = 0$
   - For Laplacian operator: $\nabla^2\Psi+\frac{8\pi^2 m}{h^2}(E - P.E)\Psi = 0$
   - Hydrogen like Atoms : $\frac{d^2\Psi}{dx^2}+\frac{d^2\Psi}{dy^2}+\frac{d^2\Psi}{dz^2}+\frac{8\pi^2 m}{h^2}\left(E+\frac{e^2}{r}\right)\Psi = 0$
2. **Bonding Molecular Orbitals** -When addition of wave function takes place, the type of molecular orbitals formed are called Bonding Molecular orbitals and is represented by

$$\Psi_{MO} = \Psi_A + \Psi_B$$

3. **Anti-Bonding Molecular Orbitals:** When molecular orbital is formed by subtraction of wave function, the type of molecular orbitals formed are called **Antibonding Molecular Orbitals** and is represented by

$$\Psi_{MO} = \Psi_A - \Psi_B$$

4. **Increasing order of energy level for MO** –
   $\sigma 1s$, σ^*1s, $\sigma 2s$, σ^*2s, $[\pi 2p_x = \pi 2p_y]$, $\sigma 2p_z$ $[\pi^*2p_x = \pi^*2p_y]$, σ^*2p_z

5. **Bond Order**- defined as the half of difference between the number of electrons present in the bonding orbitals and the antibonding orbitals that is,

   Bond Order (B.O.) = (No. of electrons in BMO – No. of electrons in ABMO)/ 2

6. **Aromaticity :** If the compound does not meet all the following criteria, it is likely not aromatic.
   - The molecule is cyclic (a ring of atoms)
   - The molecule is planar (all atoms in the molecule lie in the same plane)
   - The molecule is fully conjugated (*p*-orbitals at every atom in the ring)
   - The molecule has $(4n + 2)\pi$ electrons ($n = 0$ or any positive integer)

7. **Postulates of CFT**
   - Ligand are either negative ions e.g., F^-, Cl^-, Br^-,CN^-, etc. or neutral molecule consisting dipole e.g. NH_3, H_2O etc.
   - Complex is a group of central metal ion and ligand surrounding the central metal ion.
   - At the time of formation of complex by metal ion and ligands, ligends as point charge move towards the metal ions with their negative charge facing the metal ion.
   - Metal ion orbitals get splitted in the set of different energy due to non- uniform increase in the energy of orbitals of metal ion. This splitting of energy depends on the geometry of the complex.

8. **Spectrochemical Series:** Increasing value of crystal field splitting (Δ)
   $I^- < Br^- < S^{2-} < SCN^- < Cl^- < N_3^- < F^- <$ urea, $OH^- <$ ox, $O^{2-} < H_2O < NCS^- <$ py, $NH_3 <$ en $<$ bipy, phen $< NO_2^- < CH_3^-$, $C_6H_5^- < CN^-$
   CFSE of octahedral complex = $-0.4 \times n(t_{2g}) + 0.6 \times n(e_g)\ \Delta_0$
   For a tetrahedral complex = $0.4 \times n(t_{2g}) - 0.6 \times n(e_g)\ \Delta_t$

9. **Magnetic properties:**
   (*a*) Diamagnetism: Due to motion and spinning paired electrons
   (*b*) Paramagnetism: Due to motion and spinning of unpaired electrons,

$$\mu = \sqrt{n(n+2)}$$

10. **Conductors:** No band gap between their valence and conduction bands. Examples – Metals.

11. **Insulators:** The band gap between the valence band the conduction band is so large that electrons cannot make the energy jump from the valence band to the conduction band. Example- wood, non metals, plastics.

12. **Semiconductors:** Semiconductors have a small energy gap between the valence band and the conduction band. Electrons can make the jump up to the conduction band, but not with the same ease as they do in conductors.

13. **Doping** means the introduction of impurities into a semiconductor crystal to the defined modification of conductivity. Doping may be performed *n*-Type doping and *p*-Type doping.

EXERCISES

SUBJECTIVE QUESTIONS

1. With the help of MO diagram, arrange the following molecules/ ion in order of their increasing bond length. O_2 , O_2^- and O_2^{2-} .
2. Discuss significance of Schrödinger wave equation, write various forms of Schrödinger wave equations.
3. Draw Molecular orbital diagram of nitrogen (N_2), helium (He) and carbon monoxide (CO) molecules.
4. Explain why the Co $(NH_3)^{3+}$ ion is a diamagnetic, low-spin complex, whereas the CoF_3^- ion is a paramagnetic, high-spin complex.
5. Draw the molecular orbital diagram for the molecular ion, N_2^+. Calculate the number of electrons in the 2*p* molecular orbital and also find out bond order of N_2^+ ion.
6. When the situation of Low Spin and High Spin may arises? Explain it with the help of CFT and draw the diagram with taking a suitable example.
7. Discuss the importance of valence shell and valence electrons? Where it may be applicable in case of molecules and ions?
8. Differentiate between intrinsic semiconductors and intrinsic semiconductors with suitable examples.
9. Define aromaticity. Why benzene is more stable than other aromatic compound? Explain with taking reference of MOT and aromaticity.
10. Name the $(4n + 2)\pi$ Rule. Write any three points of this rule taking suitable example.
11. Name the metal which may be used as semiconductor. What is its requirement and how any element may convert into semiconductor.
12. What is doping? How many types of it? What happed when anyone may mix third or fifth group element in semiconductor?
13. Who discovered Crystal Field Theory? Write the salient features of CFT. Also mention two application of it in determination of structure of metal complexes.
14. What you mean by Crystal Field stabilization Energy? How it helps to explain geometry of metal complexes? Draw energy level splitting sketch octahedral and tetrahedral complexes.

SHORT ANSWER AND SUBJECTIVE QUESTIONS

Q.1 Why silicon and germanium are the two widely used semiconductor materials?

Ans. Because the energy required to release an electron from their valence band (*i.e.* to break their covalent bonds) is very small (1.12eV for Si and 0.72 eV for Ge).

Q.2 What happens to the conductivity of semiconductor with the rise in temperature? Compare with the conductivity of metals.

Ans. With the increase in temperature, the concentration of charge carriers increases resulting in increase in conductivity of semiconductors. The conductivity of metal decreases with the increase in temperature.

Q.3 How do you distinguish between a valence band and a conduction band?

Ans. The valence band is the highest band with electrons in it, and the conduction band is thehighest band with no electrons in it.

Q.4 Is the energy gap between an insulator smaller or larger than the energy gap between a semiconductor?

Ans. Larger

Q.5 What two methods bring conductivity to semiconductors?

Ans. Electron transport and hole transport

Q.6 You are more likely to find electrons in a conduction band if the energy gap is smaller/larger?

Ans. Smaller

Q.7 The values of Energy for which Schrodinger's steady state equation can be solved is called as

(a) Eigen Vectors (b) Eigen Values

(c) Eigen Functions (d) Operators [**Ans.** (c)]

Feedback: Eigen values are the value of Energy for which Schrodinger's steady state equation can be solved. The corresponding wave function is called **Eigen Function**.

Q.8 Which function is considered independent of time to achieve the steady state form?

(a) Ψ (b) $d\Psi/dt$

(c) $d^2\Psi/dx^2$ (d) P.E [**Ans.** (d)]

Feedback: The potential energy of a particle is considered to not depend on time explicitly, the forces that act on it, and hence U, vary with the position only.

Q.9 Among the following ions the pπ dπ overlap could be present in -

(a) NO_2^- (b) NO_{3-}

(c) PO_4^{3-} (d) CO_3^{2-} [**Ans.** (d)]

Feedback: In P=O bond, π–bond is formed by the sidewise overlapping of *d*–orbital of P and *p*-orbital of oxygen. Hence, it is formed by pπ and dπ over lapping. In nitrogen and carbon, no vacant d-orbital is present. So, they do not form pπ–dπ bond.

Q.10 Which of the following is the correct electron configuration for C_2?

(a) $\sigma_{1s}^2\ \sigma_{2s}^2\ \pi_{2py}^2\ \sigma^*_{1s}{}^2\ \sigma^*_{2s}{}^2\ \pi^*_{2py}{}^2$ (b) $\sigma_{1s}^2\ \sigma^*{}_{1s}{}^2\ \sigma_{2s}^2\ \sigma^*{}_{2s}{}^2\ \pi_{2py}^2\ \pi^*{}_{2pz}{}^1\ \sigma_{2p}^1$

(c) $\sigma_{1s}^2\ \sigma^*{}_{1s}{}^2\ \sigma_{2s}^2\ \sigma^*{}_{2s}{}^2\ \pi_{2py}^2\ \pi_{2pz}^2$ (d) $\sigma_{1s}^2\ \sigma^*{}_{1s}{}^2\ \sigma_{2s}^2\ \sigma^*{}_{2s}{}^2\ \pi_{2py}^1\ \pi_{2pz}^1$ [**Ans.** (c)]

Feedback: Because C_2 is a diamagnetic compound and C_2 have $(12e^-)$

Electronic Configuration will be = $\sigma_1 s^2 \sigma^* 1s^2 \sigma^2 s^2 \sigma^* 2s^2 \pi^2 px^2 = \pi^2 p^2 y$

It does not contain any unpaired electrons.

Q.11. What is the bond order in O_2^+?

(a) 3.5 (b) 2.0

(c) 1.5 (d) 2.5 [**Ans.** (d)]

Feedback: The molecular configuration of O_2^+ is as

$\sigma_{1s}^2, \sigma^*{}_{1s}{}^2, \sigma_{2s}^2, \sigma^*{}_{2s}{}^2, \sigma^*{}_{2pz}{}^2, \pi_{2py}^2 \approx \pi_{2pz}^2, \pi^*{}_{2py}{}^1 \approx \pi^*{}_{2pz}{}^0$

Bond order = Nb–Na /2 = 10–5/2

∴ Bond order = 2.5

Q.12 If the sign of the wave function is unchanged when the orbital is reflected about its centre, the orbital is -

(a) Gerade (b) Ungerade

(c) Gerade as well as Ungerade (d) None of the mentioned [**Ans.** (a)]

Feedback: If the sign of the wave function is unchanged when the orbital is reflected about its center (*i.e.* , x, y and z are replaced by –x, –y and –z), the orbital is gerade. ...

Q.13 Bond Order of O_2, F_2, N_2 respectively are ___________

(a) +1, +2, +3 (b) +2, +3, +1

(c) +2, +1, +3 (d) +3, +2, +1 [**Ans.** (c)]

Feedback: Bond Order = [[Number of electrons in bonding molecular orbital]–[Number of electrons in antibonding molecular orbital]]/2.

Q.14 Arrange the following molecules in decreasing bond length.

(a) $O_2 > O_2^- > O_2^+ > O_2^{2-}$ (b) $O_2^{2-} > O_2^- > O_2 > O_2^+$

(c) $O_2^{2-} > O_2^- > O_2^+ > O_2$ (d) $O_2^- > O_2^+ > O_2^{2-} > O_2$ [**Ans.** (b)]

Feedback: The bond length is inversely proportional to the bond order. Therefore, the correct is: $O_2^{2-} > O_2^- > O_2 > O_2^{+}$.

Q.15 The relative energies of molecular orbitals in increasing order have been found to be as follows.

$(\sigma_{1s}) < (\sigma^*_{1s}) < (\sigma_{2s}) < (\sigma^*_{2s}) < [(\pi_{2py})(\pi_{2pz})] < (\sigma_{2px}) < [(\pi^*_{2py})(\pi^*_{2pz})] < (\sigma^*_{2px})$

(a) For O_2 to Ne_2 (b) For H_2 to N_2

(c) For H_2 to Ne_2 (d) For N_2 to Ne_2 [**Ans.** (b)]

Feedback: The relative energies of molecular orbitals in increasing order have been found to be $(\sigma_{1s}) < (\sigma^*_{1s}) < (\sigma 2s) < (\sigma^*_{2s}) < [(\pi_{2py})(\pi_{2pz})] < (\sigma_{2px}) < [(\pi^*_{2py})(\pi^*_{2pz})] < (\sigma^*_{2px})$ for H_2 to N_2 only.

Q.16. Which of the following doping will produce a p-type semiconductor?

(a) Germanium with phosphorus (b) Silicon with germanium

(c) Germanium with antomony (d) Silicon with indium [**Ans.** (d)]

Feedback: Doping of third group element in silicon or germanium will form p-type semiconductor.

DESIGN INNOVATIVE PROJECTS / ACTIVITIES

Project 1. Enlist 5-10 metal complexes of your choice and compare it's characteristics under following heads

- State of spin {Low spin/ High spin}
- Geometry
- Magnetic properties
- Colour

Project 2. Tremendous example of n and p-type semiconductors are available around us at every electrical and electronic devices. Make a list of devices which you are using from morning to night contains semiconductors.

SUGGESTED READINGS

BOOKS

1. Selected Topics in Inorganic Chemistry by Wahid U Malik , GD Tuli & RD Madan , S Chand Publishing , ISBN: 81-219-0600-8.
2. Atkins' Physical Chemistry by Peter Atkins & Julio de Paula, et al. Oxford publishing.

E-RESOURCES

- https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Map%3A_Physical_Chemistry_(McQuarrie_and_Simon)/03%3A_The_Schrodinger_Equation_and_a_Particle_in_a_Box
- https://en.wikipedia.org/wiki/Crystal_field_theory
- https://chem.libretexts.org/Bookshelves/Inorganic_Chemistry/Map%3A_Inorganic_Chemistry_(Housecroft)/06%3A_Structures_and_energetics_of_metallic_and_ionic_solids/6.08%3A_Bonding_in_Metals_and_Semicondoctors/6.8B%3A_Band_Theory_of_Metals_and_Insulators

KNOW MORE

1. **The Spectrochemical Series**

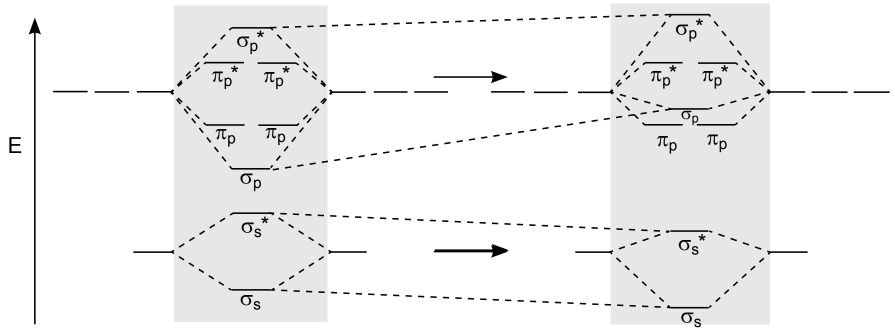
   The variation of the magnitude of the crystal field splitting (Δ) with the nature of the ligand followsa regular order, known as spectrochemical series. This series is given below in the order in which they produce increasing value of Δ.

   $I^- < Br^- < S^{2-} < SCN^- < Cl^- < N^- < F_3^- <$ urea, $OH^- <$ ox, $O_2^- < HO < NCS^- < py_2$, $NH < en <$ bipy$_3$, phen $< NO_2^- < CH_3^-$, $C_6H_5^- < CN^-$

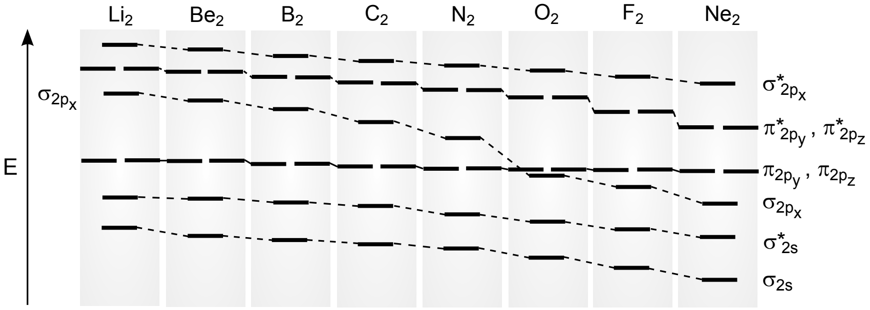
   - Weak field ligands have small Δ and will form high spin complexes.
   - Strong field ligands have large Δ and will form low spin complexes.

2. Schematic representation about transition and distribution of energy levels in various orbitals in molecules

   (a) Oxygen and Nitrogen molecules



(b) In second period of periodic Table



3. Types of Magnetic properties

Properties	Description	Alignment of magnetic dipoles	Examples	Application
Diamagnetic	They are weakly repelled by the magnetic fields	All the electrons in theorbitals are paired andare completely filled.	NaCl, Benzene	Behaves like an insulator.
Paramagnetic	They are weakly attracted by the magnetic fields.	Contains at least one unpaired electron in the orbital.	O_2, Cu^{2+} etc.	Electronic appliances
Ferromagnetic	Strongly attracted by the magnetic field. They can be magnetised permanently	Consists of unpaired electrons, all having the same direction	Cobalt, Nickel, CrO_2 etc.	CrO_2 is commonly used in making cassette recorder.
Antiferromagnetic	Net magnetic moment is zero.	Dipole moments are arranged in a compensatory way	NiO, MnO, V_2O_3 etc.	–
Ferrimagnetic	Possess small net magnetic moments	Unequal number of parallel and antiparallel arrangement of magnetic moments	Fe_3O_4	–

4. CFSE for d^1 to d^{10} electrons for low spin and high spin complexes

The Electron Arrangement and CFSE for Octahedral Complexes				
Configuration	**Strong field (low spin)**	**CFSE**	**Weak filed (high spin)**	**CFSE**
d^1	$t_{2g}{}^1e_g{}^0$	4Dq	$t_{2g}{}^1e_g{}^0$	4Dq
d^2	$t_{2g}{}^2e_g{}^0$	8Dq	$t_{2g}{}^2e_g{}^0$	8Dq
d^3	$t_{2g}{}^3e_g{}^0$	12Dq	$t_{2g}{}^3e_g{}^0$	12Dq

The Electron Arrangement and CFSE for Octahedral Complexes				
Configuration	**Strong field (low spin)**	**CFSE**	**Weak filed (high spin)**	**CFSE**
d^4	$t_{2g}^4e_g^0$	16Dq – p	$t_{2g}^3e_g^1$	6Dq
d^5	$t_{2g}^5e_g^0$	20Dq – 2p	$t_{2g}^3e_g^2$	0Dq
d^6	$t_{2g}^6e_g^0$	24Dq – 2p	$t_{2g}^4e_g^2$	4Dq
d^7	$t_{2g}^6e_g^1$	18Dq – p	$t_{2g}^5e_g^2$	8Dq
d^8	$t_{2g}^6e_g^2$	12Dq	$t_{2g}^6e_g^2$	16Dq
d^9	$t_{2g}^6e_g^3$	6Dq	$t_{2g}^6e_g^3$	6Dq
d^{10}	$t_{2g}^6e_g^4$	0	$t_{2g}^6e_g^4$	0

P = Pairing Energy

Note that Dq for strong field is higher as compare to Dq for weak field.

2

Spectroscopic Techniques and Applications

UNIT SPECIFIC

This unit discusses the topics: Principles, selection rules and applications of Electronic, Fluorescence,Vibrational and rotational spectroscopy. Applications of MRI, NMR and XRD techniques.

RATIONALE

This unit deals with the identification and characterization of molecules and compounds through interaction with electromagnetic radiations. It is the backbone of the analytical chemistry. High sensitivity and accuracy of the spectroscopic instruments with reproducible results play a very important role in research and development.

PRE-REQUISITES

Chemistry: Electromagnetic spectrum, Structure and formula of simple Organic compounds

Maths: Basic Algebra

Physics: Electromagnetic interaction and nature of waves.

LEARNING OUTCOMES

After this Unit, students must be able to:

U2-O1: Apply principles of UV-Visible & fluorescence spectroscopy for simple organic compounds

U2-O2: Interpret vibrational and rotational spectroscopy for simple organic compounds

U2-O3: Correlate the structure of simple organic compounds using NMR spectra

U2-O4: Techniques related to surface characterization, diffraction and scattering techniques.

U2-O5: State the applications of different spectral techniques including MRI in medical and other fields.

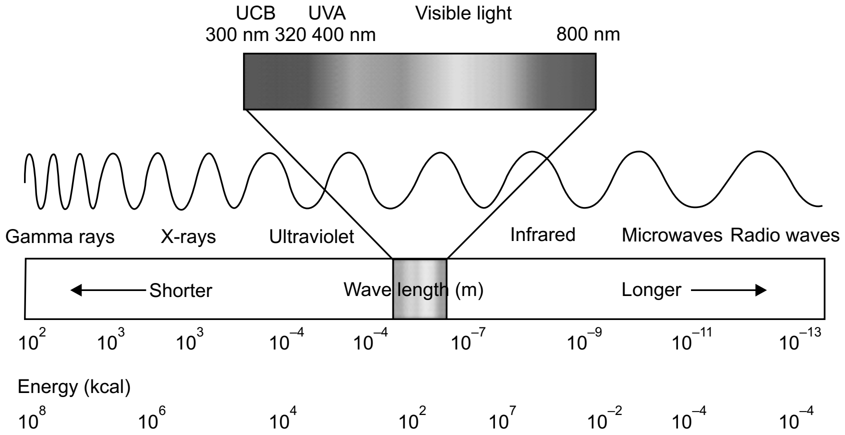
MAPPING OF UNIT WISE LEARNING OUTCOMES WITH THE COURSE OUTCOMES

Outcome	EXPECTED MAPPING WITH COURSE OUTCOMES (1- Weak Correlation; 2- Medium correlation; 3- Strong Correlation)				
	CO-1	CO-2	CO-3	CO-4	CO-5
U2-O1			3		
U2-O2			3		

Outcome	EXPECTED MAPPING WITH COURSE OUTCOMES (1- Weak Correlation; 2- Medium correlation; 3- Strong Correlation)				
	CO-1	CO-2	CO-3	CO-4	CO-5
U2-O3	2				1
U2-O4			3		
U2-O5			2		

INTRODUCTION

Spectroscopy is a technique that uses the interaction of energy with a sample toper form an analysis. The optical system which allows production and viewing of the spectrum is called a spectroscope.



The electromagnetic spectrum

Fig. 2.1: Region of Electromagnetic radiations

Let us know the historical background of its evolution –

HISTORICAL TIME LINES

S. No.	Period	Name	Discovery
1.	1814	Joseph von Fraunhofer.	first spectroscope was invented
2	1860	Robert Bunsen and Gustav Kirchhoff	The systematic attribution of spectra to chemical elements began
3.	1911-1913	Otto Heimstaedt and Heinrich Lehmann	First fluorescence microscopes as an outgrowth of the UV microscope
4	1941	Arnold Beckman	Introduced DU UV-vis spectrophotometer.
5.	1944	Isidor Isaac Rabi	Discovery of NMR and got Nobel Prize in Physics

Basis of spectroscopy is the study of nature and characters of Electromagnetic waves while interaction with molecules. Figure 2.1 shows brief detail of spectrophotometric parameters-

2.1 BASIC PRINCIPLES OF SPECTROSCOPY

(a) Born Oppenheimer Approximation
(b) Franck–Condon principle
(c) Jablonski Diagram

2.1.1 Born Oppenheimer Approximation

The atomic spectra arises from the transition of an electron between the atomic energy levels, whereas the molecular spectra arise from three types of energy changes (molecular rotation, molecular vibration and electronic transition). According to Born Oppenheimer approximation, the total energy of a molecule is given by ,

$$E = E_{\text{translational}} + E_{\text{rotational}} + E_{\text{vibrational}} + E_{\text{electronic}} \quad \text{...(2.1)}$$

All of these energies are quantized except translational energy. It is negligibly small and so the Born Oppenheimer approximation can be represented as

$$E = E_{\text{rotational}} + E_{\text{vibrational}} + E_{\text{electronic}}$$

Increasing order of energy represented as -

$$E_{\text{electronic}} >> E_{\text{vibrational}} >> E_{\text{rotational}} >> E_{\text{translational}}$$

Table 2.1 Energy in diatomic molecules

S. No.	Type of energy	Arises in molecule	Electromagnetic spectrum.
1.	Translational energy	When its center of gravity changes as a consequence of motion	–
2.	Rotational energy	When a molecule undergoes rotation about an axis perpendicular to the inter nuclear axis and passing through the center of gravity of the molecule.	Microwave region
3.	Vibrational energy	Because of to and fromotion of the nuclei of the molecule in such a way that center of gravity does not change	Infrared region
4.	Electronic energy	Associated with the transition of an electron from the ground state energy level to an excited state energy level of the molecule because of the absorption of a photon of a suitable frequency.	UV and visible region

2.1.2 Franck–Condon principle

The Franck–Condon principle is a rule in spectroscopy and quantum chemistry that explains the intensity of vibronic transitions. Vibronic transitions are the simultaneous changes in electronic and vibrational energy levels of a molecule due to the absorption or emission of a photon of the appropriate energy.

Franck–Condon principle is the approximation that an electronic transition is most likely to occur without changes in the positions of the nuclei in the molecular entity and its environment.

Franck-Condon principle (vertical transitions):

- Electrons respond much faster than nuclear motion, therefore an excitation proceeds without a change to the nuclear geometry.
- Light will be resonant with electronic energy gap at equilibrium nuclear geometry.

2.1.3 Jablonski Diagram: Relaxation Mechanism for Excited State Molecules

Once a molecule has absorbed energy in the form of electro magnetic radiation, there are a number of routes by which it can return to ground state (the statistically most common energy state for room temperature chemical species). The graph, termed a Jablonski diagram, shows a few of these processes.

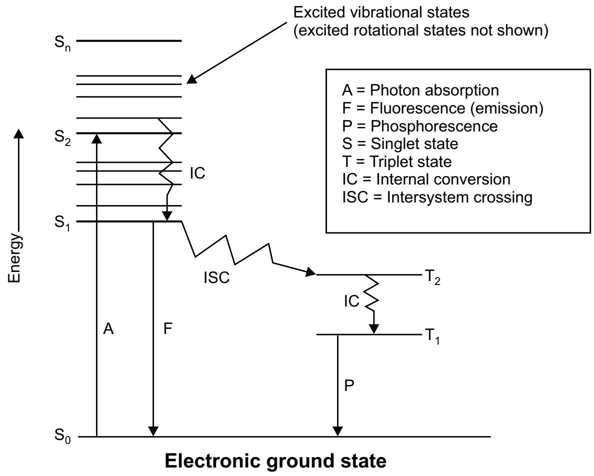
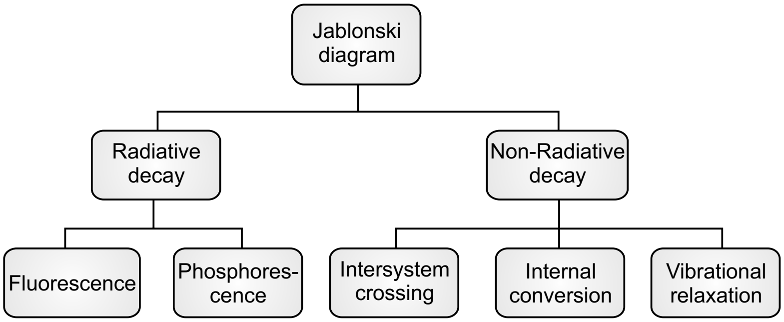


Fig. 2.2: Jablonski diagram



Flow Chart. 2.1: Tabular information of modes of decay of electromagnetic radiations

Radiative Decay

Florescence: If the photone emission (shown here as a short wave length, that is downward pointing, "long" line in the diagram) occurs between the same spin state (*e.g.* $S_1 \rightarrow S_0$) this is termed fluorescence. Lifetimes of fluorescent states are very short (1×10^{-5} to 10^{-8} seconds)

Phosphorescence: If the spin state of the initial and final energy levels are different (e.g. $T_1 \rightarrow S_0$), the emission (loss of energy) is called phosphorescence. It has longer wave length with lower energy so represented by shorter length line. Lifetimes of phosphorescence is 1×10^{-4} seconds to minutes or even hours.

Non-radiative Decay

1. **Internal conversion (IC):** Internal conversion is the **radiation less** transition between energy states of the same spin state(compare with fluorescence—a radiative process).
2. **Inter system crossing (ISC):** Inter system crossing is a radiation less transition between different spin states (compare to phosphorescence).
3. **Vibrational relaxation (VR):** Relaxation of the excited state to its lowest vibrational level is called vibrational relaxation. It is the most common way among all three modes of dissipation of energy. It occurs very quickly ($<1 \times 10^{-12}$ sec).

Points to Remember

- Electronic transitions involve much larger energies than vibrational and rotational transitions.
- Each electronic transition is accompanied by vibrational and rotational transitions.
- he combination of vibrational transitions with electronic transitions is called "vibronic" transitions.
- There is no selection rule for vibrational transitions between two electronic states.
- The Franck-Condon principle governs the intensity distribution of vibronic transitions.

2.2 ELECTRONIC SPECTROSCOPY

Electronic spectroscopy is reliable and accurate analytical method that measures absorption, transmission and emission of UV and visible light by matter.

Visible region corresponds to 800-400 nm and Ultra violet region corresponds to 400-100 nm.

When UV or visible light strikes on atoms or molecules, electronic transition between energy levels may occur. Absorption of UV or visible light results in transition of electron from lower energy level to higher energy level.

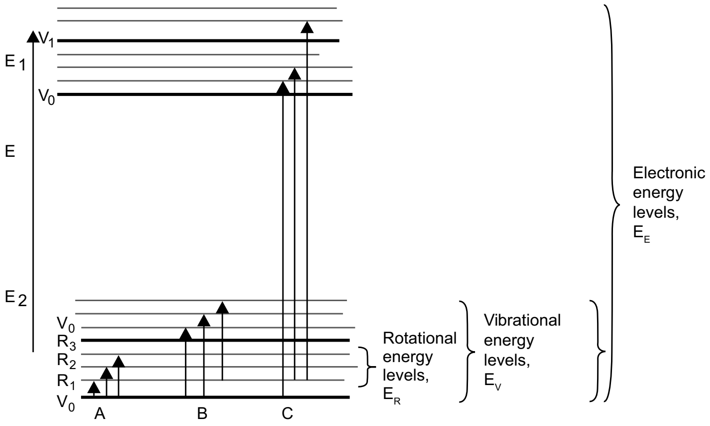


Fig. 2.3: Transition of spectrum in various energy levels
$E_R < E_V < E_E$

The energy differences between the electronic states in a molecule are much larger than those between the successive vibrational levels. It has been observed that a smallest change in electronic energy will produce a large change in the vibrational energy. A change in the vibrational energy produces change in vibrational quantum number giving bands in the electronic spectra. Similarly a small change in the vibrational energy produces a large change in rotational quantum number as a result of which rotation transition occurs resulting in rotational spectra in the same electronic spectra. Thus we can see that each electronic transition includes electronic, vibrational and rotational transitional complications in the spectrum.

2.2.1 Types of Electronic Transitions

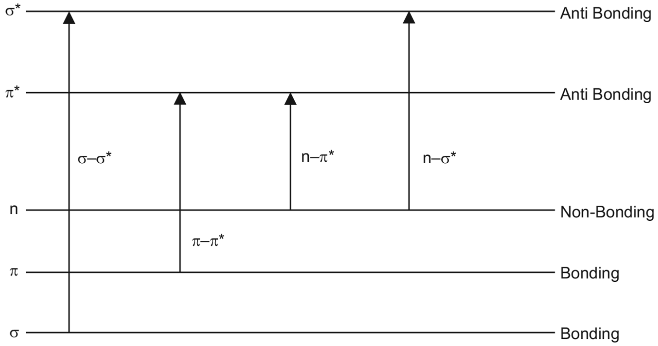


Fig. 2.4: Electronic energy levels and Electronic Transitions

The electronic transitions in decreasing order of energy are:

$\sigma\text{–}\sigma^* > n\text{–}\sigma^* > \pi\text{–}\pi^* > n\text{–}\pi^*$

(i) **$\sigma \rightarrow \sigma^*$ transition:** A electronic transition from a bonding sigma orbital to antibonding sigma orbital (higher energy) is designated as σ to σ^*. These transition occur in compound having single bond only. In alkanes, this is only transition available. Absorption band occurs in far UV region~150nm. Such transition is studied in vacuum UV region since below 200 nm, Oxygen present in air begins to absorb.

(ii) **$n \rightarrow \sigma^*$ transition:** Saturated compounds having lone pair of electrons undergo $n \rightarrow \sigma^*$ transition along with σ to σ^* transition e.g. saturated halides, alcohols, ethers, aldehydes, ketones, amines, etc. Absorption bands appear at longer wave length~ 180-200 nm (near UV region).

(iii) **$\pi \rightarrow \pi^*$ transition:** These transitions occur in unsaturated compound. Since n electrons are loosely held, hence electronic transition require comparatively less energy. Absorption bands appear around 170-190 nm in unconjugated alkenes *e.g.* dienes, trienes, aromatic compound.

(iv) **$n \rightarrow \pi^*$ transition:** Unsaturated compound having hetero atom with lone pair of electrons like S, N, O show this type of transition. This transition involves least amount of energy than all transition and occur at longest wavelengths(> 200 nm). *e.g.* : Ketones, aldehydes.

2.2.2 Applications of Electronic Spectroscopy

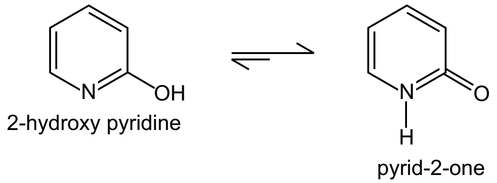
(a) **Extent of conjugation:** Longer the conjugation, longer the maximum wave length of absorption spectrum (λ_{max}) Sufficient conjugation shifts λ_{max} to visible region of spectrum. Compound becomes coloured on sufficient conjugation. Tomato is red coloured due to Caretenoid, Lycopene which has 11 conjugated double bonds.

(b) **Distinction between conjugated and non-conjugated compounds:** UV spectroscopy helps to distinguish conjugated dienes from non-conjugated one, conjugated dienes from conjugated trienes etc.

(c) **Detection of functional group:** UV spectroscopy help us to detect certain functional group. For example absence of any absorption above 200 nm shows the absence of conjugation, benzenering, carbonyl compound.

(d) **Study of Geometrical isomerism:** Trans isomer absorbs at higher wave length than C is isomers.

(e) **Study of Tautomerism:** UV spectroscopy can be used to identify the stable tautomeric species. For *e.g.*



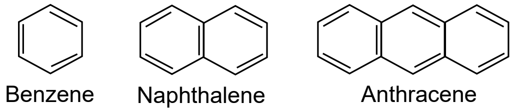
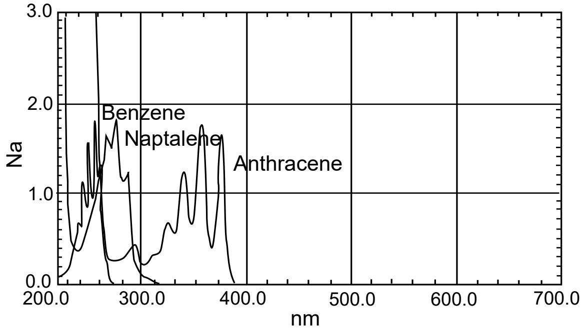
Above equilibrium is more shifted towards right side i.e. UV spectrum of solution resembles that of a solution of pyrid-2-one and is different from that of 2-hydroxypyridine. Thus UV spectrum showsketone isomer predominates.

(f) **Identification of an unknown compound:** An unknown compound can be identified by comparing its spectrum with known spectra. If the spectra coincide, the two compounds must be identifical. If spectra don't coincide, the two compounds must be different.

(g) **Electronic spectroscopy** is widely used to detect environmental pollution.

Let us discuss UV spectra by taking example of some simple molecules–

1. **UV spectra for determination of extent of Conjugation–**

 Structures of Benzene, Naphthalene and, Anthracene  **Fig. 2.5:** Absorption Spectra of Benzene,Naphthalene and Anthracene	1. Extent of conjugation is more in anthracene as compare to Naphthalene and benzene. 2. The molar absorption coefficient is a measurement of how strongly a substance absorbs light. The larger its value, the greater the absorption. 3. The peak wavelengths tend to be shifted toward the long wavelength region as the conjugated system gets larger. 4. λ_{max} shifted from 256nm benzene to 375 nm in anthracene

2. **Identification of unknown Compound–** With the help of standard values of λ_{max} in UV spectral region one can predict unknown Compound.

2.2.3 Selection Rules For Electronic Transition

During absorption of electromagnetic radiations all transitions are not equally effective to observed desired changes. To predict effective transitions certain guidelines are formed, that is known as selection rules. Simply we can understand it – **A selection rule is a statement about which transitions are allowed and thus which lines may be observed in a spectrum.**

For electronic transitions selection rules can be summarizes as–

- The total spin cannot change, $\Delta S = 0$;
- The change in total orbital angular momentum can be $\Delta L = 0, \pm 1$, but $L = 0 \leftrightarrow L = 0$ transitions are not allowed.
- The change in the total angular momentum can be $\Delta J = 0, \pm 1$, but $J = 0 \leftrightarrow J = 0$ transitions are not allowed.

Introduction to Spectroscopy

2.3 FLUORESCENCE SPECTROSCOPY

Fluorescence spectrometry is a fast, simple and inexpensive method to determine the concentration of an analyte in solution based on its fluorescent properties.

2.3.1 Principle

As we discussed earlier in Jablonski diagram regarding phenomenon of fluorescence and phosphorescence. Influorescence spectroscopy, a beam with a wave length varying between 180 and 800 nm passes through a solution in a cuvette. Atom or molecule first absorbs energy for instance a photon, this is called excitation. Very shortly (in the order of nano seconds)after excitation item its aphoton of a longer wave length named that fluorescence. If the emission takes longer time in the order of milli seconds then will be known as phosphorescence. It can be measured from an angle the light that is emitted by the sample. In fluorescence spectrometry both an excitation spectrum (the light that is absorbed by the sample) and/or an emission spectrum (the light emitted by the sample) can be measured. The concentration of the analyte is directly proportional with the intensity of the emission.

2.3.2 Applications

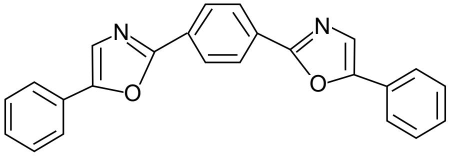
(a) Medicalmicrobiology– Fluorescence spectroscopy is being applied in medical micro biology field, for diagnostic technique with high sensitivity and specificity specially for microorganisms associated diseases.

(b) Pathology– Fluorescence spectroscopy and Fluorescence correlation spectroscopy (FCS) may be applied to understand various pathophysiological steps of various microorganisms.

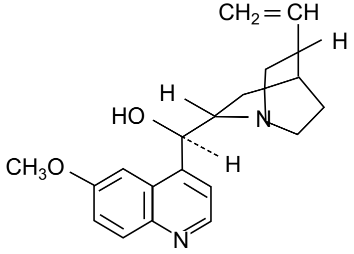
(c) Biochemistry– Fluorescence-based technology include assays for biomolecules, metabolic enzymes, DNA sequencing, research into biomolecule dynamics cell signalling and adaptation, and fluorescence in situ hybridisation (FISH) to identify specific DNA and/or RNA sequences in tissues.

(d) Genetics– Recently, molecular methods have been applied to fuse the gene for Green Fluorescent Protein (GFP) to other genes leading to its expression in living cells. This allows sophisticated analysis of gene expression and cellular location of important structural proteins and enzymes.

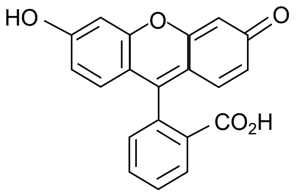
We can see Fluorescence spectrum of organic molecule with this figure



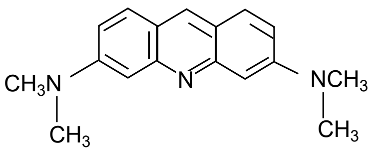
POPOP



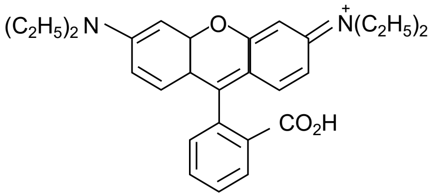
Quinine



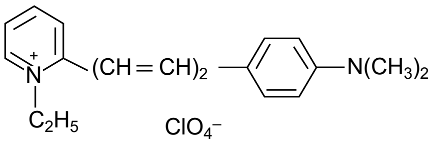
Fluorescein



Acridine Orange



Rhodamine B



Pyridine 1

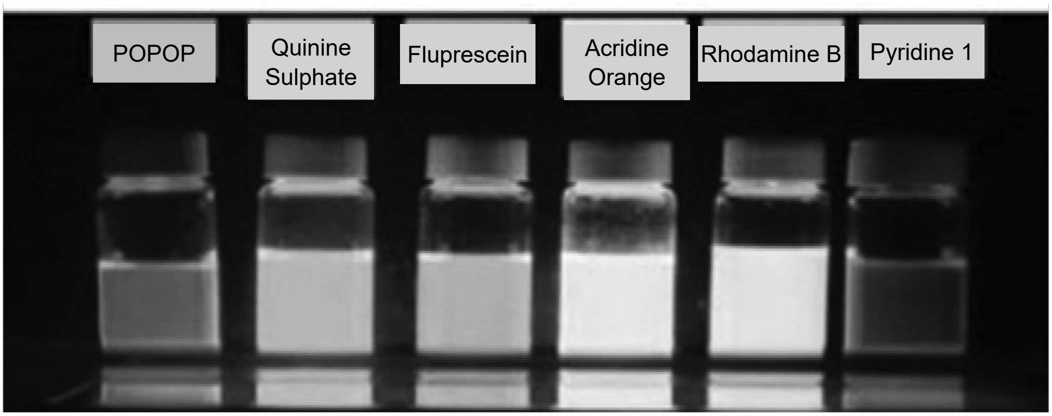


Fig. 2.6 : Fluorescence spectrum of organic molecules

Interesting Facts

- Fluorescence spectroscopy has the potential to be used as a technique to analyze microbial contamination on food.
- It is used to detect dissolution testing of tablets and products in the pharmaceutical industry when the use of UV absorption is not appropriate.
- It is a noninvasive technique and has been applied successfully for the diagnosis of multisystem cancers with high sensitivity and specificity.

VIDEO RESOURCES

Atomic and Molecular Absorption Spectrometry

Chemistry and Physics of Surfaces and Interfaces

2.4 ROTATIONAL AND VIBRATIONAL SPECTROSCOPY

Free atoms do not rotate or vibrate. The rotation and vibrational energies are usually much smaller than the energies required to break chemical bonds.

- The rotational energies correspond to the microwave region of electromagnetic radiation (3×10^{10} to 3×10^{12} Hz; energy range around 10 to 100J mol^{-1}).
- The vibrational energies are in the infrared region (3×10^{12} to 3×10^{14} Hz; energy range around 10 kJ/mol) of the electromagnetic radiation.

2.4.1 Energy of Rotational Transitions

When a molecule is irradiated with photons of light it may absorb the radiation and undergo an energy transition. The energy of the transition must be equivalent to the energy of the photon of light absorbed given by: $E = h\nu$. For a diatomic molecule the energy difference between rotational levels (J to J + 1) is given by:

$$EJ + 1 - EJ = B(J+1)(J+2) - BJ(J=1) = 2B(J+1) \qquad ...(2.3)$$

with $J = 0, 1, 2, \ldots$

Because the difference of energy between rotational levels is in the microwave region (1–10 cm^{-1})rotational spectroscopy is commonly called microwave spectroscopy. In spectroscopy it is customary to represent energy in wave numbers (cm^{-1}), in this notation B is written as $\tilde{B}$. To convert from units of energy to wave numbers simply divide by hand c, where c is the speed of light in cm sec^{-1} ($c = 2.998 \times 10^{-8}$ cm sec^{-1}). In wave numbers $\tilde{B} = h8\pi cI$.

Figure 2.7 predicts the rotational spectra of a diatomic molecule to have several peaks spaced by 2B. This contrasts vibrational spectra which tational spectrum of a diatomic molecule the bond length can be determined.

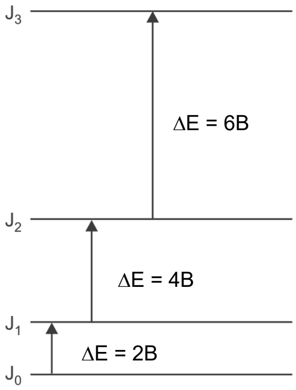


Fig. 2.7: Rotational Energy Levels

Selection rules only permit transitions between consecutive rotational levels: $\Delta J = J \pm 1$, and require the molecule to contain a permanent dipole moment. Due to the dipole requirement, molecules such as HF and HCl have pure rotational spectra and molecules such as H_2 and N_2 are rotationally inactive.

2.4.2 Selection Rule for A Rotational Transition is,

$$\Delta J = \pm 1$$

In addition to this requirement, the molecule has to possess a dipole moment. Molecules such as HCl and CO will show rotational spectra while H_2, Cl_2 and CO_2 will not.

2.4.3 Vibrational Transitions (Infrared Spectroscopy)

Infrared region results in changes in vibrational energy of molecules. Since changes in vibrational energy levels are accompanied by transitions between rational energy levels also, as a result, each line in vibrational structure is accompanied by rotational fine structure. Thus this spectrum is known as vibrational rotational spectrum which is highly complicated. This complication can be avoided by taking IR spectrum for liquid or in solution or solid sample.

2.4.4 Principle of Infra Red Spectroscopy

For a molecule to absorb IR, the rotation or vibration must be accompanied by a net change in dipole moment.

Molecular vibrations: Molecules are never at rest, they are continuously vibrating even at absolute zero temperature. In general a poly atomic molecule composed of n atoms has $3n$ degrees of freedom, six of which are translational and rotational. Modes of vibration calculated for liner and non- linear molecules as below–

$3n - 6$: For non-linear molecules degrees of vibrational freedom.

$n - 5$: For linear molecules degrees of vibrational freedom.

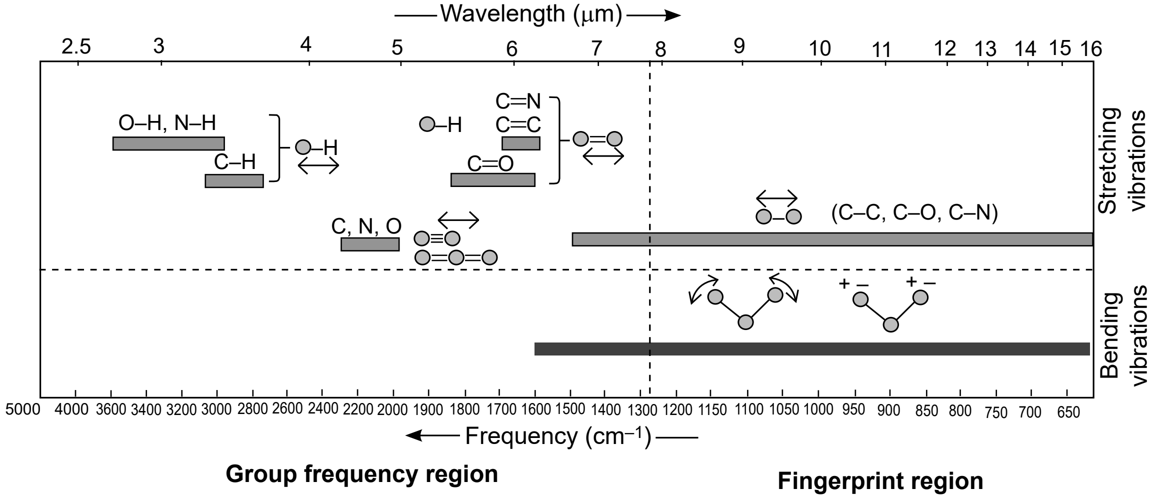


Fig. 2.8: Functional Group region and Finger print region in IR spectra

Mainly two modes of vibrations

(a) Stretching

(b) Bending

(*i*) **Functional group region (4000-1500 cm^{-1}):** In this region bands are associated with changes in vibrational states of various bonds. This region is important for characterization of a molecule or functional group.

(*ii*) **Finger print region (1500-600 cm^{-1}):** In this region bands are associated with changes in complex vibrational and rotational energy of entire molecule. This region is helpful in identification of organic compound.

2.4.5 SELECTION RULE FOR VIBRATIONAL TRANSITION

Only those transitions are allowed for which $\Delta v = \pm 1$ that is decrease or increase in vibrational quantum number is by one unit.

Thus spacing between 2 successive vibrational energy level will be always hv .

2.4.6 Applications of IR Spectroscopy

(i) **Identification of an organic compound:** An unknown organic compound can be confirmly identified, if its spectra in finger print region super impose with that of known organic compound. If two pure samples give different IR spectra, the compounds must be different but if they give super imposable spectra, then they represent the same compound. Since each organic compound has its own unique absorption pattern in fingerprint region.

(ii) **Identification of functional group:** The presence or absence of bands help in predicting the presence of certain functional groups in the compound. For e.g., bands in the region 1650–1850 cm^{-1} suspects presence of carbonyl group in the compound.

(iii) **Distinction between Hydrogen bonding:** In general hydrogen bonding lowers the absorption frequency. Intra molecular hydrogen bonding can be distinguished from inter molecular hydrogen bonding by IR technique. For e.g. o–Nitrophenol exhibits intramolecular hydrogen bonding and on dilution, it does not show any shift in absorption whereas p-nitrophenol which exhibits intermolecular hydrogen bonding,on dilution shows shift in absorption.

(iv) **To distinguish between primary, secondary and tertiary amines:** 1° amines give several peaks, 2° amines give one peak while 3° amines give no peaks.

(v) **To predict hybridization of Carbon:** Absorption frequency of O(C — H) increases with increase in ‘s’ character.

(vi) **Detection of impurities:** Spectrum of pure sample always consists of sharp peaks and bands while impure sample has poor bands and some additional bands of impurities.

Let us discuss an example of an IR spectra to know more. In the below Fig we may able to distinguished the two regions Functional group region and Figure print regions.

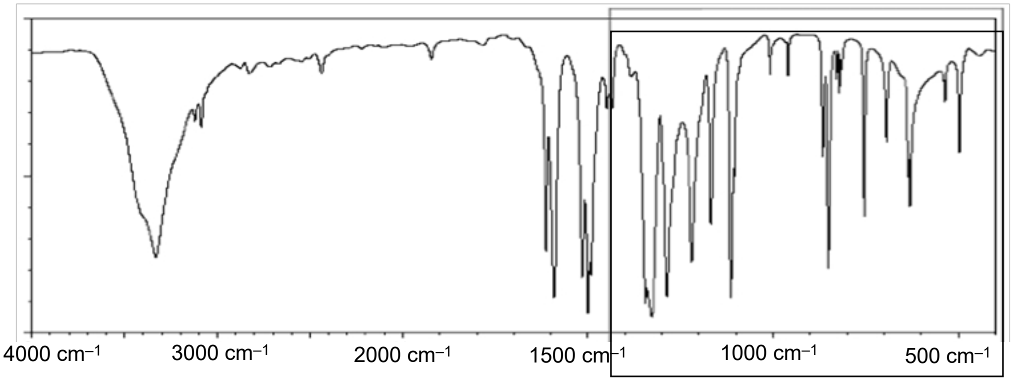


Fig. 2.9: Finger print region in IR spectrum

Taking example of the spectrum of ethanol in Fig we can apply and identify these regions.

1. **Functional group region**– Polar covalent bonds are IR "active" and its excitation can be observed in an IR spectrum. In organic molecules these polar covalent bonds represent the functional groups which are present within the molecule.

   Alcohols have IR absorptions associated with both the O–H and the C–O stretching vibrations.

   - O–H stretch, hydrogen bonded 3500-3200 cm^{-1}
   - C–O stretch 1260-1050 cm^{-1} (s)

Fundamentals of Spectroscopy

2. **Fingerprint region**, the spectra tend to be more complex and much harder to assign.

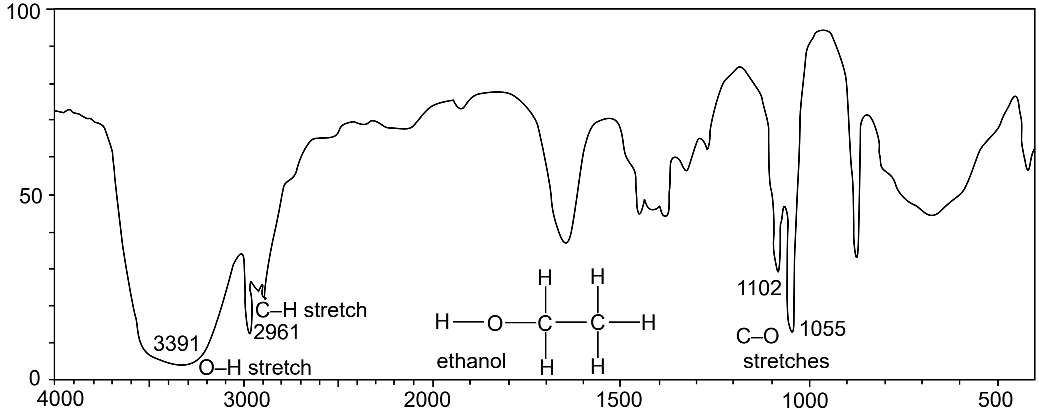


Fig. 2.10: IR spectrum of Ethanol

APPLICATION IN DAILY LIFE

- IR spectroscopy is used in forensic analysis in both criminal and civil cases. It can be used in determining the blood alcohol content of a suspected drunk driver and poisonous substances found during postmortem.
- IR used in analysis and identification of pigments in paintings and other art objects such as illuminated manuscripts.
- It is extensively used in pharmaceutical industries during various stages of drug manufacturing.

2.5 NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY (NMR)

Nuclear magnetic resonance spectroscopy involves the absorption of electromagnetic radiation in radio frequency region. It involves the interaction between oscillating electromagnetic forces and magnetic energy of nuclei usually hydrogen.

2.5.1 Rules for determining net spin (I) of a nucleus

Nuclei of certain atoms behave as if they are spinning charges. Any spinning charge creates a magnetic field and behave as if it were a tiny magnet.

(i) If the **number of protons and the number of neutrons are both even**, the nucleus has no spin i.e., $I = 0$, for example, ^{12}C, ^{16}O, ^{32}S etc.

(ii) If the **sum of number of protons and number of neutrons is odd**, the nucleus has half-integer spin i.e., $\frac{1}{2} \frac{3}{2} \frac{5}{2}$ For example ^{1}H, ^{13}C, ^{19}F, ^{31}P etc.

(iii) If **number of protons and number of neutrons are both odd** then the nucleus has an integer spin i.e. $I = 1, 2, 3$. For example, N^3.

The nuclei which are most commonly study by NMR spectroscopy are **^{1}H, ^{13}C, ^{19}F, ^{31}P**.

2.5.2 Theory of NMR Spectroscopy

Spinning nuclei behave just like a bar magnet with small magnetic field whose magnitude and direction can be described by a vector called a magnetic moment.

These magnetic moments are oriented in random fashion in absence of applied field. For ^{1}H, nuclear spin can have only two values associated with quantum numbers. $+\frac{1}{2}$ (α) $+\frac{1}{2}$ (β). There is no difference in energy between two nuclear spin states. But in presence of external magnetic field, two spin states remain no longer degenerate. Their magnetic moments tend either to align with the field (α-spin) or against the field (β-spin). The energy difference between α and β-spin states is very small, although, α spin state is of lower energy. The energy is needed in order to flip the proton from lower energy state (α) to higher energy state (β). This energy is provided by electromagnetic radiation in radio frequency region.

2.5.3 Chemical Shift

A nucleus does not observe the field equal to applied field as it is surrounded by electrons. The difference between the applied magnetic field and field observed by nucleus is called **nuclear shielding**.

All protons are not equivalent, they do not processes with same frequency, thus absorptions depend on their environment. Depending on local environment, different protons in a molecule resonate at slightly different frequencies. The shift in peak of NMR spectrum due to chemical environment is called chemical shift.

Formula of chemical shift-

$$\text{Chemical Shift} = \frac{\text{Peak position in Hz (relative to TMS)}}{\text{Spectro meter frequency in MHz}}$$

On the δ (delta) scale $$\delta = \frac{\nu' - \nu_{\text{TMS}}}{\nu_0} \times 10^6 \qquad \text{... (2.4)}$$

ν' = frequency of unknown group of protons in Hz

ν_{TMS} = frequency of reference, TMS in Hz

ν_0 = Operating frequency of spectro meter in MHz

On τ (tau) scale

On the δ (delta) scale, the position of TMS signal is taken as 0.0 ppm. On τ (tau) scale, the reference is assigned arbitrary position of 10.0.

$$\tau = 10 - \delta \qquad \text{... (2.5)}$$

Chemical shift is measured relative to a reference compound. For ^{1}H NMR most appropriate reference is tetra methyl silane (Si $(CH_3)_4$, TMS.

2.5.4 Application of NMR Spectroscopy

1. **NMR spectroscopy** is the use of NMR phenomena to study the **physical, chemical, and biological properties of matter** – In analytical chemistry NMR technique used in quality control and research for determining the content and purity of a sample as well as its molecular structure.
2. **Chemists use** it to determine molecular identity and structure like - From coupling constant, J, we can distinguish between cis and trans isomers $J_{trans} > J_{cis}$.
3. Medical practitioners employ magnetic resonance imaging (MRI), a multidimensional NMR imaging technique, for **diagnostic purposes**.
4. In the field of **engineering** it opens a new horizon for the study of image processing and correlating and mapping with various diseases.
5. MRI (Magnetic Resonance Imaging) is based on ^{1}H NMR. MRI is **image of section** of human body. Brightness of various regions of an image is related to two factors :
   (a) The number of protons in the tissue at particular place.
   (b) The relaxation times of protons.

   For example, H of H_2O in some cancerous tumours has shorter relaxation time than in healthy cells. Thus MRI can detect brain tumour.
6. Once the basic structure is known, NMR can be used to determine **molecular conformation insolution** as well as studying physical properties at the molecular level such as conformational exchange, phase changes,solubility, and diffusion.

Let us interpret the splitting of protons with the help of known NMR spectrum of some simple molecules.

Example 1: ***Figure a. shows NMR spectra of ethanol and figure b shows splitting of protons.***

Solution: Formula of ethanol is = $CH_3 - CH_2 - OH$

Means three types of protons are present here with different environments

1. Three Protons in CH_3 and CH_3 protons splits into a ratio of 1 : 2 : 1 triplet
2. Two Protons in CH_2 and after resonance is split into ratio of 1 : 2 : 2 : 1 quartet
3. One Proton in OH and as a singlet

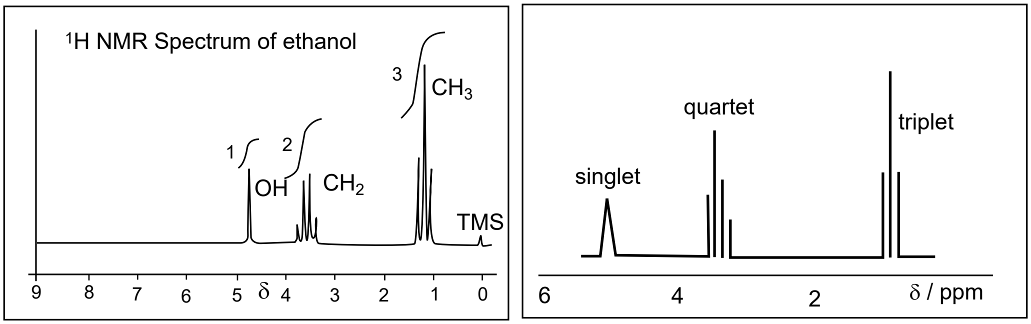


Fig. 2.11 : ^{1}H NMR Spectrum of ethanol

Example 2 : Butan-1-ol – *Let us interpret NMR spectra of buten-1-ol*

Solution: The proton ratio observed 3 : 2 : 2 : 2 :1, corresponds with the structural formula of butanol.

a – CH_3 protons splits into a 1 : 2 : 1 triplet

b – 1st CH_2 proton resonance is split by the CH_3 protons into a 1 : 5 : 10 : 10 : 5 : 1 sextet

c – 2nd CH_2 proton splits on either side by the 1st and 3rd CH_2 protons into a 1 : 4 : 6 : 4 : 1 quintet

d – 3rd CH_2 proton splits into a 1 : 2 : 1 triplet

e – OH proton as a singlet

Note that no splitting due to OH proton is detected.

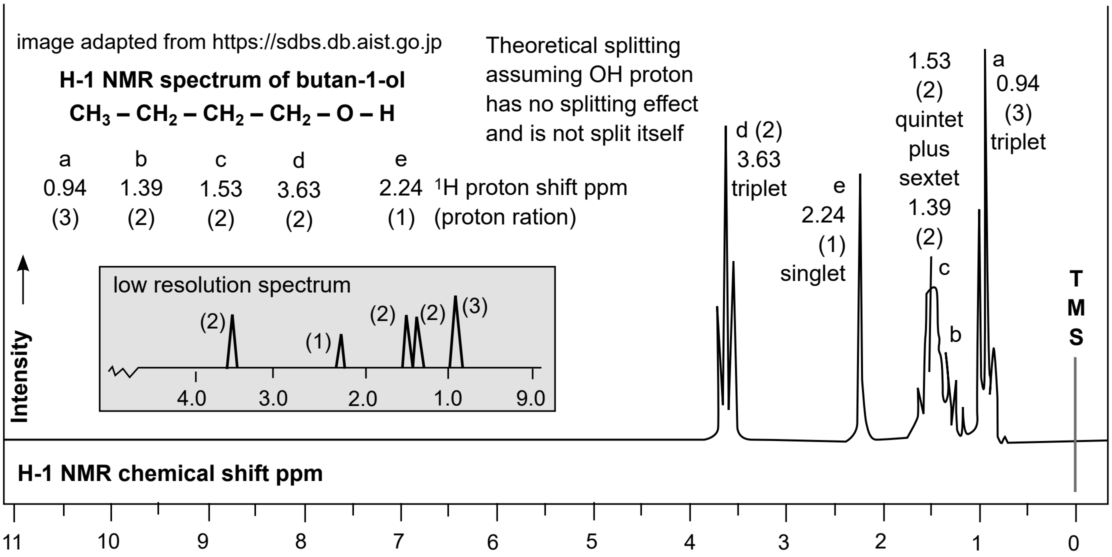


Fig. 2.12 : NMR spectrum of butan-1-ol

Example 3: ***Butanone***

Solution: NMR spectra of Butanone

The proton ratio observed 3 : 2 : 3, corresponds with the structural formula of butanone.

The CH_2 protons splits into a 1 : 3 : 3 : 1 quartet

The CH_3 protons splits into a 1 : 2 : 1 triplet

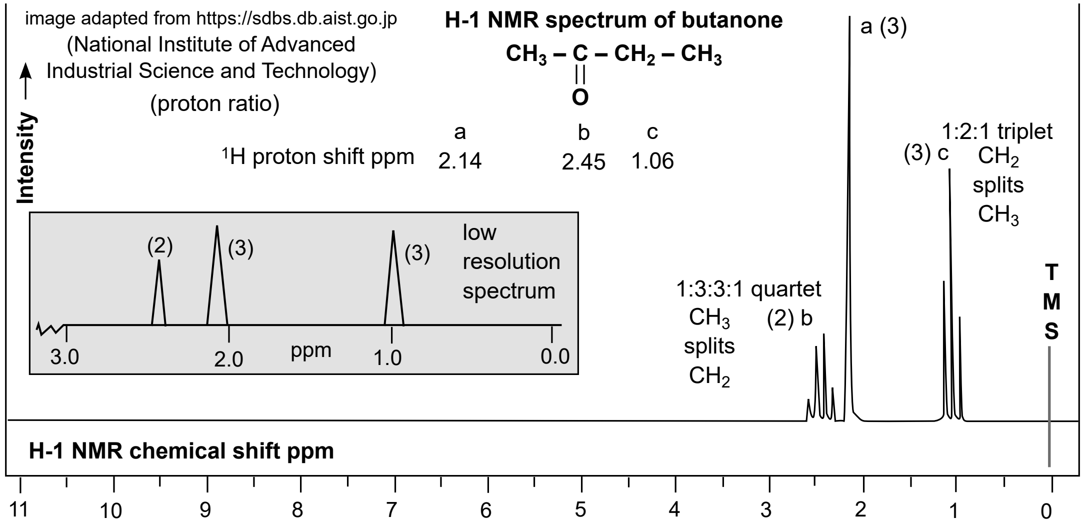


Fig. 2.13 : NMR spectrum of butanone

Problem–1: ***Calculate the NMR signals and splitted signals in $CH_3—O—CH_2—CH_3$ molecules.***

Sol. : There are three types of proton, hence 3 main peaks will be obtained:

'a' peak will not split.

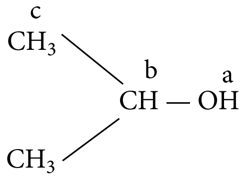
'b' peak will split into quartet (3 + 1)

'c' peak will split into triplet (2 + 1)

Problem–2: ***Predict number of NMR peaks with relative intensity in low resolution spectrum of following compounds.***

(i) $CH_3CH_2—CH_2—OH$

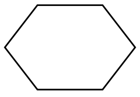
(ii)



(iii) Toluene

(iv) $CH_2—O—CH_3$

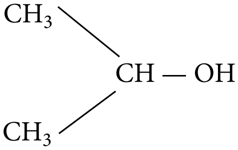
(v)



Sol.

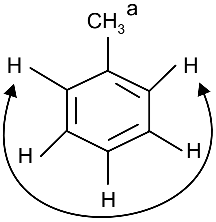
(i) $CH_3CH_2—CH_2—OH$ → 4 peaks in intensity ratio 3 : 2 : 2 : 1

(ii)



→ 3 peaks in intensityh ratio 6 : 1 :

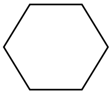
(iii)



→ 2 peaks in intensity ratio 3 : 5

(iv) $CH_2—O—CH_3$ → 1 peak

(iv)



→ 1 peak

APPLICATION IN DAILY LIFE

- NMR metabolomics is used in the search for biomarkers of infectious diseases like tuberculosis, malaria and pneumonia, neurological disorders and Parkinson's disease.
- In Food industry, NMR helpful to determine structure of proteins, aminoacid profile, carotenoids, organic acids, lipid fractions, the mobility of the water in foods.

VIDEO RESOURCES

Introduction to NMR spectroscopy

NMR Spectroscopy for Chemists and Biologists

2.6 MAGNETIC RESONANCE IMAGING (MRI)

Magnetic resonance imaging is a medical application of NMR develop during period of 1970s and 1980s. MRI is a medical imaging technique used in radiology to form pictures of the anatomy and the physiological processes of the body in both health and disease. MRI uses powerful magnets, radio waves, and a computer to make detailed pictures of the inside of your body. MRI does not involve X-rays and the use of ionizing radiation, which distinguishes it from CT or CAT scans.

It is very good at imagining soft tissue, like ligaments, spinal nerve roots, the spinal column, the brain showing an ischemic infarction shortly after it took place, while CT would only show it after a delay of 3 days.

MRI with the right software is able to show us the fluid in tube like structures like bile ducts, pancreatic ducts, blood vessels so sometimes is a good screening tool for obstructions and narrowings of these tubes instead of invasive procedures we had to perform before MRI.

Images of MRI – Let we observe few images of MRI of various organs –

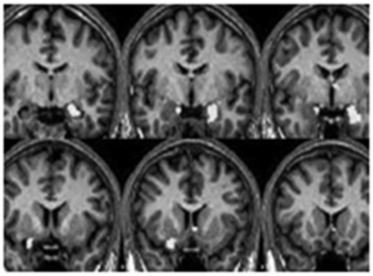


Fig 2.14 : MRI Image of Brain

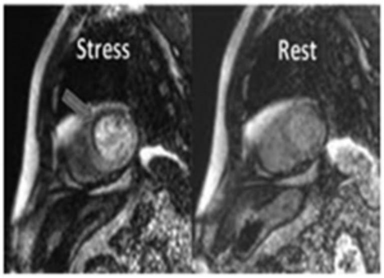


Fig. 2. 15: MRI Image of Cardiac

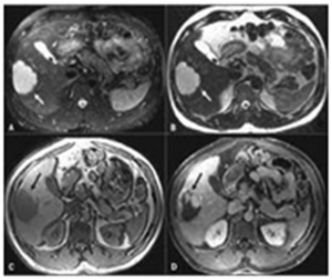


Fig. 2. 16: MRI Image of Abdomen

2.6.1 Applications of MRI

MRI is widely used in hospitals and clinics for medical diagnosis, staging of disease and follow-up without exposing the body to radiation. Applications are –

(a) **Neuro imaging:** MRI isuse for neurological cancers, as it has better resolution than CT and offers better visualization of the posterior fossa.

(b) **Cardiovascular:** Cardiac MRI is complementary to other imaging techniques, such as echo cardiography, cardiac CT, and nuclear medicine. Its applications include assessment of myocardial ischemia and viability, cardiomyopathies, myocarditis, iron overload, vascular diseases, and congenital heart disease.

(c) **Musculoskeletal:** Applications in the musculoskeletal system include spinal imaging, assessment of joint disease, and soft tissue tumors.

(d) **Liver and gastro intestinal:** Hepatobiliary MR is used to detect and characterize lesions of the liver, pancreas, and bile ducts. Extra cellular contrast agents are used widely in liver MRI and newer hepatobiliary contrast agents also provide the opportunity to perform functional biliary imaging.

(e) **Angiography:** Magnetic resonance angiography (MRA) is a group of techniques based on magnetic resonance imaging (MRI) to image blood vessels. MRA is often used to evaluate the arteries of the neck and brain, the thoracic and abdominal aorta, therenal arteries, and the legs.

2.7 X- RAY DIFFRACTION (XRD ANALYSIS)

XRD Analysis is the technique which, uniquely provides phase identification (e.g. graphite or diamond), along with phase quantification, % crystallinity, crystallite size and unit cell size.

For layered materials, Grazing Incidence XRD (GIXRD) allows compositional depthpro filing of phases with in the structure.

2.7.1 Principles of X-Ray Powder Diffraction (XRD)

Maxvon Laue, in 1912, discovered that crystalline substances act as three-dimensional diffraction gratings for X-ray wavelengths similar to the spacing of planes in a crystallattice. X-ray diffraction is now a common technique for the study of crystal structures and atomic spacing.

X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample. These X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate, and directed toward the sample. The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray) when conditions satisfy Bragg's Law ($n\lambda = 2d\sin\theta$). This law relates the wave length of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample. These diffracted X-rays are then detected, processed and counted. By scanning the sample through arange of 2θ angles, all possible diffraction directions of the lattice should be attained due to the random orientation of the powdered material. Conversion of the diffraction peaks to d-spacings allows identification of the mineral because each mineral has a set of unique d-spacings. Typically, this is achieved by comparison of d-spacings with standard reference patterns.

All diffraction methods are based on generation of X-rays in an X-ray tube. These X-rays are directed at the sample, and the diffracted rays are collected. A key component of all diffraction is the angle between the incident and diffracted rays. Powder and single crystal diffraction vary in instrument at ion beyond this.

2.7.2 APPLICATIONS

(a) X-ray powder diffraction is most widely used for the identification of unknown crystalline materials (e.g. minerals, inorganic compounds).

(b) Determination of unknown solids is critical to studies in geology, environmental science, material science, engineering and biology.

(c) Typical Industries using XRD are Aerospace, Automotive, Materials, Minerals, Glass, Ceramics and Refractories, Healthcare, Medical Devices, Semiconductors, Electronics.

(d) Some Typical Applications

1. Phase composition determination
2. Identification of fine-grained minerals such as clays and mixed layer clays that are difficult to determine optically
3. Characterization of doped cell structures for electro ceramics
4. Measurement of hard coating composition and structure e.g. carbides, nitrides on machine tools
5. Characterization of hydroxy-apatite coatings on medical implant materials.
6. In-depth analysis of silicon wafers, ITO coated glasses and solar cells.

Identification of synthesized silver nano composites and silver nano crystals through X-ray diffraction pattern may be observed through the below Figure.

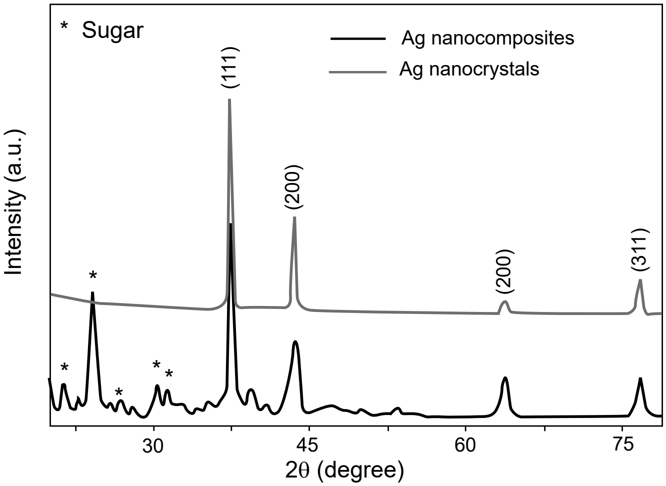


Fig. 2.17: Silver nanocomposites and silver nanocrystals through X-ray diffraction pattern

SUMMARY

- **Spectroscopy** is a technique that uses the interaction of energy with a sample to perform an analysis. Electromagnetic waves : EM waves are composed of oscillating magnetic and electric fields.
- **Born Oppenheimer Approximation –** the total energy of a molecule is given by ,

  $E = E_{translational} + E_{rotational} + E_{vibrational} + E_{electronic}$

  $E_{electronic} >> E_{vibrational} >> E_{rotational} >> E_{translational}$
- **The Franck–Condon principle** is a rule in spectroscopy and quantum chemistry that explains the intensity of vibronic transitions. Vibronic transitions are the simultaneous changes in electronic and vibrational energy levels of a molecule due to the absorption or emission of a photon of the appropriate energy.
- **Jablonski Diagram:** Once a molecule has absorbed energy in the form of electromagnetic radiation, there are a number of routes by which it can return to ground state. Graphical representation of this is termed as Jablonski diagram.
- **Types of Electronic Transitions:** $\sigma - \sigma^*$ transition, $n - \sigma^*$ transition, $\pi - \pi^*$ transition, $n - \pi^*$ transition.
- **Fluorescence:** If the photon emission occurs between states of the same spin state (e.g. $S_1 \rightarrow S_0$) this is termed fluorescence.
- **Phosphorescence:** If the spin state of the initial and final energy levels are different (e.g. $T_1 \rightarrow S_0$), the emission (loss of energy) is called phosphorescence.
- **Fluorescence spectroscopy:** Fluorescence spectrometry is a fast, simple and inexpensive method to determine the concentration of an analyte in solution based on its fluorescent properties.
- **Infrared Spectroscopy:** The infrared absorption spectrum of a substance is sometimes called its molecular fingerprint. Although frequently used to identify materials, infrared spectroscopy also may be used to quantify the number of absorbing molecules.
- **Normal modes of vibrations:** nonlinear: 3N – 6 independent vibrational modes. linear: 3N – 5 independent vibrational modes
- **Raman Spectroscopy:** Raman scattering of light by molecules may be used to provide information on a sample's chemical composition and molecular structure.
- **Nuclear Magnetic Resonance:** The principle behind NMR is that many nuclei have spin and all nuclei are electrically charged. The energy transfer takes place at a wavelength that corresponds to radio frequencies and when the spin returns to its base level, energy is emitted at the same frequency. The signal is NMR spectrum.
- **Chemical shift** is a function of the nucleus and its environment. It is measured relative to a reference compound. For ^1H NMR, the reference is usually tetra methyl silane, $Si(CH_3)_4$ TMS.

  $$\delta = \frac{H_0\,(\text{reference}) - H0\,(\text{sample})}{H_0\,(\text{reference})} \times 10^6\ \text{ppm.}$$
- **Magnetic resonance imaging (MRI):** Magnetic resonance imaging is a medical application of nuclear magnetic resonance (NMR) develop during period of 1970s and 1980s. MRI scanners use strong magnetic fields, electric field gradients, and radio waves to generate images of the organs in the body.

- **X-Ray Diffraction:** XRD provides detailed information on the crystallographic structure and physical properties of materials and thin films.

EXERCISES

SUBJECTIVE QUESTIONS

1. Explain the following

(i) Electromagneticspectrum, (ii) Born Oppenheimer Approximation

(iii) Franck–Condon principle (iv) Fingerprintarea,

(v) TypeofModesVibrations, (vi) Selectionrule

2. How is the concentration of an unknown solution determined with the help of UV spectroscopy?

3. Describe diagrammatically the various electronic transitions that take place when an organic compound absorbs radiation in ultraviolet or visible region.

4. What is XRD technique? Write principle of XRD Spectroscopy with giving application of it in daily life.

5. Now a days MRI become reliable technique for diagnosis of diseases in human being. Explain its principle and uses in detail with reference to medical sciences.

6. What is the basic difference between ultra violet spectroscopy and infrared spectroscopy. Describe how many types of molecular vibrations are possible in I.R. Spectroscopy.

7. What does the finger printing region of IR spectrum show?

8. How do UV and IR spectrum differ from each other with respect to electron transitions?

9. Compare and differentiate Selection rules of Electronic, Infrared and NMR spectroscopy examples.

10. How will you differentiate between the following pairs of compounds:

(i) o- and p-$HO—C_6H_4—CHO$

(ii) $C_6H_5COC_2H_5$ and p-$CH_3C_6H_4COCH_3$?

11. Assign and explain the wave numbers (C = C stretching) 1600, 1670 and 1950 cm

$CH_2 = CH—CH = CH_2$, $CH_2 = CH—CH = CH—CH_3$ and $CH_2 = C = CH—CH_3$.

12. What functional groups give the following signals in an IR spectrum?

(i) 1700 cm^{-1} (ii) 1550 cm^{-1}

(iii) 1700 cm^{-1} and 2510-3000 cm^{-1}

13. How can you distinguish the following pairs of compounds through IR analysis?

(i) CH_3OH (Methanol) and $CH_3CH_2OCH_2CH_3$ (Diethylether)

(ii) Cyclopentane and 1-pentene.

SHORT ANSWER

Q.1. Why are pure rotational spectra studied only in the gaseous states of atoms and molecule?

Ans. The rotational energy levels are not quantized in condensed phases; i.e., in the solid and liquid states. They are quantized in the gaseous states of chemical systems. Thus the microwave spectra are observed in the gaseous state.

Q. 2. How many rotational lines will be observed in the microwave spectrum of HCl gas?

Ans. The rotational energy level population is considerable and the ground rotational level is not the most populated, the number of rotational levels is subjected to the selection rule.

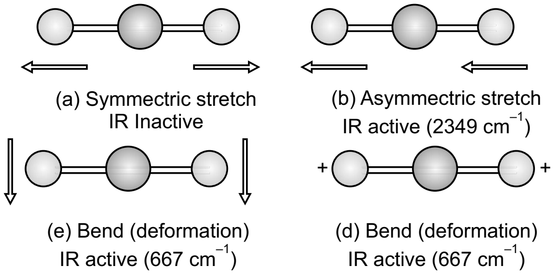
Q.3. How many normal modes of vibrations are possible in the linear molecule ethane, C_2H_6, and non-linear molecule benzene, C_6H_6?

Ans. Ethane has – $3n - 5 = 3(2 + 6) - 5 = 19$ possible normal modes of vibrations. Benzene has – $3n - 6 = 3(6 + 6) - 6 = 30$ possible normal modes of vibrations.

Q.4. How many fundamental vibrational frequencies would you predict during IR absorption spectrum of CO_2?

Ans. CO_2 is linear, it has $3n - 5 = 4$ fundamental modes of vibrations, which may be represented as–

Vibrational modes for linear CO_2



Linear CO_2 – number of modes = 3(3) – 5 = 4

Q.5. The force constant for the b and in HF is about 9×10^5 dynes cm^{-1}. Calculate the vibrational spectrum peak for HF.

Ans. (a) 3.99×103 cm^{-1} (b) 2.99×103 cm^{-1}

Q.6. Write a short note on–

(i) IR spectra

(ii) Application of IR Spectra

(iii) Selection rule for Electronic spectroscopy

(iv) Image of MRI

(v) Application of NMR

Q.7. How many fundamental modes of vibration you predict for–

(a) Benzene (b) Toluene

(c) Methane

Ans. a = 30, b = 39, c = 9

Q.8. How will you differentiate between CH_3CH_2CHO and $CH_2 = CH - CH_2OH$ with the help of IR spectrum?

Q.9. Explain the different electronic transitions in UV spectroscopy with the help of UV spectrum, how will you differentiate between cis and trans isomers?

Q.10. What information can be obtained about following compounds with the help of UV and IR spectroscopy:

(i) Acetophenone (ii) Cinnamicacide

(iii) Phenol (iv) Benzamide.

OBJECTIVE QUESTIONS

1. The compound showing absorbance at 1690 $cm^{-1}$is

(*a*) Acid (*b*) Alcohol

(*c*) Ether (*d*) Carbonyl [**Ans.** (*d*)]

Feedback: The carbonyl stretch C=O of a carboxylic acid appears as an intense band from 1760-1690 cm.

2. The nature of electronic transitions in alkene is

(a) $\pi \rightarrow n^*$ (*b*) $\pi \rightarrow \pi^*$

(*c*) $\sigma \rightarrow \pi^*$ (*d*) $\sigma \rightarrow \sigma^*$ [**Ans.** (*b*)]

Feedback: Alkene have double bond with no heteroatom, so preferred electronic transition will be $\pi \rightarrow \pi^*$.

3. How many signals do the aldehyde $(CH_3)_3CCH_2CHO$ have in ^1H NMR and ^{13}C NMR spectra?

(*a*) Five ^1H signals and six ^{13}C signals (*b*) Three ^1H signals and four ^{13}C signals

(*c*) Five ^1H signals and four ^{13}C signals (*d*) Three ^1H signals and six ^{13}C signals

Ans. (*b*) Three ^1H signals and four ^{13}C signals

Feedback: We need to find non-equivalent hydrogen and carbon atoms. This aldehyde has three kinds of hydrogen and four kinds of carbon atoms. For proton and carbon chemical shifts

4. Which spectroscopy exploits the fact that many atoms are able to emit or absorb visible light.

(a) UV-Visible spectroscopy (b) X-ray Spectroscopy

(c) IR spectroscopy (d) NMR spectroscopy [**Ans.** (*a*)]

Feedback: UV– Visible spectroscopy works in the range of visible and UV regions.

5. Identify which of the following pairs of molecules exhibit both a pure rotational spectrum and a rotational Raman spectrum.

(*a*) O_2 and H_2O (*b*) CO_2 and N_2O

(*c*) CO and CH_4 (*d*) NO and DCCH [**Ans.** (*d*)]

Feedback: Condition for display a pure rotational spectrum, it must have a permanent electric dipole and for a rotational Raman spectrum, its polarizability must anisotropic i.e. not be the same in all directions. Thus, O_2, CO_2, N_2O will all fail to display a pure rotational spectrum. All molecules possess an anisotropic polarizability except CH_4 and so the only pair of molecules to display both a pure rotational spectrum and a rotational Raman spectrum are NO and DCCH.

6. How many normal modes of vibration are there for C60?

(*a*) 174 (*b*) 180

(*c*) 60 (*d*) 175 [**Ans.** (*a*)]

Feedback: C60 is a non-linear molecule composed of 60 atoms. In total it has 3N degrees of freedom and with 60 atoms, so we have $3N - 6 = 180 - 6 = 174$ vibrational modes.

7. Which of the following molecules will not display an infrared spectrum?

(*a*) CO_2 (*b*) N_2

(*c*) Benzene (*d*) HCCH [**Ans.** (*b*)]

Feedback: Homonuclear diatomic molecule N_2 will not display an infrared spectrum. All polyatomic molecules, even if they possess no permanent electric dipole, will have at least two vibrational modes which break the overall symmetry of the molecule, thereby creating a dipole.

8. For which of the following molecules would you expect the infrared active fundamentals to be Raman inactive and vice versa?

(*a*) NO_2 (*b*) Fluorobenzene

(*c*) Benzene (*d*) Fluoroethene [**Ans.** (*c*)]

Feedback: Molecules which display mutual exclusivity in their infrared and Raman activity are those with an inversion centre. Benzene is the only molecule whose infrared active fundamentals will be Raman inactive and whose Raman active modes will be infrared inactive.

DESIGN INNOVATIVE PROJECTS / ACTIVITIES

Activity 1. -https://sdbs.db.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi

2. Enhance list of application of spectroscopy in daily life as provided below–

S. No.	Area	Application
1.	Medical or Nursing	UV lamps used to disinfect surgical operating rooms Using MRI spectroscopy to detect tumors
2.	CIA Agents/Spies	Tech to Identify Deadly Chemicals From 30 Meters Away

S. No.	Area	Application
3.	Forensics	Using bloodstains at crime scenes to determine age of a suspect or victim
4.	Material scientists / Civil Engg.	study icy roads
5.	Material scientists / Civil Engg.	Farming, Grain fed beef or grass fed beef Energy Content of Silage
6.	Career in the Outdoors	UV lamp used to disinfect water Using Infrared Light to help manage wildlife Environmental Analysis/ Science

Project 1. Collect 2-3 discarded MRI, XRD images from nearby center and observe them and try to find out the following-

- Model of spectrophotometer
- Range of spectrum
- Working wavelength
- Image characteristic
- Other observation made

SUGGESTED READINGS

BOOKS

1. Spectroscopy in Inorganic Chemistry by C.N.R. Rao, Academic Press, ISBN: 97-801-25802024.
2. Basic Principles of Spectroscopy By Raymond Chang, McGraw-Hill, 1970ISBN:97-800-70105171.
3. Fundamentals for Molecular Spectroscopy by Colin Banwell& Elaine McCash, McGrew Hill (UK) ISBN0-07-70797b-09 9780077079b5.

E-RESOURCES

- https://nptel.ac.in/courses/104/106/104106122/
- https://onlinecourses.nptel.ac.in/noc20_cy36/preview

KNOW MORE

Electromagnetic radiations, name of spectroscopy its theory and applications

Electro-magnetic Region/source	Name of Spectroscopy	Theory	Application
Ultraviolet/Visible	Electronic	Electron Transitions between Orbitals	Determination of impurities in molecules & M. wt. determination

Electro-magnetic Region/source	Name of Spectroscopy	Theory	Application
Infrared	Vibrational	(i) Simple Stretching Vibrations (ii) Higher Order Vibrations	Analysis of Vibrational Banding Patterns
Between IR and microwave	Raman	Change of frequency between incident and transmitted radiations due to scattering	To identify molecules and Study chemical bonding. Functional group determination
Microwave	Rotational	Measurement of the energies of transitions between quantized rotational states of molecules in the gas phase	Identifying stable reaction products For purity analysis and reaction efficiency.
Radiowaves	Nuclear Magnetic Resonance	(i) Nuclei with Spin 1/2 (ii) The Chemical Shift Scale (iii) Scalar Coupling between Nuclei (iv) Analysis of 1DNMR Spectra (v) Nuclear Overhauser Effect	Introduction to analysis of 2DNMR Spectra
Ionization of atom	Mass	(i) Ionization Techniques (ii) Mass Analyzers (iii) Molecular Ions and High Resolution MS	Analysis of Mass Spectral Fragmentation Patterns

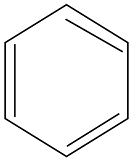
WHICH IMPARTS COLOR IN ORGANIC MOLECULES?

Chromophore: It is a part of molecule which when exposed to visible light will absorb and reflect a certain colour. It is a covalently unsaturated group responsible for electronic absorption e.g. C=O, C=C, NO_2.

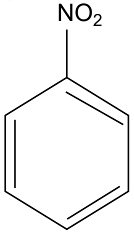
It is responsible for imparting colour to compounds. For e.g. nitro compounds are yellow in colour due to chromophore – NO_2.

Auxochrome : It is a saturated group with lone pair of electrons, when attached to a chromophore shifts the absorption maximum towards longer wavelength alongwith increase in intensity of absorption OH, NH_2, Cl.

It does not impart the colour but only deepens the colour. Due to lone pair of electrons they helpchromophore in extending the conjugation.



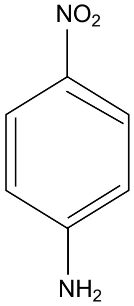
Benzene (Colorless)



Yellow in Color

NO_2 → auxochrome

Nitrobenzene



Orange in Color NH_2, NO_2 → auxochrome p-Nitroaniline

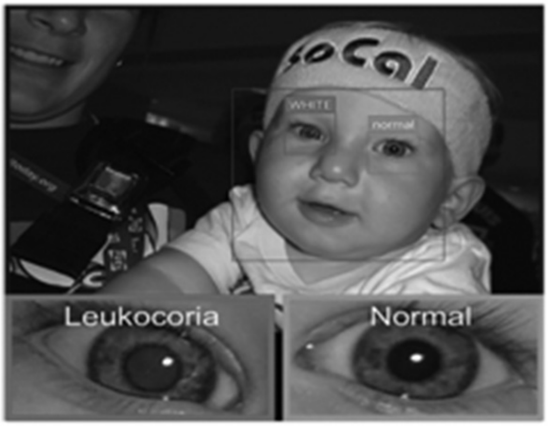
TYPICAL PROTON CHEMICAL SHIFTS

	Type of Protons	Chemical Shift (ppm)
Primary	$R—CH_3$	0.9
Secondary	$R_2—CH_2$	1.3
Tertiary	$R_3—CH$	1.5
Vinylic	$R_3—CH$	4.6—5.9
Acetylinic	—C—H	2–3
Aromatic	Ar—H	6–8.5
Benzylic	$Ar—CH_3$	2.2–3
Alcohol	R—OH	3.4–4
Phenolic	Ar—OH	4–12
Aldehydic	R—CHO	9–10
Carboxylic	RCOOH—	10.5–12
Amino	$R—NH_2$	1–5

INTERESTING FACTS OF SPECTROSCOPY IN DAILY LIFE

- Monitoring dissolved oxygen content in freshwater and marine ecosystems
- Studying spectral emission lines of distant galaxies
- Space exploration.
- Visible and ultraviolet spectroscopic methods have been used for analysis of environmental samples by environmental scientists.
- UV lamps used to disinfect surgical operating rooms.

- Characterization of proteins and Respiratory gas analysis in hospitals
- Spectroscopic sensor installed in new smartphone app which gives snapping pictures of children to look for signs that a child might be developing a serious eye disease in future or not.

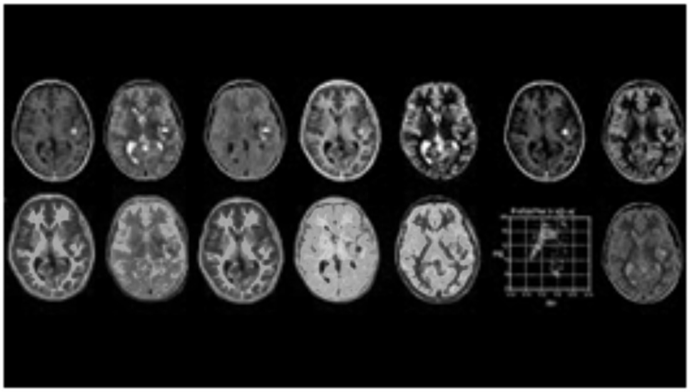


WORKING OF MRI MACHINE

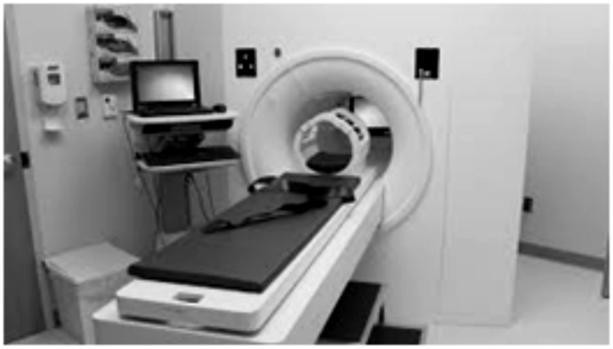
Components of an MRI Scanner

The major components of an MRI scanner are: the main magnet, which polarizes the sample, the shimcoils for correcting shifts in the homogeneity of the main magnetic field, the gradient system which is used to localize the MR signal and the RF system, which excites the sample and detects the resulting NMR signal. The whole system is controlled byone or more computers.

Working of MRI machine during diagnosis



MRI Images



- First, energy from an oscillating magnetic field temporarily is applied to the patient at the appropriate resonance frequency.
- The excited hydrogen atoms emit a radio frequency signal, which is measured by a receiving coil.
- The radio signal may be made to encode position information by varying the main magnetic field using gradient coils.
- As these coils are rapidly switched on and off they create the characteristic repetitive noise of an MRI scan.
- The contrast between different tissues is determined by the rate at which excited atoms return to the equilibrium state.
- Exogenous contrast agents may be given to the person to make the image clearer.

3

Intermolecular Forces and Potential Energy Surfaces

UNIT SPECIFIC

This unit discusses the topics: Ionic, dipole-dipole and van Der Waals interactions. Equations of state of real gases and critical phenomena. Potential energy surfaces of H_3, H_2F and HCN on these surfaces.

RATIONALE

Intermolecular forces are very significant to understand the physical properties. Hydrogen bond is a special case of dipole forces and explains numerous properties of life. Gases which have negligible intermolecular forces of attraction deviate from ideal behavior and can be understood from Van der Waals' Real gas equation. Whether or not a chemical bond is formed can be interpreted from potential energy surfaces of various chemical compounds. Let us understand all these in this unit.

PRE-REQUISITES

Chemistry : Periodic properties, Periodic Table
Maths : Basic Algebra and Trigonometric Functions
Physics : Forces and interactions

LEARNING OUTCOMES

After this Unit, students must be able to:

U3-O1: Interpret the properties arising due to different types of molecular interactions.
U3-O2: Apply the concept of hydrogen bond in real life
U3-O3: Analyse the real gases deviation from ideal gases and critical phenomena
U3-O4: Comprehend the potential energy surfaces of various chemical compound

MAPPING OF UNIT WISE LEARNING OUTCOMES WITH THE COURSE OUTCOMES

Outcome	EXPECTED MAPPING WITH COURSE OUTCOMES (1- Weak Correlation; 2- Medium correlation; 3- Strong Correlation)				
	CO-1	CO-2	CO-3	CO-4	CO-5
U3-O1	3				
U3-O2				2	
U3-O3	2				
U3-O4	1			3	

3.1 INTRODUCTION

Molecular Interactions are attractive or repulsive forces between molecules and between non-bonded atoms. Molecular interactionsare important in diverse fields of protein folding, drug design, material science, sensors, nanotechnology, separations, and origin of life.

Types of Molecular Interactions

1. Intramolecular interaction
2. Intermolecular interaction

1. **Intramolecular interaction:** An intramolecular interaction develops in same molecule. They are usually stronger than intermolecular forces, which are present between atoms or molecules that are not bonded.
2. **Intermolecular interaction:** Intermolecular interactions occur between all types of molecules or ions in all states of matter. The physical properties of melting point, boiling point, vapour pressure, evaporation, viscosity, surface tension, and solubility are related to the strength of attractive forces between molecules. These attractive forces are called **Intermolecular Forces**.

3.2 TYPES OF INTERMOLECULAR FORCES

Mostly the intermolecular forces are of three types-

(a) Ionic interaction
(b) Dipole-dipole interaction
(c) Van der Waals interactions

3.2.1 Ionic Interaction or Ionic Forces

Ionic Forces are interactions between charged atoms or molecules. This interactions arise from electrostatic attraction between two groups of opposite charge. Ions are of two types according to charges –

- **Cations :** Positively charged ions, such as Na^+, Li^+, and Ca^{2+}, are termed cations.
- **Anions :** Negatively charged ions, such as Cl^-, Br^-, HO^- are called anions.

The attractive forces between oppositely charged ions is described by **Coulomb's Law,** in which the force increases with charge and as decreases as the distance between these ions is increased. The highly polarized (charged) nature of ionic molecules is reflected in their high melting points (NaCl has a melting point of 801°C) as well as in their high water solubility.

3.2.2 Dipole-Dipole Interaction

Dipole-dipole interaction occurs whenever two polar molecules get near each other. The positively charged portion of one molecule is attracted to the negatively charged portion of another molecule. Since many molecules are polar, this is a common intermolecular force.

Dipole-dipole forces: Molecules that have dipole moments tend to align with the positive and negative ends of the dipole toward one another.

- These are highly directional forces, but tend to be disrupted by thermal motion of the molecules especially in the liquid state.
- The magnitude of such interactions is only about 1% that of covalent or ionic bonds.
- These interactions become weak rapidly as the distance between the dipoles increases; $E = -2\mu_1\mu_2/\alpha r^3$ (μ_1 and μ_2 are the individual dipole moments).

By taking example of Hydrogen bonding we may be described as the dipole-dipole interaction.

3.2.3 Hydrogen Bond

Hydrogen bond is an electrostatic attractive force between covalently bonded hydrogen atom of one molecule and an electronegative atom (such as F, O, N) of another molecule (or same molecule).

- A dipole-dipole interaction where the H atom is noncovalently attracted to an electronegative atom
- The H must have a large positive delta and the other atom must have a source of electrons to be attracted to H
- Usually negatively charged F, O, N is attracted to the positively charged H
- Use of it is very important in biology.

3.2.4 Characteristics

- A H bond is a weak bond and is dynamic [3×10^{-12} lifetime]
- In solid phase H-bond is static
- H-bonds between molecules continually form and break in liquid.

For **example in H-F**, there is a covalent bond between H and F. Since F is more electronegative than H, so it acquires partial negative charge (as it attracts shared pair of electrons more) and Hydrogen acquires partial positive charge.

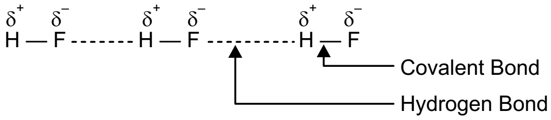
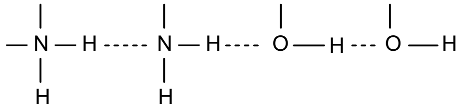


Fig. 3.1: Hydrogen Bonding in H-F

3.2.5 Types of Hydrogen Bonding

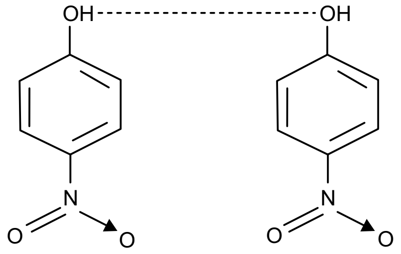
1. **Intermolecular Hydrogen bonding:** *This type of Hydrogen bonding occurs between atoms of two same or different molecules.*



Hydrogen Bonding in NH_3 and H_2O

Fig. 3.2: Hydrogen Bonding in NH_3 and H_2O

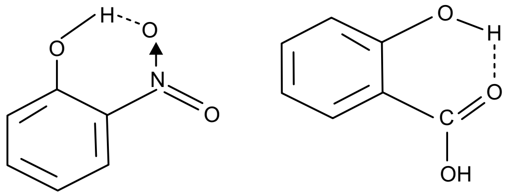
Intermolecular Hydrogen bonding increases the boiling point of the compound and also its solubility in water.



p - nitrophenol

Fig 3.3: p - nitrophenol

2. **Intramolecular Hydrogen bonding:** *This type of hydrogen bonding occurs between two atomsof the same molecule.*



O-Nitrophenol

O-hydroxy benzoic acid

Fig. 3.4: O-Nitrophenol and p-nitrophenol

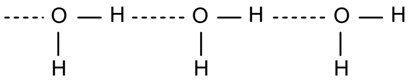
Intramolecular hydrogen bonding decreases the boiling point of the compound and also its solubility in water, as it prevents the association between molecules, which would have raised boiling point and it also prevents hydrogen bonding between compound and water thereby decreasing its solubility in H_2O.

3.2.6 Importance of Hydrogen Bonding in Daily Life

1. Boiling Point: As we know that boiling point increases with increase in intermolecular forces which is greater for heavier molecules.

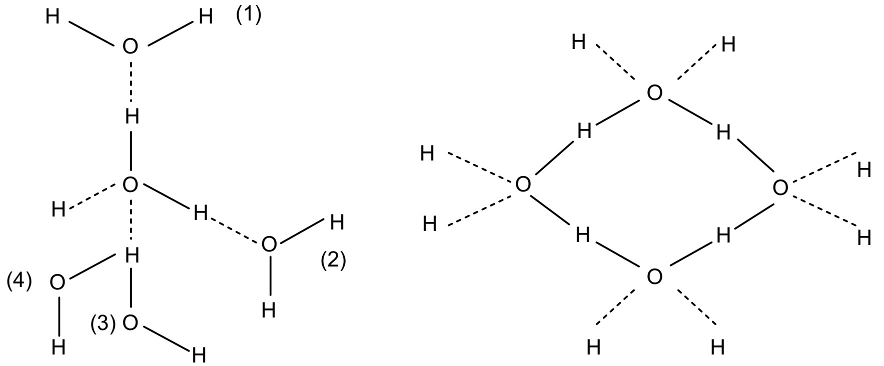
(a) **Higher B. P. of water**-Although water has the lowest molecular weight among hydrides of 16th group of the periodic table,it has the highest melting and boiling points and is liquid (while hydrides of other members are gases) under ordinary conditions.

This can be explained on the basis that water molecules are associated through hydrogen bonding.



$$\cdots\underset{\displaystyle H}{\underset{|}{O}} - H \cdots \underset{\displaystyle H}{\underset{|}{O}} - H \cdots \underset{\displaystyle H}{\underset{|}{O}} - H$$

(b) **The two unusual properties of water** ***i.e.*** (a) low density in solid state than that in the liquid state (b)contraction when heated between 0°C and 4°C can be explained on the basis of hydrogen bonding in water.



Hydrogen bonds in Water

Hydrogen bonds in in Ice
(Cage Like Structure)

Fig. 3.5: Hydrogen bond in water and ice

2. Water Solubility: A substance, which is capable of forming hydrogen bond with water molecules, are soluble in water. On the other hand substances incapable of forming hydrogen bond with water are insoluble in water.

Example - Organic molecule like alcohol, acid are soluble in water while alkanes, alkenes, ether which are incapable of forming hydrogen bond are insoluble in water.

3. Hydrogen bonding in biological systems: Hydrogen bonding also plays very important role in biological system. There are hydrogen bonding between base pairs, (purine and pyrimidine) of D.N.A.

These are 2 hydrogen bonds between Adenine and Thymine, while 3 between Guanine and Cytosine. Primary structure of protein is stabilized by hydrogen bonding.

3.2.7 VAN DER WAALS FORCES

Van der Waals forces are the interaction between uncharged atoms or molecules. The Van der Waals forces include Keesom interaction, the Debye force, and the London dispersion force. So, Van der Waals forces include intermolecular forces and also some intramolecular forces.

The forces are used to explain the universal attraction between bodies, the physical adsorption of gases, and the cohesion of condensed phases.

There are four types. It all flows from this general principle: as bonds become more polarized, the charges on the atoms become greater, which leads to greater intermolecular attractions, which leads to higher boiling points.

Ionic Bonds > H Bonding > Van der Waals Dipole-Dipole Interactions > Van der Waals Dispersion Forces.

The intermolecular forces increasein strength according to the following:

London dispersion < dipole-dipole < H-bonding < ion-ion

Now, as these things increase in strength it becomes harder to remove the molecules from each other.

3.2.8 London Dispersion Force

The London dispersion force is the weakest of the intermolecular forces. This is the force betweentwo nonpolar molecules. The electrons of one molecule are attracted to the nucleus of the other molecule, while repelled by the other molecule's electrons. A dipole is induced when the electron clouds of the molecules are distorted by the attractive and repulsive electrostatic forces.

Example: Interaction between two methyl ($-CH_3$) groups, nitrogen gas (N_2) and oxygen gas (O_2) molecules.

USE OF ICT

https://phet.colorado.edu/sims/html/atomic-interactions/latest/atomic-interactions_en.html

APPLICATIONS IN DAILY LIFE

- Human DNA is an interesting example of a hydrogen bond. It actually enables the replication of DNA strands.
- It help us to understand a protein's function and behavior during biological process.
- Formic acid is most frequently used as a way to preserve food for livestock so that it stays fresh as long as possible due to symmetric H-bond.
- Synthesis of polymer may possible because of the dipole-dipole interactions.

3.3 EQUATION OF REAL GAS AND CRITICAL PHENOMENA

The states of matter are liquid, solid, and gas which can be recognized through their key characteristics. Here we will be able to note some differences between ideal gas and real gas.The behavior of real gases are very much complex while the behavior of ideal gases are much simpler.

Ideal gases–A gas which obeys Boyle's law, Charles' law etc. under all condition of temperature and pressure is known as an ideal gas or a perfect gas.

Gas equation ($PV = nRT$) derived from Boyle's law and Charles' law so an ideal gas may be defined as –

A gas which obeys the gas equation ($PV = \boldsymbol{n}RT$) under all conditions of temperature and pressure is known as ideal gas.

It is observed that no gas which obeys the gas law or the gas equation under all condition of temperature and pressure. Hence concept of ideal gas is hypothetical or only theoretical so.

Real gas : A real gas is one which obeys the gas law fairly well under low pressure or high temperature.

Real gases are non-hypothetical gases whose molecules occupy space and have interactions; consequently, they adhere to gas laws. To understand the behavior of real gases, the following must be taken into account:

- Compressibility effects
- Variable specific heat capacity

- Van der Waals forces
- Non-equilibrium thermodynamic effects
- Issues with molecular dissociation and elementary reactions with variable composition

3.3.1 Differences between Ideal and Real Gases

The main differences between ideal and real gases are summed up as under in Table 3.1

Table 3.1: Differences between ideal and real gases

S. No.	Characteristics	Ideal gas	Real gas
1.	Definition	A gas which obeys the gas equation under all conditions of Temperature and pressure is known as ideal gas	A real gas is one which obeys the gas law fairly well under low pressure or high temperature
2.	Equation	It obeys ideal gas equation (PV = nRT)	It obeys Vander Waal's equation : $\left(P^2 + \frac{an^2}{V^2}\right)$ (V-b) = nRT
3.	Definite volume	Ideal gas has no definite volume, volume of gas will be zero at –273°C	Real gas has definite volume as gas will liquefy before reaching +273°C
4.	Mass	Ideal gas has no mass	Real gas has mass
5.	Collision	Collision of ideal gas particles is elastic	Collision for real gas is non-elastic.
6.	Thermal effect	There will be no thermal effect on expansion or compression without external pressure	There will be some thermal effect
7.	Compressibility Factor	Compressibility Factor Z (PV/nRT)is always 1	Value of Z is not always 1 for real gases
8.	Force of attraction	The force of attraction among the molecules of the gas are negligible	The force of attraction among the molecules of the gas are not negligible at all temperature and pressure

3.3.2 Deviation of real gases and Van der Waal's equation

The ideal gas laws derived from the kinetic theory of gases which is based on the following important assumptions:

- The volume occupied by the molecules is negligible in comparison to the total volume of the gas.
- The molecules exert no force of attraction upon one another.

These assumptions can not be regarded as applicable to real gases. Therefore real gases show deviation from the ideal behaviour. The molecules of a gas, do occupy a certain volume as the gases can be liquefied and solidified at low temperatures and high pressures. On decreasing the temperature of a gas, and applying high pressure molecules come closer to one another, thereby increasing the forces of attraction between them. Both these factors favour liquefaction and solidification. It is, therefore, apparent that the molecules of a gas must have an appreciable volume.

The molecules in gases also have weak forces of attraction (called Van der Waals attractions) between them. This is supported by the fact that gases can be liquefied.

Van der Waals was the first to introduce systematically the correction terms due to the above two invalid assumptions in the ideal gas equation $p_i V_i = nRT$. The corrections are given below.

Correction for Volume

In the ideal gas equation $p_i V_i = nRT_i$, where V_i represents an ideal volume where the molecules can move freely.In real gases, a part of the total volume is, however, occupied by the molecules of the gas. Hence, the free volume V_i is the total volume V minus the volume occupied by the molecules. If b represents the effective volume occupied by the molecules of 1 mole of a gas, then for n moles of the gas V_i is given by

$$V_i = V - nb \qquad \text{...(i)}$$

where b is called the excluded volume. The numerical value of b is four times the actual volume occupied by the gas molecules. This can be shown as follows:

Correction for forces of attraction

Consider a molecule A in the bulk of a vessel as shown in Fig. This molecule is surrounded by other molecules symmetrically in all directions with the result that this molecule on the whole experiences no net force of attraction.

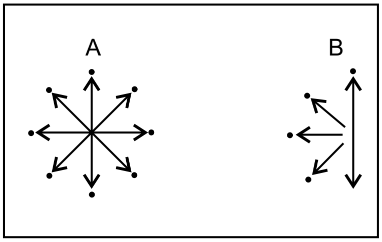


Fig. 3.6: Forces of attraction between molecules of a gas

Now, consider a molecule B near the side of the vessel, which is about to strike one of its sides, thus contributing towards the total pressure of the gas. There are molecules only on inner side of the wall. This molecule experiences a net force of attraction towards the centre of the vessel. This results in decreasing the velocity of the molecule. Thus, the molecule does not contribute as much force as it would have, had there been no force of attraction towards the centre. Thus, the pressure of a real gas would be smaller than the corresponding pressure of an ideal gas, *i.e.*

$$p_i = p + \text{correction term}$$

This correction term depends upon two factors:

(i) The number of molecules per unit volume of the vessel.

(ii) The number of molecules striking the side of the vessel per unit time.

$$p_i = p + a\frac{n^2}{V^2} \qquad \text{... (ii)}$$

where '*a*' is the proportionality constant

The unit of the term $\frac{an^2}{V^2}$ will be the same as that of the pressure. The SI unit of '*a*' will be Pa m^6 mol^{-2}. It may be conveniently expressed in kPa dm^6 mol^{-2}.

Substituting the value of V and *p* from equations (i) and (ii) in the ideal gas equation $p_iV_i = nRT_i$ we get,

$$p + a\frac{an^2}{V^2}(V - nb) = nRT$$

This equation is applicable to real gases and is known as the Van der Waals equation. The constants *a* and *b* in Van der Waals equation are called Van der Waals constants which may vary from gas to gas. pV and T are the observed pressure, volume and temperature for the gas under study.

3.3.3 Significance of Van der Waals Constants

(i) The value of '*a*' is higher for easily liquefiable gases (as SO_2, NH_3, H_2S, CO_2 etc.) while lower for permanent gases (as H_2, N_2, O_2, He etc.).Order of liquification of some gases:

Gas SO_2 > Cl_2 > NH_3 > CO_2 > N_2 > O_2 > H_2 > Ne > He

$a \rightarrow$ 6.71 6.5 4.17 3.58 1.39 1.36 0.24 0.03

Since the constant '*b*' is the effective volume of the gas molecules hence it indicates that the gas molecules are incompressible.

3.3.4 Liquefaction of Gases and Critical Temperature

The liquefaction of a gas takes place when the intermolecular forces of attraction become so high that they bind the gas molecules together to form the liquid state. The intermolecular forces of attraction can be increased either by increasing the pressure so that the molecules come close together or by cooling the gas so that the kinetic energy of the molecules decreases and they become slower.

Gases like hydrogen, helium, oxygen, nitrogen could not be liquefied at room temperature by application of pressure alone. For each gas, there is a particular temperature above which it cannot be liquefied, howsoever, high pressure may be applied on the gas. This temperature is called critical temperature.

Critical temperature : Critical temperature of a gas may be defined as that temperature above whichit cannot be liquefied however high pressure may be applied on the gas.

Critical Pressure : The pressure required to liquefy the gas at the critical temperature is called critical pressure .

Critical volume : The volume occupied by 1 mole of the gas at critical temperature and critical pressure is called critical volume.

All the three are called critical constants of the gas and are represented by T_c, T_p, T_v. This phenomenon may be explained by Andrew's experiments on CO_2 gas.

3.3.5 The Critical Point

Liquid and gas can coexist only within the regions indicated by the green-shaded area in the diagram above. As the temperature and pressure rise, this region becomes more narrow, finally reaching zero width at the critical point. The values of P, T, and V at this juncture are known as the critical constants P_c, T_c, and V_c. The isotherm that passes through the critical point is called the critical isotherm. Beyond this isotherm, the gas and liquids become indistinguishable; there is only a single fluid phase, sometimes referred to as a supercritical liquid figure 3.7.

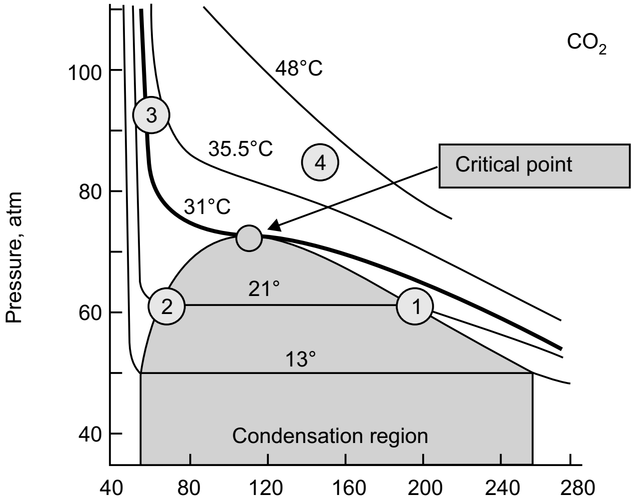


Fig. 3.7: Critical Points

At temperatures below 31°C (the critical temperature), CO_2 acts somewhat like an ideal gas even at a rather high pressure (4). Below 31°C, an attempt to compress the gas to a smaller volume eventually causes condensation to begin. Thus at 21°C, at a pressure of about 62 atm (1), the volume can be reduced from 200 cm^3 to about 55 cm^3 without any further rise in the pressure. Instead of the gas being compressed, it is replaced with the far more compact liquid as the gas is essentially being "squeezed" into its liquid phase. After all of the gas has disappeared (2), the pressure rises very rapidly because now all that remains is an almost incompressible liquid. Above this isotherm (3) CO_2 exists only as a supercritical fluid.

3.3.6 Critical Phenomena

The essential condition for the liquefaction of the gas is described by the study of critical temperature, critical pressure and critical volume and their inter relationships.

When a gaseous system is transformed to its liquid state, there is a tremendous decrease in the volume. This decrease in volume can be effectively brought about by lowering of temperature, or by increasing pressure (or) by both. In both these effects the gaseous molecules come closer to each other and experience an increase in force of attraction which results in liquefaction of gases. At any constant temperature when pressure is increased, volume is decreased and vice versa. Such P-V curves at constant temperature are known as isotherms. There is a definite deviation exhibited by the real gas from ideal gas behaviour at high pressure and low volumes.

3.3.7 Critical Temperature (T_c)

It is defined as the characteristic temperature of a gas at which increase in pressure brings in liquefaction of gas above which no liquefaction occurs although the pressure may be increased many fold. For instance T_C of CO_2 is 31.1°C. This means that it is not possible to liquefy CO_2 by applying pressure when its temperature is above 31.1°C.

Critical Pressure (P_c)

It is defined as the minimum pressure required to liquefy 1 mole of a gas present at its critical temperature.

Critical Volume (V_c)

The volume occupied by 1 mole of a gas at its critical pressure and at critical temperature is the critical volume (V_c) of the gas.

A gas is said to be at its critical state when its pressure, volume and temperature are P_c, V_c and T_c.

3.3.8 Thomson's experiment

Thomson (1871) studied the isotherm of CO_2 drawn by Andrews. He suggested that there should be no sharp points in the isotherms below the critical temperature. These isotherms should really exhibit a complete continuity of state from gas to liquid. This, he showed as a theoretical wavy curve. The curve MLB represents a gas compressed in a way that it would remain stable. The curve MNC represents a superheated liquid because compression above Tc, leads to heating effects. This type of continuity of state is predicted by Van der Waal's equation of state which is algebraically a cubic equation. The Van der Waal's equation may be written as

$$PV^3 - (RT + Pb)\,V^2 + aV - ab = 0$$

Thus, for any given values of P and T there should be three values of V. These values are indicatedby points B, M and C of the wavy curve. The three values of V become closer as the horizontal part ofthe isotherm rises. At the critical point the three roots of Van der Waal 'V' become identical and there isno longer any distinction between the gas and liquid states. Here, the gas is said to be in critical state. This effect enables the calculation of T_c, P_c and V_c in terms of Van der Waal's constants.

Derivation of critical constants from Van der Waal's constants

Let us derive the values of critical constants T_c (critical temperature), V_c (critical volume) and P_c(critical pressure) in terms of the Van der Waal's constants '*a*' and '*b*'. The Van der Waal's equation is given by

$$\mathbf{T_c = 8a / 27Rb}$$

Hence the critical constants can be calculated using the values of Van der Waal's constants of a gas and vice versa. Since P_c and T_c can often be determined experimentally, these values may be employedto calculate the constants *a* and *b*.

$$a = 3V_c^2 P_c$$
$$b = V_c / 3$$

Based on the critical temperature values, gases are categorized as "permanent" and "temporary" gases. H_2, N_2, He gases having very low critical temperature belong to the permanent type. Gases like NH_3, CO_2, SO_2, HCl etc. having critical temperature in the ordinary range of temperatures belong to the temporary gases type.

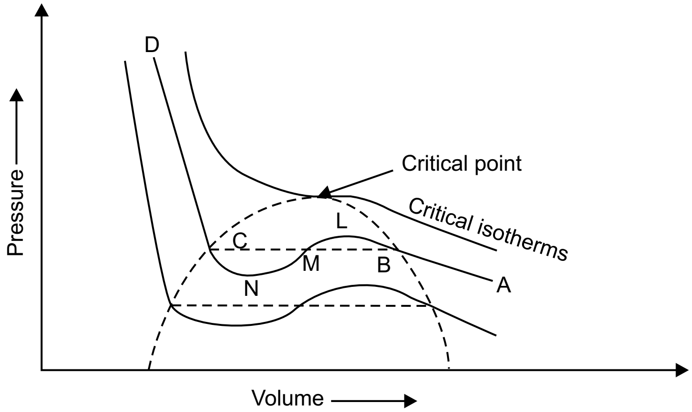


Fig. 3.8: Thomason's Isotherms of Carbon dioxide

3.3.9 Joule-Thomson Effect and Inversion Temperature (T_i)

Joule-Thomson Effect

Joule-Thomson showed that when a compressed gas is forced through a porous plug into a region of low pressure, there is appreciable cooling. The phenomenon of producing lowering of temperature whena gas is made to expand adiabatically from a region of high pressure into a region of low pressure, is known as Joule - Thomson effect.

When the gas is allowed to escape into a region of low pressure the molecules move apart rapidly against the intermolecular attractive forces. In this case work is done by the gas molecules at the expense of internal energy of the gas. Therefore cooling occurs as the gas expands. This reduction in the temperatureis generally referred as Joule-Thomson effect and is used in the liquefaction of gases.

Inversion temperature (T_i)

The Joule-Thomson effect is obeyed by a gaseous system only when its temperature is below a characteristic value. The characteristic temperature below which a gas expands adiabatically into a region of low pressure through a porous plug with a fall in temperature is called as inversion temperature (T_i).

T_i is characteristic of a gas and it is related to the Van der Waal's constant '*a*' and '*b*',

$$2a\,T_i = 2a/Rb$$

At the inversion temperature there is no Joule Thomson effect (*i.e.*) there is neither fall nor rise in temperature. Only when the temperature of the gas is below the inversion temperature there is a fall in temperature during adiabatic expansion. If the temperature of the gas is above T_i there is a small rise in temperature. For gases like H_2 and He whose T_i values are very low –80°C and –240°C respectively, these gases get warmed up instead of getting cooled during the Joule-Thomson experiment. These gaseswill obey Joule-Thomson effect only when they are cooled to a temperature below these T_i values.

APPLICATION IN DAILY LIFE

- Ideal gas laws are used for the working of airbags in vehicles.
- Coolant and radiator used in home appliance like Air condition and refrigerator are working on the same principle.
- There are infinite applications of Ideal Gas Laws in real life. It is used to calculate variation of density with pressure in different flows. Ex: Rockets, Fluid motion, Compressibility Analysis, Engines, etc.

3.4 POTENTIAL ENERGY SURFACES OF H_3, H_2F, HCN

A **potential energy surface** is a mathematical function that gives the **energy** of a molecule as a function of its geometry. Molecular Mechanics provides this **energy** as a function of stretches, bends, torsions, etc.

A potential energy surface (PES) describes the potential energy of a system, especially a collectionof atoms, in terms of certain parameters, normally the positions of the atoms.

The surface might define the energy as a function of one or more coordinates; if there is only one coordinate, the surface is called a potential energy curve or energy profile. It is helpful to use the analogy of a landscape: for a system with two degrees of freedom (*e.g.* two bond lengths), the value ofthe energy (analogy: the height of the land) is a function of two bond lengths (analogy: the coordinates of the position on the ground). The Potential Energy Surface represents the concepts that each geometry(both external and internal) of the atoms of the molecules in a chemical reaction is associated with it a unique potential energy. This creates a smooth energy "landscape" and chemistry can be viewed from atopology perspective (of particles evolving over "valleys" and "passes").

3.4.1 Potential Energy Curves (1-D Potential Energy Surfaces)

The PES is the energy of a molecule as a function of the positions of its nuclei r. This energy of a system of two atoms depends on the distance between them. At large distances the energy is zero, meaning "no interaction". At distances of several atomic diameters attractive forces dominate, whereas at very close approaches the force is repulsive, causing the energy to rise. The attractive and repulsive effects are balanced at the minimum point in the curve. Plots that illustrate this relationship are quite useful in defining certain properties of a chemical bond.

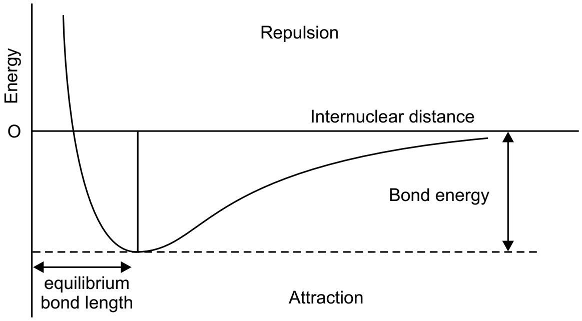


Fig. 3.9: A potential Energy Curve for a covalent bond.

The internuclear distance at which the potential energy minimum occurs defines the bond length. This is more correctly known as **the equilibrium bond length**, because thermal motion causes the two atoms to vibrate about this distance. In general, the stronger the bond, the smaller will be the bond length.

Attractive forces operate between all atoms, but unless the potential energy minimum is at least of the order of RT, the two atoms will not be able to withstand the disruptive influence of thermal energy long enough to result in an identifiable molecule. Thus we can say that a chemical bond exists between the two atoms in H_2.

3.4.2 Potential, Kinetic, and Total Energy for a System

Potential energy and kinetic energy quantum theory tells us that an electron in an atom possesses kinetic energy K as well as potential energy V, so the total energy E is always the sum of the two:

$$E = V + K.$$

The relation between them is surprisingly simple: $K = -0.5\ V$.

This means that when a chemical bond forms (an exothermic process with $\Delta E < 0$), the decrease in potential energy is accompanied by an increase in the kinetic energy (embodied in the momentum of the bonding electrons), but the magnitude of the latter change is only half as much, so the change in potential energy always dominates. The bond energy $-\Delta E$ has half the magnitude of the fall in potential energy.

3.4.3 The Dimensionality of A Potential Energy Surface

To define an atom's location in 3-dimensional space requires three coordinates (*e.g.*, x, y, and z or r, θ and ϕ in Cartesian and Spherical coordinates) or degrees of freedom. However, a reaction and hence the corresponding PES do not depend on the absolute position of the reaction, only the relative positions (internal degrees). Hence both translation and rotation of the entire system can be removed (each with 3 degree of freedom, assuming non-linear geometries). So the dimensionality of a PES is

$$3\ N-6$$

where N is the number of atoms involves in the reaction, *i.e.*, the number of atoms in each reactants). The PES is a hypersurface with many degrees of freedom and typically only a few are plotted at any one time for understanding.

For very simple chemical systems or when simplifying approximations are made about inter-atomic interactions, it is sometimes possible to use an analytically derived expression for the energy as a function of the atomic positions. An example is

$$H + H_2 \rightarrow H_2 + H$$

system as a function of the three H–H distances. For more complicated systems, calculation of the energy of a particular arrangement of atoms is often too computationally expensive for large scale representations of the surface to be feasible.

3.4.4 APPLICATION OF POTENTIAL ENERGY SURFACES

- A PES is a conceptual tool for aiding the analysis of molecular geometry and chemical reaction dynamics.
- It can be used to theoretically explore properties of structures composed of atoms, for example, finding the minimum energy shape of a molecule or computing the rates of a chemical reaction.

- Potential Energy Surfaces are widely used for the Study of Enzymatic Reactions
- Application of potential energy surfaces are more popular in optimization analysis of matter globally.

Interesting Facts

- Real life examples of potential energy are a bicycle on top of a hill, a book held over your head, and a stretched spring all have potential energy**.**
- Pendulum, springs, bow and arrow, food we eat all works under principle of potential energy.
- For more detail of daily life examples, may click the link - https://www.youtube.com/watch?v=NW0mNe9S5dM

SUMMARY

- **Molecular Interactions may be two types –** Intramolecular interaction and Intermolecular interaction
- **Three types of intermolecular forces** – Ionic interaction,Dipole-dipole interaction and Van der Waals interactions.
- **Ionic Forces or Ionic interaction** are interactions between charged atoms or molecules. This interactions arise from electrostatic attraction between two groups of opposite charge.
- **Dipole-Dipole Interaction –** Dipole-dipole interaction occurs whenever two polar molecules get near each other. The positively charged portion of one molecule is attracted to the negatively charged portion of another molecule.
- **Hydrogen Bonding –** A dipole-dipole interaction where the H atom is noncovalently attracted to an electronegative atom like F, O, N.
- **Van der Waals Forces –** Van der Waals forces are the interaction between uncharged atoms or molecules.
- Ionic Bonds > H Bonding > Van der Waals Dipole-Dipole Interactions > Van Der Waals Dispersion Forces.
- **Ideal gases –** A gas which obeys Boyle's law, Charles' law etc. under all condition of temperature and pressure is known as an ideal gas or a perfect gas.
- **Real gas** – A real gas is one which obeys the gas law fairly well under low pressure or high temperature.
- **Critical temperature –** Critical temperature of a gas may be defined as that temperature above which it cannot be liquefied however high pressure may be applied on the gas.
- **Critical Pressure –** The pressure required to liquefy the gas at the critical temperature is called critical pressure .
- **Critical volume** – The volume occupied by 1 mole of the gas at critical temperature and critical pressure is called critical volume.
- **Potential energy surfaces of H_3, H_2F, HCN – Potential energy surface** is a mathematical function that gives the **energy** of a molecule as a function of its geometry.
- **A potential energy surface** (PES) describes the potential energy of a system, especially a collection of atoms, in terms of certain parameters, normally the positions of the atoms.

EXERCISE

SUBJECTIVE QUESTIONS

1. In what manner are ideal gases are different from real ? Derive Van der Waal's equation of state and explain the behavior of real gases.

2. What are critical phenomenon of gases. Deduce the relationship between critical constants and Van der Waal's equation for gas.

3. What are critical constants? Calculate the values of V_c, P_c and T_c in terms of a and b by applying Van der Waal's equation on the critical phenomenon.

4. What are the reason of deviation from ideal behavior of gas equation $PV = nRT$? Write Van der Waal's equations and give its application.

5. What do you mean by molecular interaction? How many types of it? Explain any two in detail.

6. Discuss Van der Waal's interactions in details.

7. Explain the liquefaction of gases based on Joule-Thomson effect.

8. What are the limitations of Van der Waal's equations. Write the units of Van der Waal's constants a and b.

9. Write 4 differences between ideal and real gases.

10. Write short notes on

- (a) Hydrogen bonding
- (b) Dipole - dipole interactions
- (c) Strength of molecular interactions
- (d) Real and ideal gases
- (e) Gas equation and correction in Van der Waal's.

SHORT ANSWER QUESTIONS

Q.1. Which of the following molecules have a permanent dipole moment?

(a) H_2O (b) CO_2

(c) CH_4 (d) N_2

(e) CO (f) NH_3

Ans. CO_2, CH_4 and N_2 are symmetric, and hence they have no permanent dipole moments. A moleculewith polar bonds unsymmetrically arranged will possess a permanent dipole.

Q.2. Which has the higher boiling point, Br_2 or ICl?

Ans. They have similar molecular weights: Br_2, 160; ICl, 162. Their boiling points are 332 K and 370 K respectively.

Q.3. An atom or molecule can be temporarily polarized by a nearby species. Polarization separates centers of charge giving

(a)	permanent dipole	(b)	temporary charges
(c)	hydrogen bonding	(d)	induced dipole
(e)	induced ions	(f)	radicals

Ans. Induced dipoles are responsible for the London dispersion forces. The heavier the molecule, the larger the induced dipole will be. Thus, London dispersion forces are strong for heavy molecules.

Q.4. Which has a higher boiling point, I_2 or Br_2?

Ans. Atomic weights for Br and I are 80 and 127 respectively. The higher the molecular weight, the stronger the London dispersion forces.

Q.5. If only London dispersion forces are present, which should have a lower boiling point, H_2O or H_2S?

Ans. The b.p. for H_2O is 100 °C, and that of H_2S is –70 °C. Very strong hydrogen bonding is presentin liquid H_2O, but no hydrogen bonding is present in liquid H_2S.

Q.6. Contrary to most other substances, the density of water decreases as temperature decreases between 4 and 0 °C. This is due to

(a) dipole-dipole interaction

(b) London dispersion

(c) decreasing number of hydrogen bonds

(d) increasing number of hydrogen bonds formed

Ans. As more hydrogen bonds form when the temperature decreases, the volume expands, causing a decrease in density. Above 4°C, the thermal expansion is more prominent than the effect of hydrogen bonds.

Q.7. Ethanol (C_2H_5OH, molar mass 46) boils at 351 K, but water (H_2O, molar mass 18) boils at higher temperature, 373 K. This is because:

(a) water is denser

(b) water has stronger London dispersion forces

(c) water has stronger hydrogen bonds

(d) water molecules contain no carbon

Ans. A hydrogen atom between two small, electronegative atoms (such as F, O, N) causes a strong intermolecular interaction known as the hydrogen bond. The strength of a hydrogen bond depends upon the electronegativities and sizes of the two atoms.

Q.8. Ethanol C_2H_5OH and methyl ether CH_3OCH_3 have the same molar mass. Which has a higher boiling point?

Ans. R–OH group is both proton donor and acceptor for hydrogen bonding. Methyl groups have very weak hydrogen bonding, if any.

OBJECTIVE QUESTIONS

1. The energy stored in coal is

(a) Kinetic energy (b) Potential energy

(c) Chemical energy (d) Nuclear energy [**Ans.** (c)]

Feedback: During photosynthesis solar energy is converted in the form of glucose and carbohydrate.

2. Determination of saddle point is an application of which -

(a) Potential energy surfaces (b) Kinetic energy graphs

(c) S shaped curve (d) Growth curve [**Ans.** (a)]

Feedback – Potential energy between any two minima (valley bottoms) the lowest energy path will pass through a maximum at a saddle point, which we call that saddle point a transition-state structure.

3. Which one of the following represents the weakest interaction between two species?

(a) Hydrogen bond (b) Disulfide bond

(c) Ionic bond (d) Dispersion force **[Ans.** (d)]

Feedback: For this question, you need to recall that a disulfide bond is a type of covalent bond (which operates between two sulfur atoms). The hydrogen bond is weaker than ionic or covalent bonds, but is around ten times stronger than a dispersion force.

4. What is the minimum number of hydrogen bonds that operate between base pairs in DNA?

(a) 0 (b) 1

(c) 2 (d) 4 [**Ans.** (c)]

Feedback : The base pairs that exist in DNA are joined by either two or three hydrogen bonds: C and G are joined by three hydrogen bonds, while A and T are joined by two.

5. The intermolecular forces of attraction in the above substances is described by which of the following:

(a) Dipole-Dipole Forces (Permanent Dipoles)

(b) Ion-Dipole Forces

(c) Gravitational Forces

(d) Dispersion (Or London) Forces [**Ans.** (d)]

Feedback : The right answer is dispersion (or London) forces

6. The boiling point of water is about 200°C higher than one would predict from the boiling points of hydrogen sulfide and hydrogen selenide. One may explain this apparent anomaly by which of the following?

(a) Water has the lowest molecular weight.

(b) The H-O covalent bond is much stronger than the H-S and H-Se bonds.

(c) Water is less polar than hydrogen sulfide and hydrogen selenide.

(d) The intermolecular attractive forces are much greater in water than in hydrogen sulfide and hydrogen selenide. [**Ans.**(d)]

Feedback : Correct answer is the intermolecular attractive forces are much greater in water than in hydrogen sulfide and hydrogen selenide**.**

PRACTICAL

Experiment - 1

(Student to Record the Experiment as per Template given in Annexure)

Aim: Determine the surface tension of a given liquid at room temp using stalagmometer.

Requirements:

Chemicals : Unknown liquid, Distilled water.

Glassware : Stalagmometer, Rubber tube with screw.

Theory: The number of drops formed by equal volumes of two liquid is counted, for the determination of surface tension of the provided liquid.

If m_1 and m_2 is the mass of the drops, d_1 and d_2 are densities respectively. If n_1 and n_2 are the number of drops formed by volume v of the two liquids, then their surface tensions are related as

$$\frac{\sigma_1}{\sigma_2} = \left(\frac{d_1}{d_2}\right) \times \left(\frac{n_1}{n_2}\right)$$

Procedure:

1. Attach a small piece of rubber tube having a screw pinch cock at the upper end of the dry stalagmometer.
2. Immerse the lower end of the stalagmometer in distilled water and suck the water 1-2 cm above mark A. Adjust the pinch cork so that 10-15 drops fall per minute
3. Clamp the stalagmometer allow the water drops to fall and start counting the number of drops when the meniscus crosses the upper mark A and stop counting when the meniscus passes mark B.

Precautions

- Capillary tube and water should be free from grease.
- Capillary tube should be set vertical.
- Internal diameter of capillary tube should be measured in two mutually perpendicular directions.
- Temperature of water should be noted.

Refer to the MSDS data of each chemical being used for the safety and environment friendly approach to conduct the experiment.

Observations & Calculations:

Room temperature = T^oC

Density of water = d_w

Surface tension of water= η dynes/cm

No. of drops from a fixed volume of the liquid and water as reference (in mL), calculation of mean value

Result: The surface tension of liquid is ………dynes/cm.

Discussion: The Experiment, Observations and Result(s) to be discussed while correlating with theory and real life/industrial applications.

Experiment - 2

(Student to Record the Experiment as per Template given in Annexure)

Aim: To study of models of potential energy surfaces of molecules

Requirements:

Images / spectra /diagram / graph related to potential energy surface of molecules.

Theory: A potential energy surface (PES) describes the potential energy of a system, especially a collection of atoms, in terms of certain parameters, normally the positions of the atoms.

The surface might define the energy as a function of one or more coordinates; if there is only one coordinate, the surface is called a potential energy curve or energy profile.

Observation Table:

S. No.	Name of Compound	Analogy based on degree of freedom	Interpretation

Applications:

- It is helpful to use the analogy of a landscape.
- For a system with two degrees of freedom (*e.g.* two bond lengths), the value ofthe energy (analogy: the height of the land) is a function of two bond lengths (analogy: the coordinates of the position on the ground).
- The Potential Energy Surface represents the concepts that each geometry (both external and internal) of the atoms of the molecules in a chemical reaction is associated with it a unique potential energy.
- This creates a smooth energy "landscape" and chemistry can be viewed from a topology perspective (of particles evolving over "valleys" and "passes").

Result & Discussion: The Experiment, Observations and Result(s) to be discussed while correlating with theory and real life/industrial applications.

References: The examples of potential energy surfaces of molecules may be taken from any reliable resources. One such resource is *https://pubs.acs.org/doi/pdf/10.1021/ed070p295*

Examples of Potential Energy Surface

Experiment - 3

(Student to Record the Experiment as per Template given in Annexure)

Aim: To determine the viscosity of a given unknown liquid with respect to water, at laboratory temperature, by viscometer.

Requirements:

Chemicals: Unknown liquid, distilled water.

Glassware: Ostwald Viscometer, Pinch Cock, Specific Gravity Bottle.

Theory: The force of friction which one part of the liquid offers to another part of the liquid is called viscosity. For measuring the viscosity coefficient, Ostwald viscometer method is used which is based on Poiseuille's law. Formula expressed as η having viscosity coefficient,

$$\eta = \frac{\pi r^4 tp}{8\nu l}$$

Where,

v= vol. of liquid (in mL)

t= flow time (in sec) through capillary

r= radius of the capillary (in cm)

l= length of the capillary (in cm)

P= hydrostatic pressure (in dyne/sq.cm)

η = viscosity coefficient (in poise).

Procedure:

1. Note the laboratory temperature.
2. Wash the specific gravity bottle with distilled water and dry.
3. Take the weight of the empty & filled (with distilled water) specific gravity bottle (with stopper). Then, weigh the filled with specific gravity bottle h unknown given liquid. Use the data for measuring the densities.
4. Clean and rinse the viscometer properly with distilled water. Fix the viscometer vertically on the stand and filled with specific amount (say 20 mL) of mixture (every time take the same volume).
5. Time of flows were recorded for each solutions (water and the given liquid).
6. Take 3 to 4 readings.

Precautions:

- The viscometer should be held in a vertical position during the flow of the liquids.
- While sucking the liquids, no air bubble should be formed inside the capillary tube.

Refer to the MSDS data of each chemical being used for the safety and environment friendly approach to conduct the experiment.

Observations & Calculations:

Weight of empty R.D. bottle (w_1) =…g.

Weight of R.D. bottle with water (w_2) =…g.

Weight of R.D. bottle with liquid (w_3) =…g.

So, weight of water (w_w) = (w_2-w_1) =…g.

Flow time for each set-up and Mean value (in s)

Result & Discussion: The Experiment, Observations and Result(s) to be discussed while correlating with theory and real life/industrial applications.

DESIGN INNOVATIVE / PROJECTS / ACTIVITIES

Project 1 : To Construct and Interpolate Potential Energy Surface of any bio-molecule.

Project 2 : Enlist the factors which affects energy barriers during interaction of molecules. Student may use any web-based interface to computational chemistry packages software. Example - WebMO. Webmo basic is a free software https://www.webmo.net/

SUGGESTED READINGS

BOOKS

- Selected Topics in Inorganic Chemistry by Wahid U Malik , GD Tuli & RD Madan, S Chand Publishing , ISBN: 81-219-0600-8.
- Potential Energy Surfaces, Volume 42, K. P. Lawley (Editor) , Wiley Publication, ISBN: 978-0-470-14307-0.

E-RESOURCES

- https://nptel.ac.in/courses/122/101/122101001/
- https://nptel.ac.in/courses/104/106/104106094/
- https://ncert.nic.in/textbook/pdf/kech104.pdf

KNOW MORE

Force of attraction strongest to weakest

Type of IMFA	Involves	Occurs Between	Strength of Attraction	Effect on Boiling/Melting Points	Effect on Freezing Points
London/ Dispersion	Temporary Dipoles	Nonpolar molecules	Low	Low elevation (↑BP)	(↑↑↑↑FP)
Dipole-Dipole	Permanent dipoles	Polar molecules	Medium	Medium elevation (↑↑BP)	(↑↑↑↑FP)
HydrognBonds	Permanent dipoels between H & F, O, N	Polar molecules	Medium-High	Medium-High elevation (↑↑↑BP)	(↑↑FP)
Dipole-Dipole	Full ion and dipole	Polar molecules	High	High elevation (↑↑↑↑ BP)	(↑FP)

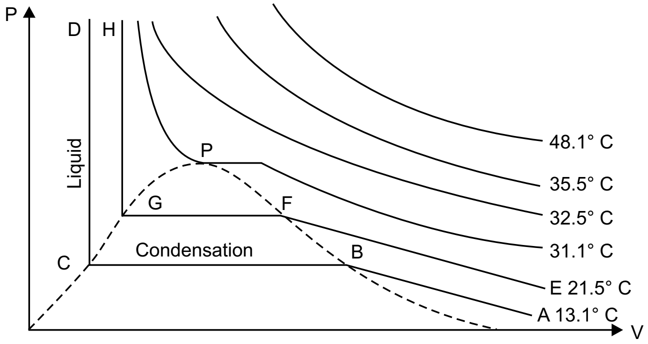
Van der Waals constants for some gases

Substance	Molar mass (g)	a (L^2- atm $mole^{-2}$)	b (L mol^{-1})
Hydrogen H_2	2	0.244	0.0266
Helium He	4	0.034	0.0237
Methane CH_4	16	2.25	0.0428
Water H_2O	18	5.46	0.0305
Nitrogen N_2	28	1.39	0.0391
Carbon dioxide CO_2	44	3.59	0.0427

Andrew's experiments on CO_2 gas

From 1861 to 1870 Andrews carried out his famous experiments on the effect of temperature and pressure on the volume of carbon dioxide. Using the experimental arrangement he plotted a series of isothermals (curves) to test the validity of Boyle's law over a wide range of pressures.The gases were compressed by tightening the screws and the pressure was estimated using air, assumingthat under the conditions of the experiment it still obeyed Boyle's law.

Andrews isothermals were drawn at temperatures 13.1°C, 21.5°C, 31.1°C, 32.5°C, 35.5°C and 48.1°C The experimental result can be depicted in the form of the following graph-



The graph between P and V for CO_2 gas.

Explanation of the graph

The curves obtained by Andrews experiment are shown in the figure 3.6. We observe that there are two types of isothermals:

(a) Above 31.1°C, the isothermals are almost rectangular hyperbola resembling the behaviour of a perfect gas.

(b) Below 31.1°C, the isothermals are not rectangular hyperbola.

At 13.1°C, the portion AB of this curve shows that with the increase of pressure, volume decreases up to the point B showing gaseous behaviour of CO_2 (Boyle's law is obeyed). From B to C, there is changeof state of CO_2 from gaseous to liquid (condensation) and the curve becomes parallel to the volume axis.This indicates that volume decreases without appreciable increase in pressure. After the point C, the curve is very steep indicating that after C, the substance becomes highly incompressible. At C, the gas gets liquefied completely. The portion CD represents the liquid phase of CO_2.

Conclusions

1. Thus the portion AB represents the gaseous phase of the substance and BC represents the conversion from vapour to liquid state. At B conversion starts and at C, it gets completed.
2. At 21.5°C, the curve is similar but only the horizontal portion BC has decreased. This shows that compression produces liquefaction.
3. At 31.1°C, the horizontal portion just disappeared which suggests that gas can be liquefied under compression.
4. Above this temperature *i.e.* 32.5°C, 35.5°C and 48.1°C, the horizontal portion vanished and the behaviour of the gas resembles that of a perfect gas.
5. SO, CO_2 cannot be liquefied by exerting pressure alone but also by cooling it below a certain temperature. This temperature is called as the **'critical temperature'**. This behavior is not specific of CO_2 only but it is common to all gases.

4

Use of Free Energy in Chemical Equilibria

UNIT SPECIFIC

This unit discusses the topics: Thermodynamic functions: energy, entropy and free energy. Cell potentials, Nernst equation, Oxidation reduction and solubility equilibria. Water chemistry. Electrochemical corrosion and Ellingham diagrams.

RATIONALE

Thermodynamics deals with energy transformations and its relation to matter. Natural phenomenon provides big canvas for learning and observing various kinds of energy, its conversion, accumulation etc. The concept of thermodynamic functions, role of electrochemistry, Chemical Equilibria. Metallurgy and Corrosion are dealt with in this Unit.

PRE-REQUISITES

Basic knowledge of thermodynamics and Electro-chemistry

LEARNING OUTCOMES

At the end of this unit, students must be able to:

U4-O1: Apply concept of thermodynamic functions to know spontaneity of a reaction and whether it is endothermic or exothermic.

U4-O2: Design a cell from two half cells and calculate its cell constant

U4-O3: Analyze theories of acids and bases and solubility as chemical equilibria

U4-O4: Apply free energy considerations in metallurgy and corrosion through Ellingham diagrams.

MAPPING OF UNIT WISE LEARNING OUTCOMES WITH THE COURSE OUTCOMES

Outcome	EXPECTED MAPPING WITH COURSE OUTCOMES (1- Weak Correlation; 2- Medium correlation; 3- Strong Correlation)				
	CO-1	CO-2	CO-3	CO-4	CO-5
U4-O1		3			
U4-O2		3			
U4-O3		3			
U4-O4		3			

4.1 INTRODUCTION

The branch of chemistry which concern with the study of inter-relations of the various forms of energy in a system is called thermodynamics.

Why Thermodynamics?

Let us think about some everyday experiences which are related with chemical reactions.

- Frying an egg is an example of an irreversible reaction.
- Why does the NaCl dissolve? Does it give off heat? Does it require energy?
- How is it that diamond, a high-pressure form of C, can coexist with the low pressure form, graphite, at Earth's surface?
- Melt and refreeze of ice shows that H_2O has two phases due to temperature.

Chemical thermodynamics provides us with a means of answering these questions and more.

4.2 FREE ENERGY (ΔG)

Free energy has the dimensions of energy, and its value is determined by the state of the system and not by its history. Free energy is used to determine how systems change and how much work they can produce. It is expressed in two forms:

1. Helmholtz free energy or work function F
2. Gibbs free energy G.

If U is the internal energy of a system, and TS the temperature- entropy product (T being the temperature above absolute zero), Then

$$F = U - TS$$
$$G = H - TS \qquad ...(4.1)$$

The Gibbs free energy (ΔG) of a reaction is a measure of the thermodynamic driving force that makes a reaction occur. **A negative value for ΔG indicates that a reaction can proceed spontaneously without external inputs, while a positive value indicates that non-spontaneous reaction.** Free energy is an extensive property.The changes in free energy, ΔF or ΔG, are useful in determining the direction of spontaneous change and evaluating the maximum work.

ΔG is negative for $T > 273.16$ K, indicating that the direction of spontaneous change is from ice to water.

ΔG is positive for $T < 273.16$ K, where the reverse reaction of freezing takes place.

4.2.1 Enthalpy (ΔH)

The enthalpy (ΔH) is a measure of the actual energy that is liberated when the reaction occurs (the "heat of reaction"). If it is negative, then the reaction gives off energy; while if it is positive, the reaction requires energy.It is another measure of energy called enthalpy 'H' a kind of measure of the thermal energy of a crystal. As we will see below,

$$dH = dQ + VdP \qquad ...(4.2)$$

Sign of dH (–) When heat absorb during chemical reaction dH will have (+) sign and when heat is evolved, then will have negative sign.

4.2.2 Entropy (ΔS)

Observe carefully about mixing of gases or the spreading of dye in water. What is it that causes these reactions to proceed spontaneously even if the heat change is zero or endothermic? The answer is **entropy S, which is a measure of the order or disorder.**

The entropy (ΔS) is a measure of the change in the possibilities for disorder in the products compared to the reactants. For example, if a solid (an ordered state) reacts with a liquid (a somewhat less ordered state) to form a gas (a highly disordered state), there is normally a large positive change in the entropy for the reaction.

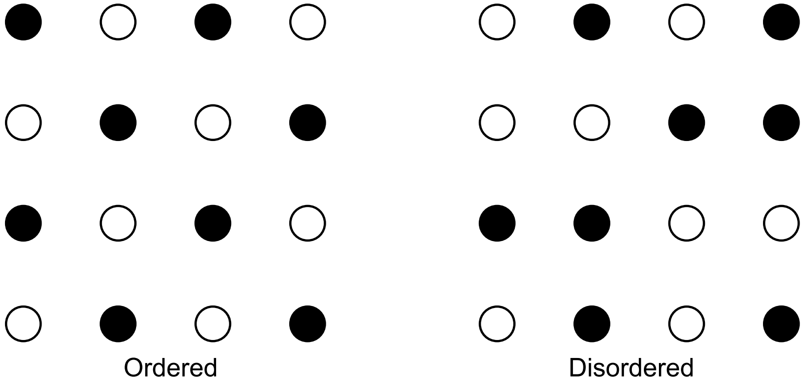


Fig. 4.1: Entropy, degree of randomness

The entropy of a system always increases during irreversible processes; *i.e.*, **for a reversible process, dS = 0, whereas for irreversible processes dS > 0. This is the Second Law of Thermodynamics.**

The change in entropy ΔS is defined as the ratio between the total heat absorbed in a change carried out isothermally and reversibly and the absolute temperature at which the heat was absorbed.

$$\Delta S = \frac{Q_{Rev}}{T} \qquad ...(4.3)$$

Unit of entropy ΔS is an extensive property. Therefore its value depends upon the quantity of substances.Its unit is calorie per degree per mol (Cal deg^{-1} mol^{-1}).

Entropy of a cyclic process– entropy is a state function in cyclic process, there will be no change in entropy of the system so, change in entropy will be

$$\Delta S = 0 \qquad ...(4.4)$$

Entropy change in adiabatic process in an adiabatic change heat is neither given to the system nor taken out of the system. Therefore, $q = 0$, and the change in entropy during the process, will be ΔS = 0 and represented as

$$\Delta S = \frac{q_{Rev}}{T} = \frac{q}{T} = 0 \qquad ... (4.5)$$

Such process are known as **iso-entropic process.**

4.3 ENTROPY CHANGE OF AN IDEAL GAS WITH CHANGE IN TEMPERATURE, PRESSURE AND VOLUME

Entropy is a thermodynamic property which depends upon the state of the system and therefore its value for a pure substance will depend upon any two out of the three independent state variables, viz., pressure, volume and temperature. Entropy changes will be considered under two heads:

(*i*) When T and V are considered variables.

(*ii*) When T and P are considered variables.

4.3.1 When T and V are Variables

We have defined increase in entropy of a gas for an infinitesimal change by the expression,

We get expression for change in entropy is

$$\Delta S = nC_v \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1} \qquad \text{... (4.6)}$$

Where,

R = Gas constant,

T_1 = Temperature in the initial state

V_1 = Volume in the initial state

T_2 = Temperature in the final state

V_2 = Volume in the final state,

In the above equation the first term on the right hand side of the equation gives the changes in entropy of n moles of an ideal gas on change of temperature at constant volume and the second term gives the ΔS due to change of volume at constant temperature. Thus , it is evident that the entropy change for change of state of an ideal gas is independent on the initial and final temperature as well as on initial and final volumes of the system. By changing the logarithm to the base 10, the equation will be

$$\Delta S = 2.303n\ C_v \log \frac{T_2}{T_1} + nR\ 2.303 \log \frac{V_2}{V_1} \qquad \text{... (4.7)}$$

4.3.2 When T and P are Considered Variables

Let P_1 be the pressure and V_1 be the volume in the initial state and P_2 be the pressure and V_2 be the volume in the final state, then we get expression for change in entropy is

$$\Delta S = nC_p \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2} \qquad \text{... (4.8)}$$

Where,

R = Gas constant,

T_1 = Temperature in the initial state

P_1 = Pressure in the initial state

T_2 = Temperature in the final state

P_2 = Pressure in the final state,

$$\Delta S = nC_p\ 2.303 \log \frac{T_2}{T_1} + nR\ 2.303 \log \frac{P_1}{P_2} \qquad \text{... (4.9)}$$

The first term in equation gives the change in entropy suffered by n moles of an ideal gas due to variation in temperature at constant pressure while the second term gives the entropy change due to variation in pressure when temperature kept constant.

Thus entropy change for the change of states of an ideal gas is dependent upon the initial and final temperature as well as on the initial and final pressure of the system.

4.4 GIBBS FREE ENERGY

The Gibbs free energy G is the thermodynamic potential. The two measures of energy (enthalpy H and entropic energy TS) are brought together in the Gibbs free energy equation: (the chemical potential is the equivalent for a component) it can write this in a more understandable way

$$\mathbf{G = H - TS} \qquad \text{...(4.10)}$$

which says that G is the difference between the heat energy and the entropic energy.

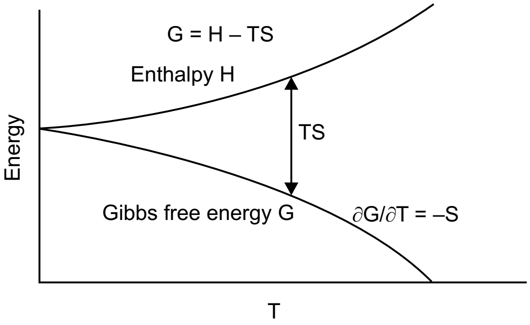


Fig. 4.2: Relationship among G, S, and H

4.4.1 Relationship Among G, S, and V

Relation among all can be write as

$$dG = VdP - SdT \qquad \text{...(4.11)}$$

It means that changes in Gibbs free energy are produced by changes in pressure and temperature acting on the volume and entropy of a phase.

May be written as

$$dG = \frac{\partial G}{\partial P}\, dP - \frac{\partial G}{\partial T}\, dT \qquad \text{...(4.12)}$$

which means that

$$\left(\frac{\partial G}{\partial P}\right)_T = V \qquad \text{...(4.13)}$$

and

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \qquad \text{...(4.14)}$$

These relations indicate that the change in Gibbs free energy with respect to pressure is the molar volume V and the change in Gibbs free energy with respect to temperature is minus the entropy S.

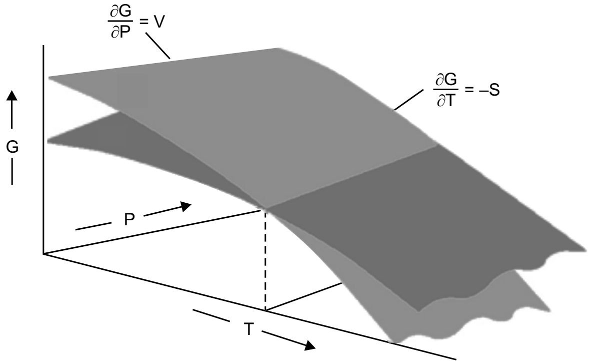


Fig. 4.3: Relationship among Gibbs free energy, volume and entropy

4.4.2 Gibbs Free Energy of Formation

Gibbs free energy of formation $\Delta_f G°$ is

$$\Delta_f G° = \Delta_f H° - T\Delta_f S° \quad \ldots(4.15)$$

APPLICATION IN DAILY LIFE

- Real life example of entropy are eating of food, Photosynthesis are examples of decrease in entropy.
- Ice melting, salt or sugar dissolving, making popcorn and boiling water for tea are processes with increasing entropy in our kitchen.
- A campfire is an example of entropy. The solid wood burns and becomes ash, smoke and gases, all of which spread energy outwards more easily than the solid fuel.

4.5 CELL POTENTIALS

The cell potential, E_{cell}, is the measure of the potential difference between two half cells in an electrochemical cell. The potential difference is caused by the ability of electrons to flow from one halfcell to the other. Electrons are able to move between electrodes because the chemical reaction is a redox reaction. During oxidation, the substance loses one or more electrons, and thus becomes positively charged. Conversely, during reduction, the substance gains electrons and becomes negatively charged. This relates to the measurement of the cell potential. The cell potential (E_{cell}) is measured in voltage (V), which allows us to give a certain value to the cell potential.

4.5.1 Electrochemical Cell

An electrochemical cell is comprised of two half cells. In one half cell, the oxidation of a metal electrode occurs, and in the other half cell, the reduction of metal ions in solution occurs. The half cell essentially consists of a metal electrode of a certain metal submerged in an aqueous solution of the same metal ions. The first half cell, will be marked as the anode. Where the metal in atoms in the electrode become oxidized and join the other metal ions in the aqueous solution. An example of this would be a copper electrode, in which the Cu atoms in the electrode loses two electrons and becomes Cu^{2+}.

Components of electrochemical cell: A typical electrochemical cell contains following components- Two half cells

1. Two metal electrodes
2. One voltmeter
3. One salt bridge
4. Two aqueous solutions for each half cell

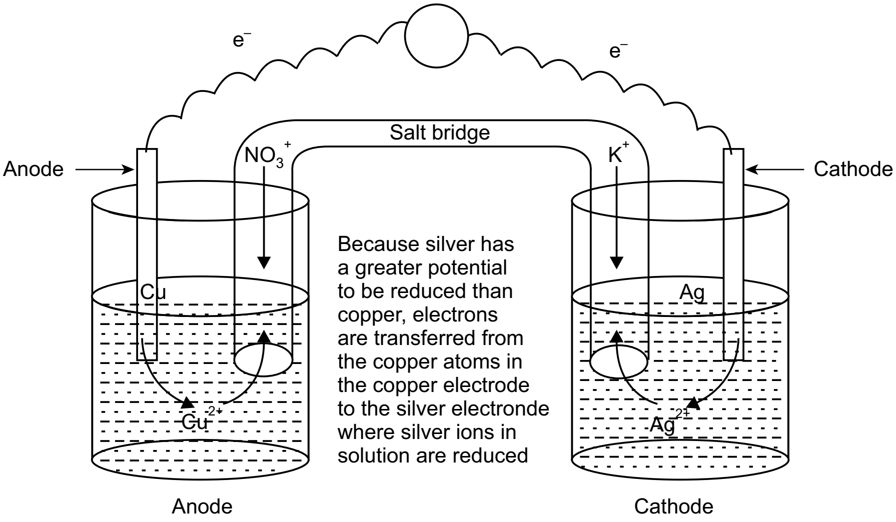


Fig. 4.4: Electro-chemical cell

4.5.2 Cell Diagram may be written as

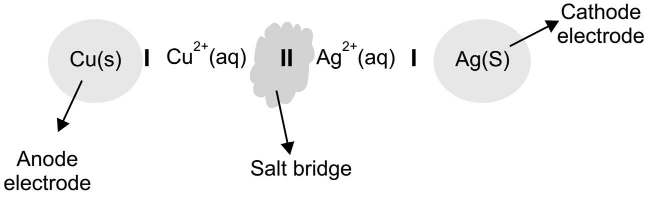


Fig. 4.5: Equation of cell

- The cell diagram is a representation of the overall reaction in the electrochemical cell.
- In the cell diagram, the anode half cell is always written on the left side of the diagram, and in the cathode half cell is always written on the right side of the diagram.
- Both the anode and cathode are separated by two vertical lines (ll) as seen in the figure.
- The electrodes of both the anode and cathode solutions are separated by a single vertical line (l).
- When there are more chemicals involved in the aqueous solution, they are added to the diagram by adding a comma and then the chemical.
- For example, in the image above, if copper wasn't being oxidized alone, and another chemical like K was involved, you would denote it as (Cu, K) in the diagram. The cell diagram makes it

easier to see what is being oxidized and what is being reduced. These are the reactions that create the cell potential.

4.6 STANDARD CELL POTENTIAL

The standard cell potential ($E°_{cell}$) is the difference of the two electrodes, which forms the voltage of that cell. To find the difference of the two half cells, the following equation is used:

$$E°_{Cell} = E°_{Red, Cathode} - E°_{Oxd, Anode} \quad ...(4.16)$$

With

- $E°_{Cell}$ is the standard cell potential (under 1M, 1 Barr and 298°K).
- $E°_{Red}$, Cathode is the standard reduction potential for the reduction half reaction occurring at thecathode
- $E°_{Oxd}$, Anode is the standard reduction potential for the oxidation half reaction occurring at theanode

The units of the potentials are measured in volts (V). Note that this equation can also be written as a sum rather than a difference

$$E°_{Cell} = E°_{Red, Cathode} + E°_{Oxd, Anode} \quad ...(4.17)$$

4.6.1 Standard Cell Potential Example

Copper and Silver cell diagram.

The oxidation half cell of the redox equation is:

$$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^- \; E°_{Oxd} = -0.340 \text{ V}$$

The reduction half cell is:

$$(Ag^+ + e^- \rightarrow Ag(s)) \text{ x2 } E°_{Red} = 0.800 \text{ V} \quad ...(4.18)$$

where we have multiplied the reduction chemical equation by two in order to balance the electron countbut we have not doubled $E°_{Red}$ since E° values are given in units of voltage. Voltage is energy per charge,not energy per reaction. The chemical equations can be summed to find:

$$Cu(s) + 2Ag^+ \rightarrow Cu^{2+}(aq) + 2Ag(s)$$

where the potentials of the half-cell reactions can be summed

$$E°_{Cell} = E°_{Red, Cathode} + E°_{Ox, Anode}$$

$$E°_{Cell} = 0.800 \text{ V} + (-0.340 \text{ V})$$

$$E°_{Cell} = 0.460\text{V}$$

to find that the standard cell potential of this cell **is 0.460 V.**

Calculating the Cell Potential

The net reaction of a voltaic cell constructed from a standard zinc electrode and a standard copper electrode is obtained by adding the two half-reactions together:

oxidation $Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$ $E° = 0.763$ V

reduction $2\,[1e^- + Ag^+(aq) \longrightarrow Ag\,(s)]$ $E° = 0.337$ V

sum

net $Zn(s) + 2\,Ag^+(aq) \longrightarrow 2\,Ag(s) + Zn^{2+}(aq)$ $E° = 1.100$ V

4.7 NERNST EQUATION

In electrochemistry, the Nernst equation is an equation that relates the reduction potential of an electrochemical reaction (half-cell or full cell reaction) to the standard electrode potential, temperature, and activities (often approximated by concentrations) of the chemical species undergoing reduction and oxidation. It is the most important equation in the field of electrochemistry. It is named after the German physical chemist who first formulated it, Walther Nernst.

A reaction may start at standard-state conditions, but as the reaction proceeds, the concentrations of the solutions change, the driving force behind the reaction becomes weaker, and the cell potential eventually reaches zero.

When the cell potential equals zero, the reaction is at equilibrium.

Nernst Equation – Can be used to find the cell potential at any moment in during a reaction or at conditions other than standard-state.

$$E = E^{o} - \frac{RT}{nF} \ln Q_c \qquad ...(4.19)$$

$E°$ = cell potential (V) under specific conditions

E = cell potential at standard-state conditions

R = ideal gas constant = 8.314 $JK^{-1}mol^{-1}$

T = temperature (kelvin), which is generally 25°C (298 K)

n = number of moles of electrons transferred in the balanced equation

F = Faraday's constant, the charge on a mole of electrons = 95,484.56 C/mol^{-1}

$\ln Q_c$ = the natural log of the reaction quotient at the moment in time

Nernst Equation

This equation can be used to calculate the equilibrium constant for any oxidation-reduction reaction from its standard-state cell potential.

APPLICATION IN DAILY LIFE

Let us know importance of Electrochemistry in our day today life.

- All sorts of batteries, from those used to power a flashlight to a calculator to an automobile, rely on chemical reactions to generate electricity.
- Electrochemistry is used to coat objects with protective and decorative metals like gold or chromium and Zinc.
- Nernst equation is widely used in the calculation of solution pH, solubility product, constant equilibrium and other thermodynamic properties, potentiometric titrationsetc.

4.8 ACID BASE THEORIES

Acid – An acid is defined as substance whose water solution has sour in taste, turns blue litmusto red, can neutralise base and evolves hydrogen gas when treated with metals like Zn, Mg, Na.

Example – HCl, H_2SO_4, HNO_3.

Base – A base is defined as substance whose water solution has bitter in taste, turns blue litmus to red, has soapy touch and can neutralise acids.

Example – NaOH, KOH, NH_4OH.

4.8.1 Limitations

- Above definition based on some observed properties of acids and base.
- Above definition are unable to explain structure, responsible for this properties. So, there is need of some conceptual definitions.

Three principal theories about acid-base are

1. Arrhenius theory
2. Bronsted-Lowry theory
3. Lewis theory

4.8.2 The Arrhenius Theory of Acids and Bases

Acid – Acids are substances which produce hydrogen ions (H^+) in solution.

Base – Bases are substances which produce hydroxide ions (OH^-) in solution. Neutralisation happens because hydrogen ions and hydroxide ions react to produce water.

$$H^+_{(aq)} + OH^-_{(aq)} \longrightarrow H_2O_{(I)}$$

4.8.3 Limitations of the theory

This theory is applicable to aqueous solutions only and not applicable to non-aqueous and gaseous reactions.

It is applicable only to compounds having formula HA for acids or BOH for bases.

The theory does not consider the role of solvent in deciding the nature of acid and base.

4.8.4 The Bronsted-Lowry Theory of Acids and Bases

In 1923, Bronsted and Lowry proposed another theory of acid and base which is applicable for wider range as compared to Arrhenius concept. It is applicable for aqueous and non-aqueous solutions both.

Acid – An acid is a proton (hydrogen ion) donor.

Base – A base is a proton (hydrogen ion) acceptor.

4.8.5 Conjugate pairs

When hydrogen chloride dissolves in water, produces hydroxonium ions and chloride ions. Hydrogen chloride is a strong acid, and can write the reaction in this way :

$$H_2O + HCl \longrightarrow H_3O^+ + Cl^-$$

In fact, the reaction between HCl and water is reversible, but only to a very minor extent. In order to generalise, consider an acid HA, and think of the reaction as being reversible.

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

- The HA is an acid because it is donating a proton (hydrogen ion) to the water.
- The water is a base because it is accepting a proton from the HA.

Back reaction between the hydroxonium ion and the A^- ion:

- The $H\,O^+_3$ is an acid because it is donating a proton (hydrogen ion) to the A^- ion.
- The A^- ion is a base because it is accepting a proton from the $H\,O^+_3$

The reversible reaction contains two acids and two bases. We think of them in pairs, called **conjugate pairs.**

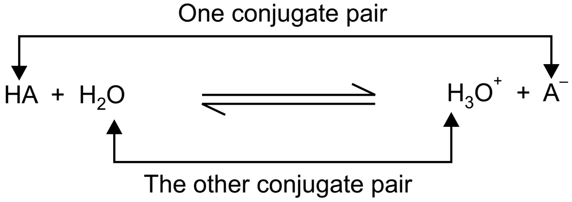


Fig. 4.6: Conjugate acid and Conjugate base pairs in water molecule

Limitations of Bronsted Lowry theory

- It cannot explain the reactions between acidic oxides like SO_3, CO_2, SO and the basic oxides like CaO, BaO, MgO.
- Cannot explain the reactions occuring in the non-protonic solvents like SO_2, N_2O_4, $COCl_2$ and many more.

4.8.6 The Lewis Theory of Acids and Bases

In 1923 Lewis suggested a theory based on transaction of electrons.

The theory

Lewis Acids : An acid is an electron pair acceptor.

Lewis Bases : A base is an electron pair donor.

Classification of Lewis acids: According to Lewis concept acids are classified into following manner

1. **Simple cations** – Strength of cations increases with–
   - Increase in charge of ion.
   - Decrease in ionic radius
   - Decrease in shielding electrons

   The order of Lewis acid strength of some cations are

   $$Na^+ < Mg^{++} < Al^{+++}$$

   $$Cs^+ < K^+ < Na^+ < Li^+$$

2. Molecule having incomplete octet in their central atom- Halides of Be, B, and aluminium.

   Example – BF_3, $AlCl_3$, $BeCl_2$ etc.

3. Molecules having vacant 'd' orbital in their central atom

   Example – SiX_4, $SnCl_4$, GeX_4, $TiCl_4$, PX_3, PF_5, SF_4 etc.

4. Molecules having the multiple bond between atoms of different electronegativity.

   Example – SO_2, CO_2.

Classification of Lewis bases : According to Lewis concept bases are classified into following manner

1. Neutral molecules having lone pair of electron on any of their atoms–

   Examples are –NH_3, RNH_2,R_2NH, R_3N, H_2O, ROH, ROR.

2. Anions – Generally all cations have one lone pair of electron which they can donate to Lewis acid. *e.g.* Cl^-, Br^-, NH_2^-, SO_3^{2-}, NO_2^-, OR^- etc.
3. A molecule having double bond or π bond $CH_2 = CH_2$.
4. Halides – Which can give halogen ions, acts as Lewis base, *e.g.* XeF_2, CsF, XeF_4, XeF_6, etc.

4.9 OXIDATION AND REDUCTION

During oxidation process oxidation number increases than participating species and during reduction oxidation number decreases than original number of participating species.

Oxidation half-reaction: This reaction include the oxidation of Zn to Zn^{++} ion by loss of two electrons.

Oxidation number of Zn is 0 (zero) after oxidation it becomes +2.

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

Reduction half-reaction: This reaction include the reduction of Cu^{++} ion to Cu by gain of two electrons. Oxidation number of Cu^{++} is +2 after reduction it becomes 0 (zero).

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

After cancelling two electrons from each side complete reaction may be written as

$$Zn + Cu^{++} \rightarrow Zn^{++} + Cu$$

Oxidation and reduction process may be defined in several ways. Some of them are mentioned below-

1. **Oxidation and reduction in terms of oxygen transfer**

   Definitions:

   - Oxidation is gain of oxygen.
   - Reduction is loss of oxygen.

   For example, in the extraction of iron from its ore:

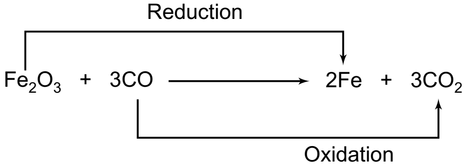


Fig. 4.7: Redox reaction between Fe_2O_3 and carbon mono-oxide

Because both reduction and oxidation are going on side-by-side, this is known as a redox reaction.

4.9.1 Oxidising and Reducing Agents

An oxidising agent is substance which oxidises something else. In the above example, the iron (III) oxide is the oxidising agent. **A reducing agent** reduces something else. In the equation, the carbon monoxide is the reducing agent. Oxidising agents give oxygen to another substance. Agents remove oxygen from another substance.

Oxidation and reduction in terms of hydrogen transfer

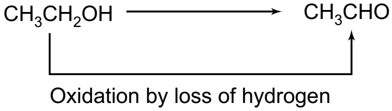
These are old definitions which aren't used very much nowadays. The most likely place you will come across them is in organic chemistry.

Definitions

- Oxidation is loss of hydrogen.
- Reduction is gain of hydrogen.

Notice that these are exactly the opposite of the oxygen definitions.

For example, ethanol can be oxidised to ethanal:



You would need to use an oxidising agent to remove the hydrogen from the ethanol. A commonly used oxidising agent is potassium dichromate (VI) solution acidified with dilute sulphuric acid. Ethanal can also be reduced back to ethanol again by adding hydrogen to it. A possible reducing agent is sodium tetrahydridoborate, $NaBH_4$.

Another update on oxidising and reducing agents – Oxidising agents give oxygen to another substance or remove hydrogen from it. Reducing agents remove oxygen from another substance or give hydrogen to it.

Oxidation and reduction in terms of electron transfer

- Oxidation is loss of electrons.
- Reduction is gain of electrons.

It is essential that you remember these definitions. There is a very easy way to do this. As long as you remember that you are talking about electron transfer

OIL	RIG
Oxidation is Loss of electron	Reduction is Gain of electron

We can summarise –

- An oxidising agent oxidises something else.
- Oxidation is loss of electrons (OIL).
- That means that an oxidising agent takes electrons from that other substance.
- So an oxidising agent must gain electrons.

4.10 WATER CHEMISTRY

Chemical formula of water is H_2O. A water molecule consists of one atom of oxygen bound to two atoms of hydrogen. The hydrogen atoms are "attached" to one side of the oxygen atom, resulting in a water molecule having a positive charge on the side where the hydrogen atoms are and a negative charge on the other side, where the oxygen atom is. Since opposite electrical charges attract, water molecules tend to attract each other, making water kind of "sticky." The side with the hydrogen atoms (positive charge) attracts the oxygen side (negative charge) of a different water molecule.

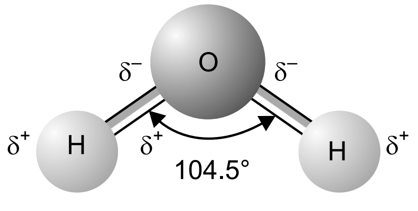


Fig. 4.8: Structure of Water

4.10.1 Hardness

The amount of dissolved calcium and magnesium in water determines its "hardness." Water hardness varies throughout the region. Where the water is relatively hard, you may noticethat it is difficult to get a lather up when washing your hands or clothes. And, industries in yourarea might have to spend money to soften their water, as hard water can damage equipment. Hardwater can even shorten the life of fabrics and clothes.

Hardness of water – Water which does not produce lather with soap are termed as hard water. On the other hand soft water readily produce a lot of lather when mixed even with little amount of soap. The hardness is mostly due to the presence of Ca and Mg metallic ions which react with soap and form precipitates. Some major cations are Mg^{++}, Ca^{++}, Al^{+++} and Fe^{+++}. Some important anions are HCO_3^-, NO_3^-, SO_4^-, etc.

The hard water causes boiler troubles like scale formation etc. Example : A reaction of soap (Sodium stearate) with calcium chloride and Magnesium sulphate is as follows–

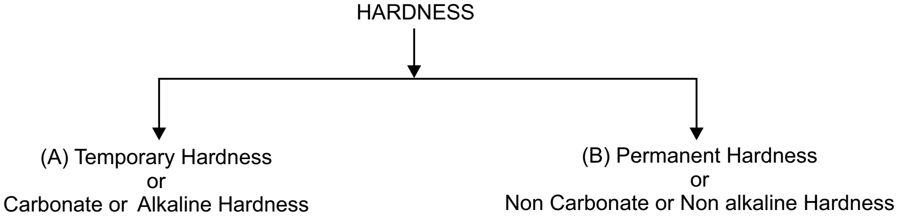
$$\underset{\text{Sodium stearate}}{2\ C_{17}H_{35}COONa} + \underset{\text{Hardness}}{CaCl_2} \longrightarrow \underset{\text{Calcium stearate (Scum)}}{(C_{17}H_{35}COO)_2Ca} + 2\ NaCl$$

$$\underset{\text{Sodium stearate}}{2\ C_{17}H_{35}COONa} + \underset{\text{Hardness}}{MgSO_4} \longrightarrow \underset{\text{Magnesium stearate (Scum)}}{(C_{17}H_{35}COO)_2Mg} + Na_2SO_4$$

The water are commercially classified on the basis of degree of hardness as follows–

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

4.10.2 Types of Hardness



(A) Temporary Hardness		(B) Permanent Hardness	
(i)	It is caused by the presence of dissolved bicarbonates of calcium, magnesium and other heavy metals.	(i)	It is caused by the presence of soluble chlorides and sulphates of calcium, magnesium, iron and other heavy metals.
(ii)	Salts responsible for temporary hardness are – $Ca(HCO_3)_2$ and $Mg(HCO_3)_2$.	(ii)	Salts responsible for permanent hardness are – $CaCl_2$, $MgCl_2$, $CaSO_4$, $FeSO_4$, $Al_2(SO_4)_3$.

(A) Temporary Hardness		(B) Permanent Hardness	
(iii)	It can be removed by simple boiling of water.	(iii)	It can't be removed by simply boiling of water.
(iv)	Bicarbonates are decomposed and are converted into insoluble carbonates or hydroxides, which precipitate and settle down at the bottom of the vessel.	(iv)	It is also known as non-carbonate or non-alkaline hardness.

Hardness of water is expressed as equivalent of calcium carbonate ($CaCO_3$).

4.10.3 The reason for choosing $CaCO_3$ as standard is

The reason for choosing $CaCO_3$ as standard is – molecular weight of $CaCO_3$ is exactly 100, so,ease in the calculations occurs. Secondly it forms most insoluble salt that can be precipitated in water treatment.

$$\textbf{Degree of hardness} = \frac{\text{Mass of hardness producing substance}}{\text{Chemical equivalent of hardness producing substance}} \times 50$$

Temporary hardness can be removed by boiling but permanent hardness cannot be removed by boiling. It requires softening methods. Theses method are–

1. Lime –Soda method
2. Zeolite Method
3. Ion-Exchange method

USE OF ICT

http://chemcollective.org/chem/electrochem/step2_cell.php

APPLICATION IN DAILY LIFE

Common acids and bases used in daily life

Acids	Name	Uses
	HCl	Production of glucose from corn starch
	H_2SO_4	Fertilisers, paints, dyes, chemicals, plastics and synthetic fibers, car batteries.
	H_2CO_3	Used in aerated drinks
	HNO_3	Manufacture of fertilizers, explosives like TNT, dyes and drugs
	HCl	Production of glucose from corn starch
Bases	**NaOH**	Production of soaps, paper and synthetic fibres like rayon
	NH_4OH	Fertilizers like ammonium phosphate and ammonium sulphate.
	$Ca(OH)_2$	Bleaching powder

Hardness of water -Hard water causes adverse effect in industry-

- Dye and textile industries face problem of excessive demand of soap and problem in imparting proper shade of colors on fabric.
- Boilers badly affected with scale and sludge problem which decreases efficiency in stem production and over use of fuels.
- Over a period of time, the mineral deposits start building up inside the pipes, fixtures, and appliances. These results in a reduced flow of water and sometimes erode it causing holes on plumbing work.
- There are no serious adverse **health problems** associated with **drinking hard water**. However, **hard water can** make to dry skin dry and hair scalp feeling itchy.

4.11 CORROSION

Any process of deterioration (or destruction) and consequent loss of a solid metal through an unwanted chemical or electrochemical attack of its environment, starting at its surface is called corrosion.

"Corrosion is a reverse process of extraction"

Most of the metals except Nobel metals (Pt, Au) are exist in combined forms as their oxide, carbonates, sulphide,chlorides etc. In this state, in the form of ore metal have very less energy so this state is a thermodynamically stable state. During metallurgical operation ore is converted into metal. In each step of metallurgy ore become superior and thermodynamically unstable by gaining energy. Formed metal gained more energy than ore and become unstable. To become stable again metal undergo corrosion.

ORE		**Pure Metal**
Have less energy,	Metallurgical Process →	Have more energy
Thermodynamically stable		Thermodynamically unstable
Not useful in this state	← Corrosion Process	Useful in this state

4.11.1 Examples of Corrosion

- Formation of ferric hydroxide on the surface of Iron metal Formula Fe_3O_4
- Formation of green layer of basic copper carbonate on the surface of Copper metal $CuCO_3.H_2O$
- Formation of MoO_3 on surface of Molybdenum

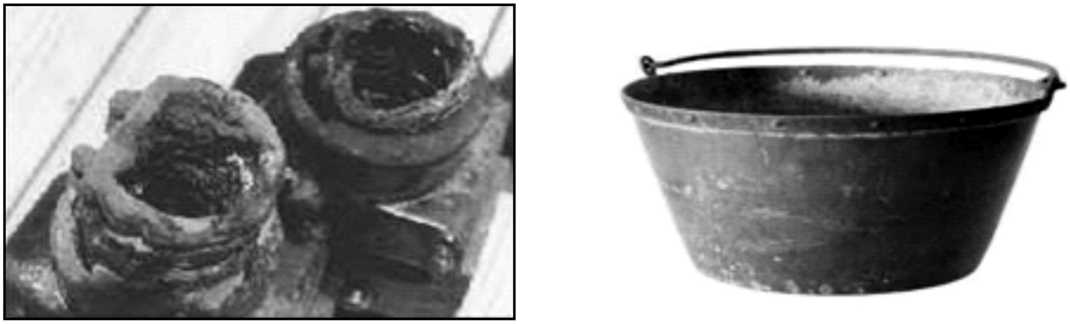


Fig. 4.9: (a) Rusting of Iron (Black and yellow rust) (b) Rusting on Copper (green Layer)

4.11.2 Corrosion can be prevented by using below mentioned techniques–

- The selection of appropriate materials.
- The design of the product.
- Protective methods (Coatings, anodes, etc.)
- Correct installation and maintenance.
- Research, development and testing.

4.11.3 Types of corrosion

Corrosion may be divided into two types—

1. **Chemical or Dry Corrosion :** Chemical corrosion can be seen as oxidation and occurs by the action of dry gases, often at high temperatures. Example – Oxidation corrosion.
2. **Electrochemical or Wet corrosion :** Electrochemical corrosion on the other hand takes place by electrode reactions, often in humid environments, *i.e.* wet corrosion. Wet corrosion covers large area of corrosion. Example Galvanic corrosion, Stress corrosion, Waterline corrosion, Concentration cell corrosion.

4.11.4 Parameters Affecting the Corrosion Rate

Some of the most important parameters affecting the corrosion rate of metals are outlined below.

1. **Oxidizing agents:** The corrosion process is conditional on an anodic reaction and a cathodic reaction taking place simultaneously. The anodic reaction causes the metal to dissolve. An oxidizing agent must be present for the cathodic reaction, and the most common agents are dissolved oxygen or hydrogen ions. If the availability of oxidizing agents is restricted, the corrosion process will be inhibited or will cease entirely.
2. **The electric conductivity of the electrolyte:** Corrosion involves electrochemical reactions, and an increase in the electrical conductivity of the electrolyte will therefore increase the corrosion rate. In sea water the chloride content causes rapidly increased conductivity.
3. **Temperature:** An increase in temperature will generally cause an increase in the corrosion rate. A rule of thumb is that temperature increases of 10°C will double the corrosion rate.
4. **Concentration:** An increased concentration will normally increase the corrosion rate up to a maximum level. Higher concentration above this will not give higher corrosion rate. *e.g.* a chloride concentration above approximately 1500 ppm will not increase the corrosion rate.

4.12 ELLINGHAM DIAGRAM – THERMODYNAMICS OF METALLURGY

An Ellingham diagram shows the relation between temperature and the stability of a compound.

It is basically a graphical representation of Gibbs Energy Flow.

Here ΔG is plotted in relation to the temperature.

The slope of the curve is the entropy and the intercept represents the enthalpy.

Gibbs equation helps us to predict the spontaneity of a reaction on the basis of enthalpy and entropy values directly.

Since ΔH and ΔS are essentially constant with temperature unless a phase change occurs, the free energy versus temperature plot can be drawn as a series of straight lines, where ΔS is the slope and ΔH is the y-intercept.

Free energy of formation is negative for most metal oxides, and so the diagram is drawn with $\Delta G = 0$ at the top of the diagram, and the values of ΔG shown are all negative numbers.

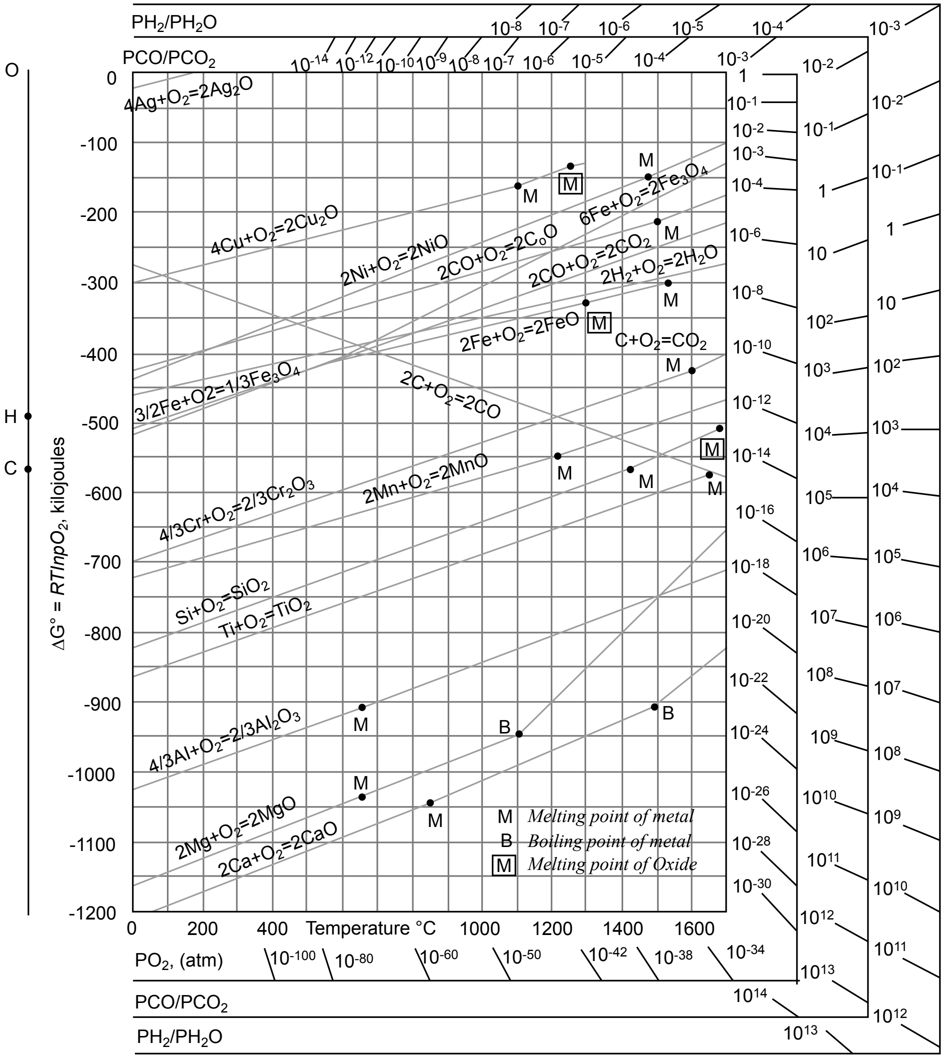


Fig. 4.10: Ellingham Diagram

Applications of the Ellingham diagram

In metallurgy, the Ellingham diagram is used to predict the equilibrium temperature between a metal, its oxide, and oxygen.

1. Ellingham diagram is used to predict thermodynamic feasibility of reduction of oxides of one metal by another metal.
2. Determination of the partial pressure of oxygen that is in equilibrium with a metal oxide at agiven temperature.
3. Determination of the ratio of carbon monoxide to carbon dioxide that will be able to reduce the oxide to metal at a given temperature.

SUMMARY

- **Free energy (ΔG):** Free energy has the dimensions of energy, and its value is determined by the state of the system and not by its history. It is expressed in two forms:

  Helmholtz free energy or work function **F_2.** Gibbs free energy **G**.

  $$G = H - TS$$

  ΔG is negative for T > 273.16 K, indicating that the direction of spontaneous change is from ice to water.

  ΔG is positive for T < 273.16 K, where the reverse reaction of freezing takes place.
- **Enthalpy :** The enthalpy (ΔH) is a measure of the actual energy that is liberated when the reaction occurs (the "heat of reaction"). $dH = dQ + VdP$, $dU = dQ - PdV$
- **Sign of dH :** When heat absorb during chemical reaction dH will have positive sign and when heat is evolved , then will have negative sign.
- **Entropy (ΔS)** -E**ntropy** S, which is a measure of the order or disorder. $\Delta S = \dfrac{Q_{Rev}}{T}$
- **Entropy change in adiabatic process** in an adiabatic change heat is neither given to the system nor taken out of the system. Therefore, q = 0, and the change in entropy during the process, will be $\Delta S = \dfrac{q_{Rev}}{T} = \dfrac{q}{T} = 0$

  change in entropy -

  $$\Delta S = 2.303\ nC_v \log \frac{T_2}{T_1} + nR\ 2.303 \log \frac{V_2}{V_1}$$
- **Gibbs Free Energy :** The **Gibbs free energy** G is the thermodynamic potential. The two measures of energy (enthalpy H and entropic energy TS) are brought together in the Gibbs free energy equation: (the chemical potential is the equivalent for a component). $G = H - TS$
- **Relationship Among G, S, and V** $dG = VdP - SdT$

  It means that changes in Gibbs free energy are produced by changes in pressure and temperature acting on the volume and entropy of a phase.
- **Cell potentials :** The cell potential, E_{cell}, is the measure of the potential difference between two half cells in an electrochemical cell.
- **Components of Electrochemical Cell :** Two half cells, Two metal electrodes, One voltmeter One salt bridge,Two aqueous solutions for each half cell
- **Standard Cell Potential**-The standard cell potential (E^ocell) is the difference of the two electrodes, which forms the voltage of that cell. To find the difference of the two half cells, the following equation is used: $E^o_{Cell} = E^o_{Red,Cathode} + E^o_{Oxd,\ Anode}$
- **Nernst Equation** – When the cell potential equals zero, the reaction is at equilibrium.

  $$E = E^o - \frac{RT}{nF} \ln Qc$$
- **Theories of acids and bases**

  The Arrhenius Theory Acid – Acids are substances which produce hydrogen ions (H^+) in solution.**Base** - Bases are substances which produce hydroxide ions (OH^-) in solution.

  The Bronsted-Lowry Theory -Acid – An acid is a proton (hydrogen ion) donor. **Base** -A base is a proton (hydrogen ion) acceptor.

  The Lewis Theory – An acid is an electron pair acceptor. A base is an electron pair donor.

- **Oxidation and Reduction –**

  Oxidation and reduction in terms of oxygen transfer – Oxidation is gain of oxygen. Reduction is loss of oxygen.

  Oxidation and reduction in terms of hydrogen transfer – Oxidation is loss of hydrogen. Reduction is gain of hydrogen.

  Oxidation and reduction in terms of electron transfer – Oxidation is loss of electrons. Reduction is gain of electrons.

Hardness of water – Water which does not produces lather with soap are termed as hard water. The hardness is mostly due to the presence of Ca and Mg metallic ions which react with soap and form precipitates.

Types of Hardness is of two types – (A) Temporary Hardness (B) Permanent Hardness

Methods for removal of hardness are- Lime-Soda method, Zeolite Method, Ion-Exchange method

- **Corrosion** -Any process of deterioration (or destruction)and consequent loss of a solid metal through an unwanted chemical or electrochemical attack of its environment , starting at its surface is called corrosion. **"Corrosion is a reverse process of extraction"**
- **Ellingham Diagram -Thermodynamics of Metallurgy** – H.G.T Ellingham proposed the Ellingham diagram to predict the spontaneity of reduction of various metal oxides. Diagram is basically a curve which related the Gibbs energy value with the temperature.

EXERCISE

LONG ANSWER TYPE QUESTIONS

1. Define below mentioned thermodynamic expression with suitable expression-

   (a) Entropy (b) Enthalpy

   (c) Gibbs free energy
2. Differentiate between adiabatic and isothermal process. Write formula during entropy changes on both of the processes.
3. How electrochemical cell works? Explain standard electrode potential in detail.
4. Write Nernst Equation. Give chemical formula of it. Discuss significance of Nernst Equation in daily life.
5. What you meant by oxidation and reduction process? Write name of two oxidizing agent and two reducing agent with complete information.
6. Define hardness of water, Differentiate between hard and soft water. Write the expression for degree of hardness.
7. What are conjugate acids and bases? How are the relative Strengths of Bronsted acids. Bases related with conjugate pair? Explain with examples.
8. What do you understand by Lewis acid and base? Describe with examples. Give, classify andthe limitations.

9. Solvent system concept is wide form of Arrhenius Concept. Explain with examples.

10. Write short notes on the following.

(a) Acid base theory on the basis of concept of solvent system.

(b) Arrhenius hypothesis.

(c) Conjugated acid base pair

(d) Lux-Fluid concept.

11. Write the difference between acids base concepts given by Bronsted Lowry and Lewis. The utility and limitation of both concepts.

12. Explain the following:

(a) Conjugate bases of strong acids are weak

(b) Mg (II) is a weak base

(c) $[COF_6]^{3-}$ is more stable than $[CoI_6]^{3-}$

(d) Arrange in increasing order of acid strength :

$ClCH_2COOH$, C_6H_5COOH, HCl, CH_3COOH

OBJECTIVE TYPE QUESTIONS

1. One mole of which of the following has the highest entropy?

(a) Liquid Nitrogen (b) Hydrogen Gas

(c) Mercury (d) Diamond [**Ans.** (b)]

Feedback: The measure of randomness of a substance is called entropy. Greater the randomness of molecules of a substance greater is the entropy.

2. Which of the following is true for the reaction? H_2O (l) ↔ H_2O (g) at 100° C and 1 atm pressure

(a) $\Delta S = 0$ (b) $\Delta H = T\ \Delta S$

(c) $\Delta H = \Delta U$ (d) $\Delta H = 0$ [**Ans.** (a)]

Feedback: Equilibrium, Therefore, $\Delta\ G = 0 = \Delta\ H - T\Delta S$, Or $T\Delta\ S = \Delta H$

3. Which thermodynamic function accounts automatically for enthalpy and entropy both?

(a) Helmholtz Free Energy (A) (b) Internal Energy (E)

(c) Work Function (d) Gibbs Free Energy [**Ans.** (d)]

Feedback: Gibbs free energy combines the effect of both enthalpy and entropy. $\Delta G = \Delta H - T\Delta S$

4. Which of the following is not a type of electrochemical cell?

(a) Voltaic cell (b) Photovoltaic cell

(c) Electrolytic cell (d) Fuel Cell [**Ans.** (b)]

Feedback: Photovoltaic cells are used to convert light energy into electrical energy. Others converts chemical energy into electrical energy.

5. What is the pH of HCl solution when the hydrogen gas electrode shows a potential of -0.22 V at standard temperature and pressure?

(a) 2.17 (b) 2.98

(c) 3.73 (d) 3.14 [**Ans.** (c)]

Feedback: Applying Nernst equation, $E_{(H+/H_2)} = E°(H+/H_2) - 0.059 \log (1/ [H^+])$ $E°_{(H+/H_2)} = 0$ for hydrogen gas electrode, $-0.22 = 0.059 \log H^+$, $-0.22 = -0.059$ pH, pH= 3.73.

6. Which gas is evolved when acids react with metals?

(a) O_2 (b) CO_2

(c) H_2 (d) N_2 [**Ans.** (c)]

Feedback: It is a characteristic property of metal

7. Which of the following gives the correct increasing order of acidic strength?

(a) Water < Acetic acid < Hydrochloric acid

(b) Water < Hydrochloric acid < Acetic acid

(c) Acetic acid < Water < Hydrochloric acid

(d) Hydrochloric acid < Water < Acetic acid [**Ans.** (a)]

Feedback: H_2O is neutral, Acetic acid is a weak acid and HCl is a strong acid.

PRACTICALS

Experiment - 1

(Student to Record the Experiment as per Template given in Annexure)

Aim: Determine the chloride content of water

Requirements:

Chemicals: NaCl, $AgNO_3$, K_2CrO_4 .

Glassware: Titration flask, Conical flask, Burette .

Theory: Chloride ions can be determined by Mohr's method. When silver nitrate solution is added to a solution of sodium chloride containing few drops of indicator (K_2CrO_4), white silver chloride is precipitated initially. The moment all the chloride ions have been precipitate of silver chromate. This indicates the end point.

As soon as all the chloride ions have been precipitated out, even a slight excess of Ag+ produces insoluble silver chromate which is red in colour.

$$AgNO_3 + NaCl \longrightarrow AgCl + NaNO_3$$

$$2Ag^+ + CrO_4^{2-} \longrightarrow Ag_2CrO_4$$

Procedure:

(i) Fill the washed and rinsed burette with unknown $AgNO_3$ solution.

(ii) Pipette out 5 mL NaCl solution into conical flask.

(iii) Add 2-3 drops of K_2CrO_4 indicator.

(iv) Add $AgNO_3$ from the burette shaking the flask constantly. A white precipitate of NaCl is obtained. After the addition of a few mL of $AgNO_3$, a red colour appears in the flask but disappears quickly upon shaking.

(v) The addition drop by drop till a permanent reddish brown colour is obtained. Take three concordant readings.

Precautions:

- Usually an air bubble is present in the nozzle of the burette; it must be removed before taking the initial reading.
- There should not be any leakage from the burette during titration.
- Always read lower meniscus in case of colourless solution and upper meniscus in case of coloured solutions.

Refer to the MSDS data of each chemical being used for the safety and environment friendly approach to conduct the experiment.

Observations & Calculations:

$$N_1V_1 \text{ of } AgNO_3 = N_2V_2 \text{ of } NaCl$$

$$N_1 = \frac{N_2V_2}{V_1}$$

$$\text{Strength of given } AgNO_3 \text{ Solution} = N_1 \text{ X Eq. Wt. of } AgNO_3$$

$$N_1 \text{ X } 169.9 \text{ g/L.}$$

Result: The strength of given $AgNO_3$ solution was found to be .... g/L.

Discussion- The Experiment, Observations and Result(s) to be discussed while correlating with theory and real life/industrial applications.

QR code can be used for more information-

Precipitation Titrations

Environmental Engineering

Experiment - 2

(Student to Record the Experiment as per Template given in Annexure)

Aim: Determination of the partition coefficient of a substance between two immiscible liquids.

Requirements:

Chemicals: Hypo Solutions (N/10 and N/100), Saturated solution of Iodine in CCl_4 Starch indicator solution

Glassware: Shaker machine, Four glass- stoppered reagent bottles of about 250 mL capacity, Separating funnel.

Theory: Iodine distributes itself in two miscible solvents as water and carbon tetra chloride and same molecular state of I_2 in both of these solvents. If C_1 and C_2 are concentrations of Iodine in water and carbon tetra chloride layers in contact with each other and forming the heterogeneous equilibrium, then the ratio of these concentrations ; i.e. = $\frac{C_1}{C_2}$ would be constant at fixed temperature.

Mathematically:

$$K = \text{Distribution or partition coefficient} = \frac{C_1}{C_2} = \frac{\text{Concentration of } I_2 \text{ in water layer}}{\text{Concentration of } I_2 \text{ in } CCl_4 \text{ layer}}$$

Procedure

1. Take clean and dry stoppered reagent bottles and label them as 1,2,3 and 4. Fill 10,20,30 and 40 mL of the solution in different glass bottles.
2. Add 40, 30, 20 and 10 mL of CCl_4 in each bottle respectively. Then add 50 mL of distilled water in each bottle.
3. Stopper these bottles and shake each bottle vigorously for about 20 minutes.
4. Allow to stand till two separated layers are formed distinctly.
5. Pour the content of each bottle separately in to a separating funnel and collect carbon tetra chloride and water layer of each bottle in separate beaker.
6. Pipette out CCl_4 layer from the separated layers. Add about 1 g of KI, 5 drops of starch solution and titrate against N/10 hypo solution.
7. Disappearance of the blue colour marks the end point. Repeat to get two concordant readings. Repeat this process with CCl_4 layer of other bottles in the same way.
8. Pipette out aqueous layer into titration flask and titrate against N/100 hypo solution as given in step 7.
9. Carry similar titration for upper and lower layers respectively in other bottles.

Precautions:

1. Do not use rubber stopper as Iodine solution in CCl_4 can react with it.
2. The reagent bottles should be thoroughly cleaned and dried.
3. The stopper are kept properly pressed during shaking of bottles
4. Loosen the stopper after shaking for releasing the pressure if any developed during the process of shaking the contents in the bottles.
5. Use only the fresh starch solution as indicator in hypo solutions.

Refer to the MSDS data of each chemical being used for the safety and environment friendly approach to conduct the experiment.

Observations & Calculations:

Room temperature = ˚C

Vol. of water layer used in each titration = mL

Vol. of CCl_4 layer used in each titration = mL

S. No.	Percentage of Iodine (V/V)	Titration with water layer				Titration with CCl_4 layer			
		Initial Reading	Final Reading	Vol. of Hypo Solution used V_1 mL	Normality of Hypo Solution	Initial Reading	Final Reading	Vol. of Hypo Solution used V_1 mL	Normality of Hypo Solution
1	10%				N/100				N/10
2	20%				N/100				N/10
3	30%				N/100				N/10
4	40%				N/100				N/10

$$\text{Concentration of water layer} = \frac{\text{Normality of hypo used with water layer X } V_1}{\text{Volume of water layer used}} \text{ g eq. } L^{-1}$$

$$\text{Concentration of layer} = \frac{\text{Normality of hypo used with } CCl_4 \text{ layer X } V_2}{\text{Volume of } CCl_4 \text{ layer used}} \text{ g eq. } L^{-1}$$

Result: The partition coefficient of Iodine between water and carbon tetra chloride is ……at ……°C.

Discussion- The Experiment, Observations and Result(s) to be discussed while correlating with theory and real life/industrial applications.

QR code can be used for more information-

Experiment - 3

(Student to Record the Experiment as per Template given in Annexure)

Aim: To determine the cell constant for a given cell at room temperature.

Requirements:

N/10 KCl Solution, Beaker, Pipette, Standard flask-100 mL, Weight box/ Digital Balance

Theory: Cell constant for a cell is defined as the constant factor which stands for the ratio of the specific conductance of a solution and its measured conductance in the cell.

$$\text{Cell constant} = \frac{l}{A} \text{ in } m^{-1}$$

Procedure:

1. Prepare 0.1M KCl solution by weighing accurately 0.7455 g of KCl into a clean 100 mL standard flask.
2. From this 0.1M KCl solution prepare 100 mL each of 0.05M, 0.02M, 0.01M, and 0.001M KCl solutions.
3. Take about 40 mL of each solution in to a clean and dry 100 mL beaker and dip the conductivity cell and make necessary connections. Measure the conductance of each solution and note down.

Precaution:

- Note the specific conductance values of each of the solution from literature.
- Use a thoroughly cleaned conductivity cell.
- Immerse the cell in the sample such that the electrode plates are completely submerged in the liquid.
- If air bubbles remain between the outer cylinder and supporting tube, remove them by shaking the cell.

Observations & Calculations:

Specific conductance = Measured conductance X Cell constant

Since for any conductor, the resistance $R = \rho \frac{l}{A}$

Where, ρ = constant, l = length and A= cross sectional area of the conductor.

Taking reciprocals $\frac{1}{R} = \frac{1}{\rho} \times \frac{A}{l}$

$$\text{Or } \frac{1}{p} = \frac{1}{R} \times \frac{1}{a}$$

Therefore specific conductance = conductance × $\frac{l}{A}$

Therefore, cell constant = $\frac{l}{A}$ in m^{-1}

Result: The cell constant observed ……. m^{-1}

Discussion: The Experiment, Observations and Result(s) to be discussed while correlating with theory and real life/industrial applications. QR code can be used for more information-

EMF Measurement

Experiment - 4

(Student to Record the Experiment as per Template given in Annexure)

Aim: Ion exchange column for removal of hardness of water.

Student may perform any practical related to hardness of water

Few experiments are listed below.

- Removal of Calcium Hardness
- Removal of Magnesium Hardness
- Determination and of Removal of Total Hardness

Hard Water

Student to Record the Experiment as per Template given in Annexure. QR code for related experiments is provided here.

SUGGESTED READING

BOOKS

- Physical Chemistry by Peter Atkins, Julio de Paula and Jame Keeler, Oxford university Press 2010.
- An Introduction To Electrochemistry by Samuel Glasstone, East-West Press (Pvt.) Ltd. January 2006.

E-RESOURCES

- http://www.che.ncku.edu.tw/FacultyWeb/ChenBH/E340100%20Thermodynamics/Supplementary/Gibbs_free_energy%20Nov%202%202011.pdf
- https://www.google.co.in/books/edition/Atkins_Physical_Chemistry_11e/0UKjDwAAQBAJ?hl=en&gbpv=1&dq=physical+chemistry+by+Atkins&printsec=frontcover

KNOW MORE

Entropy change in physical change

Change in entropy also occurs when some physical transformation such as fusion, vaporisation or transition from one crystalline state to another takes place.

- Isochoric Process – $\Delta S_v = nC_v \ln \frac{T_2}{T_1}$

- Isobaric Process – $\Delta S_p = nC_p \ln \frac{T_2}{T_1}$
- Isothermal Process – $\Delta S_T = \Delta S_p = nR \ln \frac{P_2}{P_1}$
- Adiabatic Process – $\Delta S = \frac{q}{T} = 0 \; ; \; nC_p \ln$
- Entropy Change in Physical Change – $\Delta S = \frac{q}{T} = \frac{\Delta H}{T}$
- Entropy of fusion – $\Delta S_f = \frac{\Delta H_f}{\Delta T_f}$ ΔH_f become negative, process of freezing the decrease in entropy occurs.
- Entropy of evaporation – $\Delta S_v = \frac{\Delta H_v}{T_v}$ ΔH_v = negative, the process of condensation of vapours

Ranges of Hardness

Hardness In *fh	m mol^{-1}	Water hardness range
0 to 7	0 to 0.7	Very soft
higher 7 to 15	higher 0.7 to 1.5	Soft
higher 15 to 25	higher 1.5 to 2.5	Medium hard
higher 25 to 32	higher 2.5 to 3.2	Quite hard
higher 32 to 42	higher 3.2 to 4.2	Hard
higher than 42	higher than 4.2	Very hard

5

Periodic Properties

UNIT SPECIFIC

This unit discusses the topics: Effective nuclear charges and penetration of orbitals. Variations of energies in s, p, d and f orbitals. Electronic configurations, atomic and ionic sizes. Ionization energies, electron affinity, electronegativity and polarizability. Oxidation states, coordination numbers and geometries of C.N. 4 and 6. Hard and soft acids and bases.

RATIONALE

Everything including the Universe except vacuum is constituted of chemical compounds made of one or more elements! Each element has characteristic physical and chemical properties. Periodic Table beautifully arranges properties of elements in systematic and scientific manner. Some important periodic trends will be discussed in this Unit. These will help in understanding the trends in properties like acidity and basicity. In cases of inorganic complexes, correlation of Coordination number of the central atom with molecular geometries are also discussed.

PRE-REQUISITES

Chemistry : Understanding of Elements: Atomic Structure, Electronic configuration, Atomic number & Valency

Maths : Basic Algebra and Trigonometric Functions

Physics : Electric charges, Forces and interactions

LEARNING OUTCOMES

At the end of this unit, students must able to:

U5-O1: Predict the position of any element in Periodic table based on electronic configuration and orbitals.

U5-O2: Indicate the number of valence electrons and effective nuclear charges of simple elements from their position in the periodic table.

U5-O3: Analyse the trends in properties of elements like Atomic and Ionic sizes, Ionization Energies, Electron affinity, Electronegativity, Polarizability and Oxidation states based on their positioning in Periodic Table.

U5-O4: Draw Geometries of various inorganic complexes, based on the coordination number of central atom.

MAPPING OF UNIT WISE LEARNING OUTCOMES WITH THE COURSE OUTCOMES

Outcome	EXPECTED MAPPING WITH COURSE OUTCOMES (1- Weak Correlation; 2- Medium correlation; 3- Strong Correlation)				
	CO-1	CO-2	CO-3	CO-4	CO-5
U5-O1	2			3	
U5-O2				3	
U5-O3				3	
U5-O4				3	

5.1 INTRODUCTION

Very famous iconic figure in the world of chemistry, Dmitri Mendeleev is referred as the 'Father of the Periodic Table of Chemical Elements'. Year 2019, was the 150th anniversary of Sir Dmitri Mendeleev. To honor this milestone, UNESCO proclaimed 2019 "The United Nations International Year of The Periodic Table" (IYPT 2019). Let us see the journey for Evolution of periodic Table in brief through historical timeline -

Historical Timelines

Period	Scientist	Contribution
1829	Johann Dobereiner	Discovered the halogen triad and the alkali metal triad.
1864	John Newlands	Developed the Law of Octaves.
1869	Dmitri Mendeleev	Published periodic table
1898	William Ramsey	Established the "zero" group (for "zero valency") and predicted the future discovery of the element Neon
1911	Ernest Rutherford	Established that "the nuclear charge on a nucleus was proportional to the atomic weight of the element."
1913	Henry Moseley	Established that "the properties of the elements varied periodically with atomic number," not atomic Weight. Also discovered the isotopes of elements
1940	Glenn Seaborg	Discovered plutonium and the transuranic elements from 94 to 102.

In Mendeleev's periodic table, properties of element based as a function of atomic mass of elements. He grouped the elements in 8 groups and provided gaps for undiscovered elements. But unable to explain satisfactorily the grouping of chemically dissimilar elements, anomalous pairs of elements, isotopes and place of Hydrogen. Answer of these can be given by **Modern Periodic Table by Moseley**. In Modern periodic table, the chemical properties of elements are a periodic function of their atomic number. Applying this concept all elements grouped into four blocks; s, p, d and f. This arrangement is able to justify the position of isotopes in more simple way.

As we have already learned in previous chapters about structure of atoms and molecules in microscopic way through quantum mechanics. Its shape and geometry by Molecular Orbital Theory and effect of ligand in shapes and magnetic properties of complex compound through Crystal Field Theory. With these understanding we are learning here some important periodic properties and its periodicity-

5.2 EFFECTIVE NUCLEAR CHARGE

Effective nuclear charge refers to the charge felt by the outermost (valence) electrons of a multi- electron atom after taking into account the number of shielding electrons that surround the nucleus.

The effective nuclear charge is the net charge an electron experiences in an atomwith multiple electrons.

The formula for calculating the effective nuclear charge for a single electron is $\mathbf{Z_{eff} = Z - S}$

Where, Z_{eff} is the effective nuclear charge, Z is the number of protons in the nucleus, and

S is the number of shielding electrons.

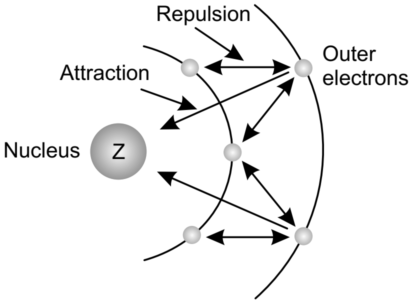


Fig. 5.1: Shielding Effect due to interaction between electron and nucleus

5.2.1 Shielding Effect

Another name of shielding effect is screening effect. **The phenomenon which occurs when the nucleus reduces its force of attraction on the valence electrons due to the presence of electrons in the inner-shell, known as a screening effect.**

The shielding effect is the name given to the balance between the attraction between valence electrons and protons and the repulsion between valence and inner electrons. The shielding effect explains the trend in atomic size on the periodic table and also why valence electrons are readily removed from an atom.

If the distance between an electron and the nucleus is–

(a) **Approaches infinity,** Z_{eff} approaches a value of 1 because all the other (Z – 1) electrons in the neutral atom is, on the average, between it and the nucleus.

(b) **Very close to the nucleus,** then at any given moment most of the other electrons are farther from the nucleus and do not shield the nuclear charge. At $r \approx 0$, the positive charge experienced by an electron is approximately the full nuclear charge, or $Z_{eff} \approx Z$.

(c) **At intermediate** values of *r*, the effective nuclear charge is somewhere between 1 and Z:$1 \leq Z_{eff} \leq Z$. Thus the actual Z_{eff}experienced by an electron in a given orbital depends not only on the spatial distribution of the electron in that orbital but also on the distribution of all the other electrons present.

For the elements of the first three rows of the periodic table. Notice that only for hydrogen does $Z_{eff} = Z$, and only for helium are Z_{eff} and Z comparable in magnitude.

5.3 PENETRATION OF ORBITALS

It's interesting to think, Are the distribution of electron inside the element is uniform or it follows any pattern? Before moving towards penetration of orbitals lets know what is orbital, how shapes are formed, what about level of energies in different orbitals and laws for filling of electrons in it.

Orbital - In an element the three dimensional space around the atom, where the probability of finding of an electron is maximum is known as orbital. Orbitals are named as s, p, d and f. Each orbital in atom has quantized size, shape and energy.

Energy is emitted from the atom when the electron jumps from one orbit to another closer to the nucleus. Penetration refers to how effectively electrons can get close to the nucleus. The electron probability density for s-orbitals is highest in the center of the orbital, or at the nucleus. Different orbitals have greater nuclear penetration than others. Let us learn these step by step.

5.3.1 s, p, d, f ORBITALS ENERGIES OF ATOMS IN PERIODIC TABLE

s, p, d and f orbitals have aligned and take positions in various axis in atoms. Details about types, shapes and energies of it are-

- ***s*-orbital:** The first shell contains orbital in which two electron can be filled. The shape is round or spherical.
- ***p*-orbital:** The second shell contain s & p subshells, the p subshells can have maximum 6 electrons. The shape of p orbital is dumbbell. It contain subshell p_x which lies on x axis, p_y lies on y axis and p_Z which lies on z axis.

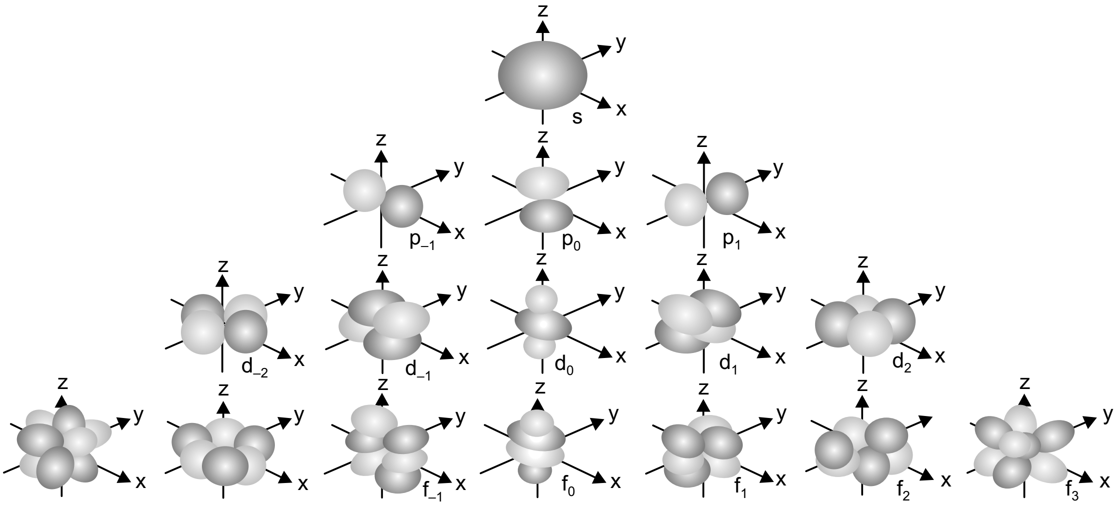


Fig. 5.2: Shapes of Atomic Orbital

- ***d*-orbital:** The third shell contain s, p & d sub shell, d sub shell can have maximum 10 electrons. The shape of d orbital is double dumbbell shape. it contain subshells known as d_{xy} lies between x andy axis, d_{yz} lies between y and z axis, d_{zx} lies between z and x axis, $d_{X^2-y^2}$ lies on the x and y axis & finally d_{z^2} which lies on z axis.
- ***f*-orbital:** The fourth shell contain s, p, d & f subshells, f can have maximum 14 electrons. Their shapes are fairly complicated.

The three major rules govern the placement of electrons in orbitals are –

- **Pauli Exclusion Principle:** According to this principle, an orbital can have maximum two electrons and these must have opposite spins. In other words, no two electrons in an atom can have all the four quantum numbers exactly the same. As we know that fourth quantum number is s, +1/2 is spin up (↿) and –1/2 is spin down (⇂) and hence if the first three quantum numbers are same for two electrons then the electrons must have opposite spins in an orbital.
- **Hund's Rule:** When assigning electrons in orbitals, each electron will first fill all the orbitals with similar energy (also referred to as degenerate) before pairing with another electron in a half-filled orbital.
- **Aufbau principle:** According to this principle, the electrons will first occupy the orbitals that have the lowest energy.

The following is the order for filling the "subshell" orbitals, which also gives the order of the "blocks" in the periodic table:

1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d, 7p

5.3.2 Penetration Power

It means the ability of an orbital to attract an electron. This process is accompanied with release of energy. The Penetration effect of s orbital is the maximum because of the closeness to the nucleus than are the *p*, *d* and *f* orbitals. Thus, an s orbital, due it's more penetration effect, releases greater amount of energy than *p* orbital when it accepts an electron. Similarly the energy released by a d orbital is more than that of a *f* orbital but less than that of a *p* orbital.

The penetration power of an electron, in a multi-electron atom, is dependent on the values of both the shell and subshell. We can learn by taking below cases:

Case 1 – Within the same shell value (n), the penetrating power of an electron follows this trend in subshells (l):

$$s > p > d > f$$

Case 2 – For different values of shell (n) and subshell (l), penetrating power of an electron follows this trend:

$$1s > 2s > 2p > 3s > 3p > 4s > 3d > 4p > 5s > 4d > 5p > 6s > 4f...$$

Case 3 – Energy of an electron for each shell and subshell goes as follows...

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p...$$

Electrons which experience greater penetration experience stronger attraction to the nucleus, less shielding, and therefore experience a larger Effective Nuclear Charge (Z_{eff}), but shield other electrons more effectively.

5.4 ELECTRONIC CONFIGURATION

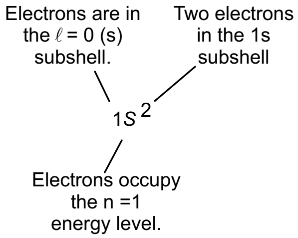
Electronic configuration is the distribution of electrons of an atom or molecule in the atomic or molecular orbitals. In atomic physics and quantum chemistry, the electron configuration is the distribution of electrons of an atom or molecule (or other physical structure) in atomic or molecular orbitals. For example, the electronic configuration of the Neon atom is $1s^2\ 2s^2\ 2p^6$.

Importance of Electronic Configuration

- To understand the structure of the periodic table of elements.
- This is also useful for describing the chemical bonds that hold atoms together.
- In bulk materials, this same idea helps explain the peculiar properties of lasers and semiconductors.
- An electron configuration describes the distribution of electrons among the various orbitals in the atom.

Electronic configuration is represented as-

The notation *n* uses numbers to designate a principal shell andletters (*s, p, d, f*) to identify a subshell; a superscript indicates thenumber of electrons in a designated subshell.



How to Write Electronic Configuration?

The electron distribution over various energylevel is governed by the following rules:

- Electrons fill orbitals in a way to minimize the energy of the atom. Therefore, the electrons in an atom fill the principal energy levels in order of increasing energy (the electrons are getting farther from the nucleus). The order of levels filled looks like this:

  1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d,** and **7p

  To help memorize this sequence check out this arrangement,

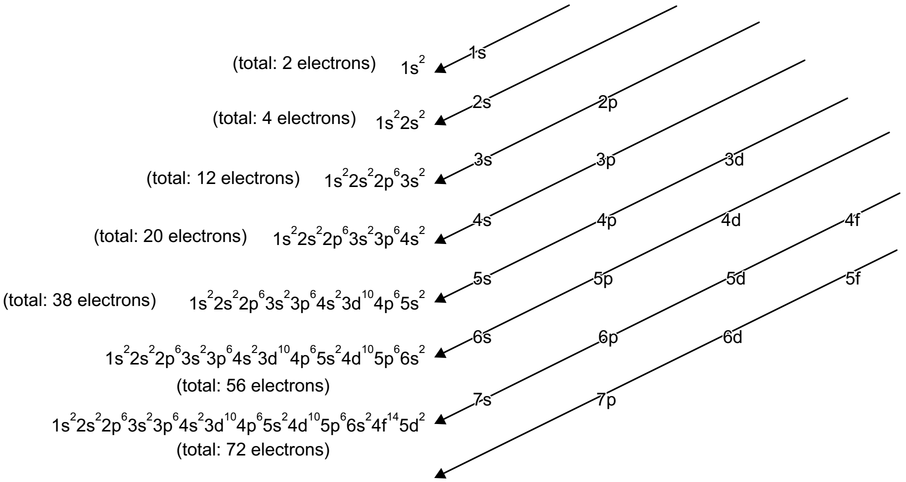


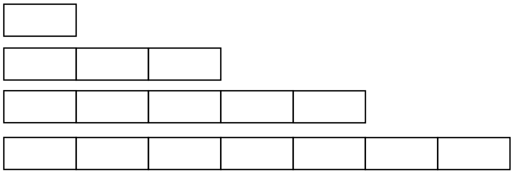
Fig. 5.3: Electronic configuration

Filling of electrons in energy levels follows Pauli Exclusion Principle, Hund's Rule and Aufbau principles. Although the Aufbau rule accurately predicts the electron configuration of most elements, there are notable exceptions among the transition metals and heavier elements. The reason these exceptions occur is that some elements are more stable with fewer electrons in some subshells and more electrons in others.

Aufbau Diagram Boxes -Orbitals are hard to draw and the Aufbau Diagram is an easierway to show electron location by using sets of boxes

Each box can hold up to $2e^-$

- s orbital – 1 box – total no. of $2e^-$
- p orbital – 3 boxes – total no. of $6e^-$
- d orbital – 5 boxes – total no. of $10e^-$
- f orbital – 7 boxes – total no. of $14e^-$



Element	Should be	Actually is
Copper	$1s^22s^22p^63s^23p^6\mathbf{3d^44s^2}$	$1s^22s^22p^63s^23p^6\mathbf{3d^54s^1}$
Chromium	$1s^22s^22p^63s^23p^6\mathbf{3d^94s^2}$	$1s^22s^22p^63s^23p^6\mathbf{3d^{10}4s^1}$

When writing an electron configuration, first write the energy level (the period), then the subshell to be filled and the superscript, which is the number of electrons in that subshell. The total number of electrons is the atomic number, Z. The rules above allow one to write the electron configurations for all the elements in the periodic table.

For example, the Electronic configuration of iron can be written as:

$$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6\ 4s^2 = [Ar]\ 3d^64s^2$$

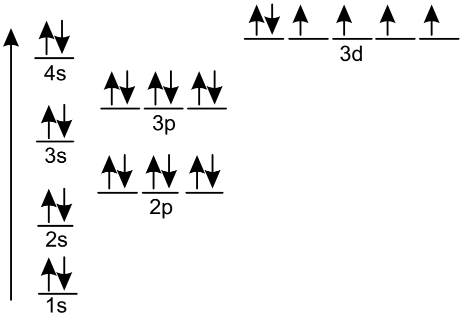


Fig. 5.4: Electronic configuration – Iron

5.5 CLASSIFICATION OF ELEMENTS BASED ON ELECTRONIC CONFIGURATION [s, p, d AND f - BLOCK ELEMENTS]

According to 'Long Form' of periodic table or Modern Periodic Table , all elements are broadly divided into four blocks *i.e.* s, p, d and f blocks. This classification of elements is based on the entry of last electron in various subshells or orbitals.

1. ***s*–Block elements.** The elements of 1 and 2 groups, hydrogen and helium belong to this group. They have one (ns^1) or two (ns^2) electrons in their outer most shell.

I ***p*–Block elements.** The elements of 13, 14, 15, 16, 17 and zero groups 9 (except He) are called p-block elements. These are those elements in which last electron enters in p-orbital of the outermost shell. Their general outermost electronic configuration ranges from ns^1p^1 to ns^2p^6. Only elements whose outermost shell is incomplete, are called representative elements. Their general outermost electronic distribution ranges from ns^2 to ns^2p^6.

2. ***d*–Block elements.** The elements of 3, 4, 5, 6, 7, 8, 9, 10, 11 and 12 groups are called d-block elements. This block lies between the s- and p-blocks. The d-orbitals of the penultimate shell (shell just below the outermost shell) are successively filled till they are incomplete. Thus the outermost two shells of such elements are incomplete. In the periodic table d-block elements are placed in long periods between s-block and p-block elements. Their general outermost electronic configuration ranges from (n–1) d^{1-10} ns^{1-2}. They are also known as **transitional elements.**
3. ***f*–Block elements.** They have last three shell which are incomplete. Lanthanides or Rare-earths (At No. 58 to 71) and Actinides or Actinons (At No. 89-103) are called f-block elements. The last electron of these elements enters f-orbitals of penultimate (n–2) *i.e.* third last orbit. Since inner f-orbitals are successively filled, these elements are also called inner transition elements.

USE OF ICT

https://phet.colorado.edu/sims/html/build-an-atom/latest/build-an-atom_en.html

Interesting Facts

- Dmitri Mendeleyev was very fond of card games. That's why he wrote the weight of each element on a separate index card and sorted them as they would be organized in solitaire. The IUPAC is responsible for maintaining and updating the periodic table. The most recent revision of the periodic table was published in December 2018.
- Electronic configuration is backbone of information of an atom. It is helpful to predict the chemical, physical, electrical and magnetic behavior of substance.
- In bulk materials, characteristics of periodicity help to explain the peculiar properties of lasers and semiconductors.

5.6 ATOMIC RADII

The shape of atom is assumed as spherical. So, its size generally expressed as the radius of the sphere. Atomic radii is the distance between the centre of the nucleus and the outermost shell of electrons.

5.6.1 Factors on which atomic size depends

(*i*) **Nuclear charge.** With increase in nuclear charge, the force of attraction between the nucleusand the electron cloud increases. Hence, the electron cloud moves closer to the nucleus andatomic size decreases.

(*ii*) **Number of orbits.** With increase in number of orbits, the distance between the nucleus and last orbit increases. Hence, atomic size increases. Similarly, with decrease in number of orbits, the atomic size decreases.

(*iii*) **Measurement.** Atomic radii are measured by electron diffraction method in angstrom units (1Å = 10^{-8} cm).

(*iv*) **Study of atomic radii.** Different types of atomic radii (which depend upon the environmentof an atom) are as follows:

(*a*) Covalent radius
(*b*) Metallic radius
(*c*) van der Waal's radius
(*d*) Ionic radius

5.6.2 Covalent Radius

The covalent radius may be defined ***as one-half of the distance between the centres of nuclear of two similar atoms held together by purely covalent single bond***.

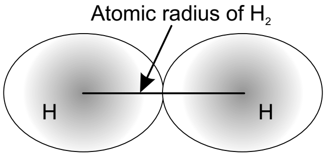


Fig. 5.5: Covalent radius of hydrogen atom

1. The inter-nuclear distance of the bonded atoms can be **determined by X-ray diffraction of spectroscopic techniques.** Half of this distance gives the covalent radius.

$$\text{Covalent radius} = \frac{\text{Inter-nuclear distance between two covalently bonded atoms}}{2}$$

Example: Inter-nuclear distance in a H_2-molecule = 0.74 Å

$$\text{Covalent radius of H-atom} = \frac{0.74}{2} = 0.37 \text{ Å}$$

5.6.3 Metallic Radii (Crystal Radii)

Half of the inter-nuclear distance between two adjacent atoms in a metallic bond represents the crystal radius or metallic radius. This is generally determined by **X-ray diffraction method**.

e.g. In solid sodium inter-nuclear distance between two adjacent sodium atoms is 3.72 Å. Therefore.

Metallic radius of Na = 1.86Å (half of 3.72Å)

5.6.4 Van der Waal's Radius

It is defined as "Half of the distance between the nuclei of two similar adjacent atoms belonging totwo neighbouring molecules in the solid state."

There are some forces of attraction, known as van der Waal's forces operating between neutral atoms of inert gases and also between non-polar molecules of various substances. Due to these forces of attraction, the neutral atoms of inert elements and non-polar molecules of other elements can come quite close together in the solid state.

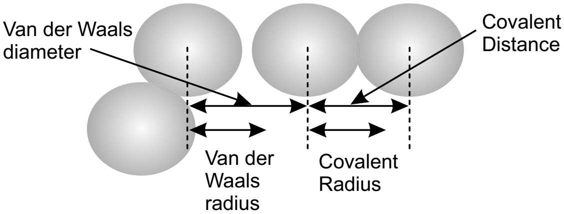


Fig. 5.6: Van der Waal's radii of chlorine and argon

It is clear from Fig. 5.9 that **van der Waal's radii must be larger than covalent radii since theinter-nuclear distance between non-bonded atoms must be more than that between bonded atoms.**

5.6.5 Ionic Radii

The ionic radii can be defined *as **the distance from the nucleus of an ion upto which it has influenceof its electron cloud.***

Inter-nuclear distance in any ionic compound is determined **from X-ray studies**. If the ions are taken as spheres, the inter-nuclear distance may be considered to be made up of the sum of the ionic radii of the two ions. For example, the inter-nuclear distance of Na–Cl is 2.76Å. this is equal to the sum of the ionic radii of Na^+ and Cl^- ions. Therefore, if we know the radius of one ion, that of other ioncan be calculated.

5.6.6 Periodic Trends of atomic radii

The atomic radius increases when we move from top to bottom in a group, because each row adds a new electron shell and greater distance between the nucleus and the outermost orbital. From left to right across a period, the ionic size decreases because total number of shells in all atoms remain same only electrons are being added to the same energy level.

5.7 IONISATION ENERGY (I.E.) OR IONISATION POTENTIAL (I.P.)

The electrons in an atom are attracted by the positively charged nucleus. In order to remove an electron from an atom, energy has to be supplied.

5.7.1 First ionisation energy (IE)

First ionisation energy or simply ionisation energy (*I.E.*) is defined as the amount of energy required to remove one valence electron from an isolated neutral gaseous atomresulting in the formation of a monovalent positive ion.

The process may be represented as :

Atom(g) + Energy → Positive ion(g) + Electron(g)

i.e., $Li(g) + Energy\ (520.1\ kJ\ mol^{-1}) \rightarrow Li^+(g) + e^-(g)$

Unit. It is expressed in either electron-volts $atom^{-1}$ or kcal mol^{-1} or kJ mol^{-1}1 eV $atom^{-1}$ = 23.06 kcal mol^{-1} = 96.5 kJ mol^{-1}.

Ionisation energy is also called ionisation potential. The ionisation energy gives the ease with which an electron can be removed from an atom. Evidently, smaller the value of ionisation energy, easier it is to remove the electron from the atom.

More than one valence electron can be removed from a neutral atom by supplying necessary energy. decreasing order of energy -

$IE_4 > IE_3 > IE_2 > IE_1$

$M_{(g)} \rightarrow M^+_{(g)} + e^-$ IE_1 (First ionisation energy)

$M^+_{(g)} \rightarrow M^{2+}_{(g)} + e^-$ IE_2 (Second ionisation energy)

5.7.2 Factors on which Ionisation Energy Depends

1. Nuclear charge.
2. Atomic size.
3. The screening or shielding effect of the inner electronic orbitals
4. Penetration of sub-shells

5.7.3 Periodic Trends of Ionisation Energy

The ionization energy of the elements within a group generally decreases from top to bottom, due to shielding of electrons. The ionization energy of the elements within a period generally increases from left to right, due to stability of valence shell.

5.8 ELECTRON AFFINITY (E.A.)

The amount of energy released when an electron is added to a neutral gaseous atom of an element to form an anion is called first electron affinity. For example,

$$\underset{\text{Neutral Atom}}{A_{(g)}} + e^- \rightarrow \underset{\text{Anion}}{A^-{}_{(g)}} + \text{Energy (called electron affinity)}$$

Unit. It is measured in kcal mol^{-1} or electron volt (eV). 1 eV = 23.06 kcal mol^{-1}.

Example. When one mole of F atom is converted into one mole of F$^-$ ions, 83 kcals of energy is released.

$$F_{(g)} + e^- \rightarrow F^-{}_{(g)} + 83 \text{ kcal mol}^{-1} (= \text{E.A.})$$

Higher the energy released, greater the value of electron affinity of an atom. Similarly higher the value of E.A. easier the formation of anion from atom and more strong the oxidising nature of element.

5.8.1 Successive Electron Affinities

When the first electron is added to the gaseous atom, it forms a uninegative ion and the energy released during the process is called **first electron affinity**. For example,

$$O_{(g)} + e^- \rightarrow O^-{}_{(g)} + \text{E.A}_1 \ (= 34.0 \text{ kcal mol}^{-1})$$

Now, if an electron is added to the uni-negative ion, it experiences a repulsive force from the anion, As a result, the energy has to be supplied to overcome the repulsive force. Thus, in order to force the second electron the energy is required rather than its release and this is called **second electron affinity**. For example,

$$O^-{}_{(g)} + e^- + \text{E.A} \ (= 168.3 \text{ kcal mol}^{-1}) \rightarrow O^{2-}{}_{(g)}$$

Thus, the value of second electron affinity is negative. The phenomenon of adding the electrons one after the other *i.e.*, in successionis called **successive electron affinity.**

5.8.2 Factors on which Electron Affinity Depends

(*i*) **Nuclear charge.** The electron affinity increases as the nuclear charge increases. This is due to greater attraction for the incoming electron if nuclear charge is high.

(*ii*) **Size of the atom.** With the increase in size of the atom, the distance between the nucleus and the incoming electrons increase and this results in lesser attraction. Consequently, the electron affinity value will decrease.

(*iii*) **Electronic configuration.** The elements having stable electronic configuration of half and completely filled valence sub-shell show very small tendency to accept additional electron and thus, electron affinities are low or almost zero in certain cases.

(*iv*) **Screening and Penetration Effects.** Value of electron affinity also depends on that orbitalin which electron enters. Value of electron affinity for the electron entering in the s-orbital isless than the p, d and f orbitals. This is due to more penetration power of s-electrons.

5.8.3 Periodic Trends of Electron Affinity

It has been observed that the electron affinity in general increases from left to right in a period and decreases from top to bottom in a group. Few exceptions observed in trend of periodicity are- Group 17 are larger (more negative) than the elements in Group 1 and Group 14 have larger (more negative) electron affinities than elements in Group 15.

5.9 ELECTRONEGATIVITY

Electronegativity is defined as a measure of the ability of an atom in a covalent molecule to attract the shared electron pair towards itself. It is denoted by Greek letter χ (chi).

Consider a covalent bond formed by two atoms (say A and B) of equal electronegativity. The bonded electron pair is equally shared between the atoms and situated between the center of two atoms. *e.g.* H_2,N_2, Cl_2, NCl_3etc. But, if atoms of dissimilar electronegativity form a covalent bond, the shared pair of electrons is not exactly in the middle but shifted towards the side of greater electronegativity.

Example- two atoms which are not identical, *e.g.*, H and Cl, forming the covalent compound H : Cl. The electronegativity of chlorine is greater than that of hydrogen, the former has the larger share in the electron pair than the latter; the chlorine end of the molecule is the negative end of the dipole, *i.e.*,

$$\overset{\delta^+}{H} - \overset{\delta^-}{Cl} \quad \text{or} \quad \overset{\delta^+}{H} : \overset{\delta^-}{Cl}$$

5.9.1 Measurement of Electronegativity

These scales of electronegativity are prevalent and used for measuring the percentage ionic character of a compound and heat of formation in a reaction.

(a) Mulliken's Scale, (b) Pauling's Scale, (c) Allred and Rochow method.

5.9.2 Application of Electronegativity

(a) **Electronegativity values and nature of bonds.** The nature of the bond formed between two atoms of different electronegativity may form polar electrovalent compound .

Example, Na(0.9) and Cl(3.0) form Na^+, Cl^-.. When two identical atoms combine *i.e.*, the difference in electronegativity values is not appreciable, they form non-polar covalent bond.

(b) **Electronegativity and nomenclature of compounds.** In binary compounds,it has become customary to put the name of the less electronegative first. For example, ICl an interhalogen compound, is called iodine chloride, ICl.

(c) Calculation of partial ionic character of a covalent bond.

(d) **Electronegativity helps to predict hydrolysis mechanism of reaction.**

(e) Calculation of bond length.

Let us calculate the bond distance N–O. Covalent radii of nitrogen and oxygen atoms are, respectively, 0.75Å and 0.74Å and the electro negativities of N and O are 3.0 and3.5, respectively.

Thus,

$$D_{N-O} = 0.75 + 0.74 - 0.09\,(3.5 - 3.0) = \mathbf{1.445Å}$$

The actual N–O bond length is 1.46Å

5.9.3 Periodic Trends of Electronegativity

In the periodic table, when we move across the period from left to right, the size of the atom gradually decreases because of gradual increase in the effective nuclear charge, so the electronegativitywill also increase gradually. Whereas, from down the group, the size of the atom goes on increasing gradually, the resultis that there is a gradual decrease in the electronegativity.

5.10 POLARIZABILITY

Polarizability is a measure of how easily an electron cloud is distorted by an electric field. The power of an ion to destroy the other ion is known as its polarizing power and the tendencyto distort is known as its polarizability.

Example in LiI, the large iodide ion, the anion is pulled towards thepositive lithium ion. The iodide ion is said to be **polarized.**

Fo polarisation (covalent character) to be significant for a bond, the cation must be polarising and the anion must be polarisable.if the cation is strongly polarising, the anion must be polarisable if the cation is moderately polarising, the anion must be very polarisable. Bonds between polarising cations and polarizable anions have significant covalent character. The polarizability of the anion depends both on its size and charge.

5.10.1 Anions of Lower Charge Density are More Polarizable

For anions having the same charge, the larger anion is polarised to a greater extent $F^- < Cl^- < Br^- < I^-$.

For anions of similar size, the more polarizable anion has a greater negative charge $S^{2-} > Cl^-$This is because a larger charge indicates a larger excess of electrons over protons.

Example 1. Why NaCl is ionic in nature but and AlI_3 is covalent.

Reason– sodium chloride, NaCl has a low positive charge (+1), a fairly large cation (~1 Å) and relatively small anion (0.2 Å) so, it is ionic in nature. But aluminium iodide AlI_3 has a high positive charge (+3) and a large anion so it is covalent in nature.

5.10.2 Polarization will be Increased by

(i) high charge and small size of the cation.

(ii) Ionic potential Å Z^+/r^+ (= polarizing power)

(iii) High charge and large size of the anion

(iv) The polarizability of an anion is related to the deformability of its electron cloud.

(v) An incomplete valence shell electron configuration.

(vi) Noble gas configuration of the cation produces better shielding and less polarizing power
e.g. Hg^{2+} (r^+ = 102 pm) is more polarizing than Ca^{2+} (r^+ = 100 pm)

5.10.3 Factors that Influence Polarizability

The relationship between polarizability and the factors of electron density, atomic radii, and molecular orientation is as follows:

1. The greater the number of electrons, the less control the nuclear charge has on charge distribution, and thus the increased polarizability of the atom.

2. The greater the distance of electrons from nuclear charge, the less control the nuclear charge has on the charge distribution, and thus the increased polarizability of the atom.
3. Molecular orientation with respect to an electric field can affect polarizibility (labelled orientation-dependent), except for molecules that are: tetrahedral, octahedral or icosahedral (labelled orientation-independent). This factor is more important for unsaturated molecules that contain areas of electron dense regions, such as 2, 4-hexadiene. Greatest polarizability in these molecules is achieved when the electric field is applied parallel to the molecule rather than perpendicular to the molecule.

5.10.4 Trend of Polarizability

A general trend is that the polarizability is lower for more electronegative atoms, and the polarizability is higher for less electronegative atoms.

Interesting Facts

(a) **Four of the elements in the table were only recently named**-On 28 November 2016, the IUPAC approved the name and symbols for four elements 113, 115, 117, and 118, named Nihonium (Nh), Moscovium (Mc), Tennessine (Ts), and Oganesson (Og).

(b) **Some elements are named after famous scientists, planets, or mythological figures**

S. No.	Element	Named after
1.	Einsteinium	Albert Einstein
2.	Germanium, Americium, and Gallium	places in which they were discovered
3.	Uranium	after the discovery of Uranus
4.	Thorium	Scandinavian god of thunder, Thor
5.	Titanium	Greek Titans

5.11 OXIDATION STATE

An oxidation state is a number that is assigned to an element in a chemical combination. This number represents the number of electrons that an atom can gain, lose, or share when chemically bonding with an atom of another element.

IUPAC definition of oxidation state is ***"Oxidation state of an atom is the charge of this atom after ionic approximation of its heteronuclear bonds, and the term oxidation number is nearly synonymous."***

The oxidation state/ oxidation number, describes degree of oxidation (lossof electrons) of an atom in a chemical compound. It is represented by integerswhich may be positive, zero, or negative. In some cases, the average oxidation state of an element is a fraction, such as 8⁄3 for iron in magnetite.

- The highest oxidation state is +9 in the iridium tetroxide cation (IrO_4^+).
- The lowest oxidation state is −4, as for carbon in methane or for chromium in $[Cr(CO)_4]^{4-}$.

Oxidation State Rules

RULE 1: Any individual atom uncombined with other elements has the oxidation state of 0(zero). Ex. The OS for Ag is 0. The oxidation state for O (oxygen) or O_2 is 0 as long as it is uncombined with any other element.

RULE 2: The total sum of the oxidation state of all atoms in any given species is equal to the net charge on that species. Ex -In neutral species, the total sum of the oxidation state of all atoms is 0. Ex. The sum of OS for NaCl is 0 since the OS of Na = +1 and the OS of Cl = –1, therefore NaCl total OS = 0.

RULE 3: In a compound, the Oxidation state for Group 1 metal is +1 and for Group 2 metal,the oxidation state is +2. Ex. In NaCl, Na has the oxidation state of +1 since it is a Group 1 Alkali metal. Cl would have an oxidation number of –1 to make the sum of the oxidation states 0 (Rule 2). In $MgCl_2$, Mg has the oxidation state of +2, since it is a Group 2 Alkaline Earth metal. Cl would have an oxidation state of –1, and since there are 2 Cl atoms, the overall charge of the species would again be 0 (Rule 2).

RULE 4: The oxidation state of FLOURINE is –1 in a compound. Ex. OS of F is –1 in HF, SF6.

RULE 5: The oxidation state of HYDROGEN is +1 in a compound.

Ex. OS of H is +1 in HI, CH_4, NH_4^+.

RULE 6: The oxidation state of OXYGEN is –2 in a compound.

Ex. OS of oxygen is –2 in OH^-, H_2O, CO_3^{2-}.

RULE 7: In two-element compounds with metals, Group 15(3A) elements have the oxidation state of –3, Group 16(6A) elements have the oxidation state of –2, and Group 17(7A) elements havethe oxidation state of –1.

5.12 COORDINATION NUMBERS AND GEOMETRY

A central metal atom or ion is called coordination centre and surrounding molecules or ions of it known as ligand, jointly they known as coordination complex. Central atom or ions are usually transition metal or inner transition metal, which donates electrons. Ligands are electron deficit groups or ions, which accepts electrons.

Coordination Number(C.N.)– "A coordination number is the number of ions and atoms around a central atom, or the total number of attachment locations to the central element in a molecule."

Thus, "The coordination number is the sum of the atoms in a given molecule bonded to the central metal atom of a compound." C.N. ranges from 2 to 16 but is usually 6.

Table 5.1: Co-ordination numbers of metal ions

Example	Metal atom	Coordinationnumber
$[Mo(CN)_8]_4$ and $[Sr(H_2O)_8]_2$	Mo, Sr	8
$[ZrF_7]_3^-$	Zr	7
$Fe(CN)_6^{4-}$, $Co(NH_3)_6^{3+}$ and $Ni(NH_3)_6^{2+}$	Fe^{2+}, Co^{3+}, Ni^{2+}	6
$[Zn(CN)_4]^{2-}$, $[Cu(CN)_4]^{3-}$, and $[Ni(CN)_4]^{4-}$	Zn, Cu, Ni	4
$[Ag(NH_3)_2]^+$, $[AuCl_2]^-$, and $[HgCl_2]$	Ag, Au, Hg	2
$[AlCl_4]^-$	Al^{3+}	4
$[AlF_6]^{3-}$	Al^{3+}	6

Example - The coordination number for the silver ion in $[Ag(NH_3)_2]^+$ is two:

5.12.1 How to Calculate Coordination Number

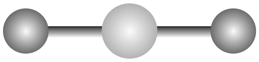
Here are the steps for identifying the coordination number of a coordination compound.

- Identify the central atom in the chemical formula. Usually, this is a transition metal.
- Locate the atom, molecule, or ion nearest the central metal atom. To do this, find the molecule or ion directly beside the metal symbol in the chemical formula of the coordination compound. If the central atom is in the middle of the formula, there will be neighboring atoms/molecules/ions on both sides.
- Add the number of atoms of the nearest atom/molecule/ions. The central atom may only be bonded to one other element, but you still need to note the number of atoms of that element in the formula. If the central atom is in the middle of the formula, you'll need to add up the atoms in the entire molecule.
- Find the total number of nearest atoms. If the metal has two bonded atoms, add together both numbers.

Complex with a specific coordination number will have a choice of several possible geometries (*i.e.*, there is not a one-to-one correspondence between coordination number and geometry).Let's discuss

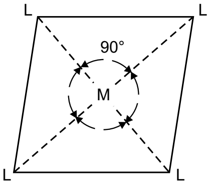
Coordination Number 2

This arrangement is not very common for first row transition metal ion complexes and some of the bestknown examples are for Silver(I). Bond angle = 180°. Shape – linear, Ex. $[Ag(CN)_2]^-$, $[Cu(CN)_2]^-$



Linear ML_2

Coordination Number 4



Two different geometries are possible tetrahedron and square planar. The tetrahedron is the more commonwhile the square planar is found almost exclusively with metal ions having a d^8 electronic configuration.

Tetrahedral Geometry: The chemistry of molecules centered around a tetrahedral C atom is covered in organic courses. To be politically correct, please change all occurrences of C to Co.There are large numbers of tetrahedral Cobalt(II) complexes known. Bond angle = 109°28'

Example: $[Zn(Cl_4)]^{2-}$, $[Hg(CN)_4]^{2-}$, $[Ni(CO)_4]^0$

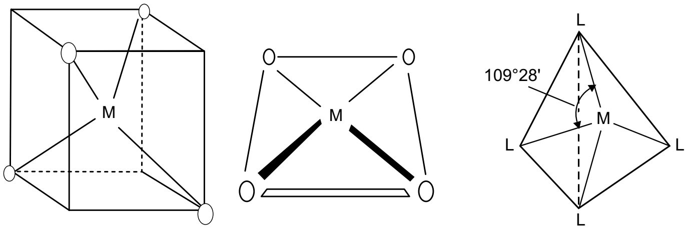


Fig. 5.7: Tetrahedral Gometry

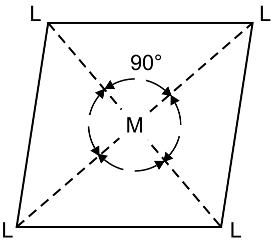
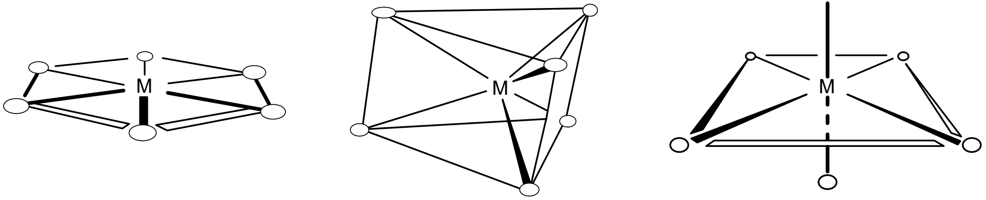


Fig. 5.8: Square Planar Geometry

Square Planar Geometry: This is fairly rare and is included only because some extremelyimportant molecules exist with this shape. Bond angle = 90° ,Example cisplatin –cis–$[PtCl_2(NH_3)_2]$

Coordination Number 6

It is most common ones formed by transition metals.



Hegagonal planner Trigonal prism Octahedral

Fig. 5.9: Coordination Number 6

- **Hexagonal planar Geometry:** Unknown for first row transition metal ions, although the arrangement of six groups in a plane is found in some higher coordination number geometries.
- **Trigonal prism Geometry:** Most trigonal prismatic compounds have three bidentate ligands such as dithiolates or oxalates and few are known for first row transition metal ions.
- **Octahedral Geometry (Oh):** The most common geometry found for first row transition metalions, including all aqua ions. In some cases distortions are observed. Ex $[Co(en)_3]Cl_3$ and $[CoCO_3(NH_3)_5]^+$

Thus, with the help of Coordination number of any molecule, we can predict the shape of that molecule. Final geometry of the molecule is further determined and confirmed by CFT which is already learned by us in unit 1.

APPLICATIONS

- **Coordination compounds** are majorly used as catalysts during synthesis of chemicals in industries and laboratories.
- These compound have peculiar properties of colour, which used in detection, identification and visualization of industrial products.

5.13 HARD AND SOFT ACIDS AND BASES

Hard and Soft Acids and Bases (HSAB) Theory is a qualitative concept introduced by Ralph Pearson to explain the stability of metal complexes and the mechanisms of their reactions.

HSAB Principle: According to HSAB concept, hard acids prefer binding to the hard bases togive ionic complexes, whereas the soft acids prefer binding to soft bases to give covalent complexes.

- The large electronegativity differences between hard acids and hard bases give rise to strong ionic interactions.
- The electronegativities of soft acids and soft bases are almost same and hence have less ionic interactions. *i.e.*, the interactions between them are more covalent.
- The interactions between hard acid - soft base or soft acid - hard base are mostly polar covalent and tend to be more reactive or less stable. The polar covalent compounds readily form either more ionic or more covalent compounds if they are allowed to react.

The Lewis acids and bases can be further divided into hard or soft or border line types.

In short, hard acids and bases are small and non-polarizable, whereas soft acids and bases are larger and more polarizable.

Characteristics of hard and soft acids, bases and borderline acids & bases are summarized in Table 5.12.

Table 5.2: Characteristics of Hard, Soft & Borderline Acids & Bases

Type of Acid/Base	CHARACTERISTICS	EXAMPLES
Hard acids	• Atomic centres of small ionic radii (<90 pm). • High positive charge. • Empty orbitals in their valenceshells. • Low electronegativity (0.7–1.6)and low electron affinity. • Likely to be strongly solvated. • High energy LUMO.	H^+, Li^+, Na^+, K^+, Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Sn^{2+} Al^{3+}, Ga^{3+}, In^{3+}, Cr^{3+}, Co^{3+}, Fe^{3+}, Ir^{3+}, La^{3+}, Si^{4+}, Ti^{4+}, Zr^{4+}, Th^{4+}, VO^{2+}, UO_2^{2+} BF_3, BCl_3, $B(OR)_3$
Soft acids	• Large radii (> 90 pm). • Low or partial positive charge. • Completely filled orbitals in their valence shells. • Intermediate electronegativities (1.9–2.5) • Low energy LUMO's with large magnitude of LUMO coefficients.	Cu^+, Ag^+, Au^+, Hg^+, Cs^+, Tl^+, Hg^{2+}, Pd^{2+}, Cd^{2+}, Pt^{2+} Metal atoms in zero oxidation states
Border line acids		Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, $B(CH_3)_3$, SO_2, NO^+
Hard bases	• Small radii (around 120pm) &highly solvated. • electronegative atomic centres • (3.0-4.0). • Weakly polarizable. • Difficult to be oxidized. • High energy HOMO.	H_2O, OH^-, F^-, Cl^-, CH_3CO_{2-}, PO_4^{3-}, SO_4^{2-}, CO_3^{2-}, NO_3^-, ClO_4^-, ROH, RO^-, R_2O, NH_3, RNH_2, N_2H_4
Soft bases	• Large atoms (> 170 pm) with intermediate electronegativity (2.5–3.0). • High polarizability • Easily undergo oxidation • Low energy HOMO's but large magnitude HOMO coefficients.	RSH, RS^-, R_2S, I^-, CN^-, SCN^-, $S_2O_3^-$, R_3P, R_3As $(RO)_3P$, RNC, CO, C_2H_4, C_6H_6, R^-, H^-
Border line bases		Aniline, pyridine, N^-, Br^-, NO_2^-, SO_3^{2-}, N_2

APPLICATIONS OF HSAB PRINCIPLE

1. **Application of hydrogen bonding:** The strong hydrogen bond is possible in cases of H_2O, NH_3 and HF, since the donor atoms (F, O & N) are hard lewis bases and their interactions with partially positively charged H, which is a hard acid, are stronger.

2. **Linkage of amphidentate ligands to metal atoms:** The amphidentate ligand, SCN^- can bind either by S end or N end. The bonding mode can be determined by using HSAB principle.
   It bonds through sulfur atom (soft base) when bonded to Pt^{2+}, a soft acid.
   However it bonds through nitrogen atom (a hard base) when linked to Cr^{3+}, a hard acid.
3. **Site preference in organic reactions:** RCOX is a hard acid and reacts with the nitrogen end of SCN^- ion to form an acyl isothiocyanate.

$$CH_3\,COX + SCN^- \xrightarrow{-X^-} RC(O)NCS$$

   Whereas the softer methyl group bonds to the sulfur atom and forms methyl thiocyanate.

$$CH_3\,X + SCN^- \xrightarrow{-X^-} CH_3\,SCN$$

4. **Inorganic reactions:** HSAB principle is used to predict the outcome of some of the reactions.
   (1) The following reaction is possible because As is softer than P and I^- is softer than F^-.

$$AsF_3 + PI_3 \longrightarrow AsI_3 + PF_3$$

   Remember that both As and P are soft but relatively As is softer.
   (2) The following reaction is possible since Mg^{2+} is harder acid than Ba^{2+} and O^{2-} is harder base than S^{2-}.

$$MgS + BaO \longrightarrow MgO + BaS$$

5. **Precipitation reactions:** The softer acids like Ag^+, Hg^+, Hg^{2+} etc., and border line acids like Fe^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+} etc., can be precipitated as sulfides from their aqueous solutions since S^{2-} ion is a softer base.

5.14 MOLECULAR GEOMETRIES

Molecular geometry is the three-dimensional arrangement of the atoms that constitute a molecule. It influences several properties of a substance including its reactivity, polarity, phase of matter, color, magnetism and biological activity.

Determination of molecular Geometry

The molecular geometry can be determined by various spectroscopic methods and diffraction methods.

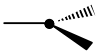
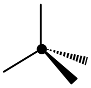
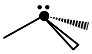
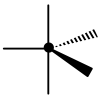
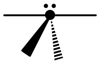
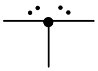
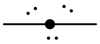
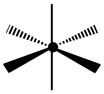
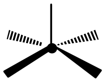
- ***IR, microwave and Raman spectroscopy*** can give information about the molecule geometry fromthe details of the vibrational and rotational absorbance detected by these techniques.
- ***X-ray crystallography, neutron diffraction and electron diffraction*** can give molecular structure for crystalline solids based on the distance between nuclei and concentration of electron density.
- ***NMR spectroscopy*** can be used to determine complementary information including relative distances dihedral angles, angles, and connectivity.

Types of molecular structure

A bond angle is the geometric angle between two adjacent bonds.

To ease of understanding and comparison molecular structure may be summarized as below mentioned Table. Shaded squares represent geometries which give non-polar molecules when all substituents X are identical

Table 5.3: The Table below summarizes the Molecular and Electron-Pair Geometries and Shapes

Total No. of Groups of ē	Electron Pair Geometry (Hybridization)	Approximate Bond Angle	No. of Bonding Directions (No. of X)	No. of Lone Pairs (No. of e)	Geometry Name (VSEPR class)	Shape	Examples
2	linear (sp)	180°	2	0	**linear** (AX_2)		BeH_2, CO_2
3	trigonal planar (sp^2)	120°	3	0	trigonal planar (AX_3)		BF_3, NO_3^-
			2	1	**bent** (AX_2E)		
4	tetrahedral (sp^3)	109.5°	4	0	tetrahedral (AX_4)		CH_4
			3	1	**trigonal pyramidal** (AX_3E)		NH_3
			2	2	**bent** (AX_2E_2)		H_2O
5	trigonal bipyramidal (sp^3d)	120° (in plane) & 90° (above& below)	5	0	**trigonal bipyramidal** (AX_5)		PCl_5
			4	1	**seesaw** (AX_4E)		SF_3
			3	2	T-shaped (AX_3E_2)		ClF_3
			2	3	**linear** (AX_2E_3)		XeF_2
6.	octahedral (sp^3d^2)	90°	6	0	octahedral (AX_6)		SF_6
			5	1	**spuare pyramidal** (AX_5E)		BrF_5
			4	2	square planar (AX_4E_2)		XeF_4

Note: For bent molecular geometry when the electron-pair geometry is trigonal planar the bond angle is slightly less than 120°, around 118°. For trigonal pyramidal geometry the bond angle is slightly less than 109.5°, around 107°. For bent molecular geometry when the electron-pair geometry is tetrahedral, the bond angle is around 105°.

APPLICATION IN DAILY LIFE

- Coordination compounds play important roles in the animals and plants life. They are essential in the storage and transport of oxygen, as electron transfer agent, as catalysts, and in photosynthesis. Hemoglobin is a well-known example of Iron metal.
- Hardness present in water is a great problem in boiler industry. It is removed by EDTA metal complex.
- We are living in the era of rapid development of new materials. Periodic variation in properties of elements have been widely used to identify the composition and structure of materials.
- These are highly helpful to calculate quantitatively various physical properties of crystal materials such as the superconductivity, electronic polarizability, elastic modulus, and hardness etc.

Interesting Facts

- **Scientists used battery polarity to weigh the elements** - Batteries were used to separate the atoms their polarity would make atoms of one element go in one direction and others in another. The atoms were then collected in separate containers and weighed.
- **Opposites of the table attract** - If you take the modern periodic table, cut out the complicated middle columns and fold it once along the middle of the Group 4 elements, the groups that "kiss" are the ones that can be stably fused together. These elements have complementary electron structures that will allow for a combination of the two.
- **Carbon is king** - Carbon atoms, from Group 4 and the carbon molecules formed can exist in a huge variety of three-dimensional structures, including rings and lattices. This flexibility makes them a key molecule in our very existence. Did you know that we are around 20 percent carbon, and that the majority of known compounds contain carbon? It is also the fourth most-abundant element in the entire universe.

SUMMARY

- **Effective nuclear charges** -The effective nuclear charge is the net charge an electron experiences in an atom with multiple electrons. $Z_{eff} = Z - S$.
- **Penetration** refers to how effectively electrons can get close to the nucleus. Different orbitals have greater nuclear **penetration** than others.
- Order for filling the electrons in orbitals-***1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d, 7p***
- **Pauli Exclusion Principle:** No two electrons in an atom can have all the four quantum numbers exactly the same.
- **Hund's Rule:** When assigning electrons in orbitals, each electron will first fill all the orbitals with similar energy (also referred to as degenerate) before pairing with another electron in a half-filled orbital.
- **Aufbau principle:** According to this principle, the electrons will first occupy the orbitals that have the lowest energy.

  Elements can be classified according to their electronic configuration are s,p,d and f-block elements

- **Atomic radii:** The atomic size is, therefore, generally expressed as the radius of the sphere or the distance between the centre of the nucleus and the outermost shell of electrons.

  Types of atomic radii - (i) Covalent radius (ii) Metallic radius (iii) Van der Waal's radius (iv) Ionic radius
- **Ionisation energy:** The electrons in an atom are attracted by the positively charged nucleus. In order to remove an electron from an atom, energy has to be supplied.

  $$IE_3 > IE_2 > IE_1$$
- **Electron affinity:** The amount of energy released when an electron is added to a neutral gaseous atom of an element to form an anion is called first electron affinity. For example,
- **Electronegativity:** Electronegativity is defined as a measure of the ability of an atom in a covalent molecule to attract the shared electron pair towards itself.
- **Polarizability** - The power of an ion to destroy the other ion is known as its polarizing power and the tendency of the ion to the ion to distort is known as its polarizability.
- **Oxidation state** - An oxidation state is a number that is assigned to an element in a chemical combination. This number represents the number of electrons that an atom can gain, lose, or share when chemically bonding with an atom of another element.
- **Coordination Number** - The coordination number is the sum of the atoms in a given molecule bonded to the central metal atom of a compound. Coordination numbers typically ranges from 2 to 16 but is usually 6.
- **Coordination Number Geometry** - Coordination Number 2 – linear, Coordination Number 4 - tetrahedral, square planar, Coordination Number 6 - hexagonal planar, trigonal prism, octahedral.
- **Hard and soft acids and bases** - According to HSAB concept, hard acids prefer binding to the hard bases to give ionic complexes, whereas the soft acids prefer binding to soft bases to give covalent complexes.
- **Applications of HSAB principle**
  (a) Application of in hydrogen bonding
  (b) Linkage of ambidentate ligands to metal atoms
  (c) Site preference in organic reactions
  (d) Inorganic reactions
  (e) Precipitation reactions
- **Molecular geometries:** Molecular geometry is the three-dimensional arrangement of the atoms that constitute a molecule. It influences several properties of a substance including its reactivity, polarity, phase of matter, color, magnetism and biological activity.

EXERCISE

LONG ANSWER TYPE QUESTIONS

1. What do you understand by periodic properties? Write the name of four periodic properties and explain in detail the factors which affect these properties.
2. Define Ionisation Potential? Describe its periodicity and the factors which affect it. Describe electrical method for its measurement.

3. Explain Electron affinity? Describe its periodicity in the periodic table. Describe the factors which influence the electron affinity.

4. What do you understand by electronegativity? Show its periodicity in the periodic table. Describe the factors which affect it.

5. Differentiate between electronegativity and electron affinity. Give application of electronegativity.

6. What is co-ordination no.? How it may calculate? Draw a neat sketch of metal complex which have octahedral geometry.

7. How lone pair of electron affects the geometry of metal complexes? Explain the role of lone pair electron by taking any suitable example of your choice.

8. Define polarizability and discuss the factors affects polarizability of molecule.

9. Explain the following giving reasons:

(i) For a metal, why is the value of second ionisation potential higher than the value of first ionisation potential?

(ii) In size, chloride ion is bigger than chlorine atom, whereas sodium ion is smaller than sodium atom.

(iii) Magnitude of electronegativity increases when we move from left to right in a period of periodic table.

(iv) Magnitude of electron affinity decreases when we move from top to bottom in a group of periodic table generally.

10. How do the following properties vary in the periodic table?

(i) Ionization energy

(ii) Atomic radii

(iii) Electronegativity.

11. Find the oxidation state of

(i) C in $C_2 H_3 O_2^-$

(ii) Mo in MoO $^{2-}$

(iii) S in SO_3^{2-}

(iv) As in AsO_4^{3-}

12. Assign the oxidation numbers of the atoms Al, Xe and Cr in the following compounds.

(a) Al_2O_3

(b) XeF_4

(c) $K_2Cr_2O_7$

13. Arrange the following compounds in order of increasing oxidation state for the carbon atom.

(a) CO

(b) CO_2

(c) H_2CO_3

(d) CH_3OH

(e) CH_4

OBJECTIVE TYPE QUESTIONS

1. Potassium Ion K+ has the same electronic configuration as that of which noble gases mentioned below?

(a) Krypton (b) Xenon

(c) Argon (d) Radon [**Ans.** (c)

Feedback: Potassium has atomic number 19, hence it has 19 electrons and therefore K^+ has 18 electrons, which is the same as noble gas Argon.

2. The electronegativity difference between the covalently bonded atoms is __________

(a) Less than 0 (b) 0-0.3

(c) 0.3-1.7 (d) Over 1.7 [**Ans.** (b)]

Feedback: The electronegativity difference between covalent bond atoms is 0-0.3, whereas for polar covalent bonded atoms it is between 0.3-1.7 and for ionic it is over 1.7.

3. On moving from left to right in a period in the periodic table, the size of the atom

(a) increases (b) first decreases and then increases

(c) does not change appreciably (d) decreases. [**Ans.** (d)]

Feedback: In periods moving from left to right principal quantum number will be same, but number of electrons gets increases, thus size decreases.

4. What is the oxidation number of chromium in calcium dichromate ($CaCr_2O_7$)?

(a) + 7 (b) – 2

(c) + 6 (d) 0 [**Ans.** (c)]

Feedback: Calcium ion has a charge of +2, the dichromate anion must have a charge of –2. Oxygen always has an Oxidation number of Oxygen is –2, so $7 \times -2 = -14$. Now , $(-2 - (-14) = 12)$. So, $12/2 = +6$.

5. The tendency of an electrode to lose electrons is known as

(a) Electrode Potential (b) Reduction Potential

(c) Oxidation Potential (d) E.M.F. [**Ans.** (c)]

Feedback: The magnitude of the electrode potential of a metal is a measure of its relative tendency to lose or gain electrons. i.e., it is a measure of the relative tendency to undergo oxidation (loss of electrons) or reduction (gain of electrons). $M \rightarrow M^{n+} + ne^-$ (oxidation potential)

6. Which of the following processes does not involve either oxidation or reduction?

(a) Formation of slaked lime from quick lime

(b) Heating Mercuric Oxide

(c) Formation of Manganese Chloride from Manganese oxide

(d) Formation of Zinc from Zinc blende [**Ans.** (a)]

Feedback: Here, in this reaction, $CaO + H_2O \rightarrow Ca(OH)_{2,}$ Oxidation number doesn't change so it's not a redox reaction.

7. Which of these statements about $[Co(CN)_6]_3^-$ is true?

(a) It has 4 unpaired electron, high spin (b) No unpaired electron, high spin
(c) No unpaired electron, low spin (d) 4 unpaired electron, low spin [**Ans.** (c)]

Feedback: $[CO(CN)_6]_3^-$ has d^2sp3 hybridisation, no unpaired electron, low spin.

8. Which of the following is wrongly mapped?

(a) Sodium carbonate – Washing soda (b) Sodium chloride – common salt
(c) Calcium carbonate – slaked lime (d) Sodium hydroxide – caustic soda [**Ans.**(c)]

Feedback: calcium hydroxide is commonly referred as slaked lime

9. Which of the following is neither an acid nor base?

(a) CH_3COOH (b) HCl
(c) KCl (d) CH_3OH [**Ans.** (c)]

Feedback: CH_3COOH and CH_3OH are organic acids, HCl is strong acid and KCl is a salt.

PRACTICAL

Experiment - 1

(Student to Record the Experiment as per Template given in Annexure)

Aim: Potentiometry - determination of redox potentials and emfs.

Student may perform any practical related to Potentiometry.

Few experiments are listed below.

- Titration of strong acid Vs strong base
- Titration of weak acid Vs strong base
- Determination of dissociation constant of a weak acid
- Determination of single electrode potential

Electro-chemistry Lab Experience

Student to Record the Experiment as per Template given in Annexure. QR code for related experiments is provided here.

Experiment - 2

(Student to Record the Experiment as per Template given in Annexure)

Aim: Chemical analysis of a salt.

This practical belongs under category of qualitative analysis. Student may identify, analyze any element of any group related to chemical analysis of salts through the provided links.

Lab

GROUP ACTIVITY

- Students may divide in s, p, d & f block elements and explain any five common character of periodic table and its periodicity along with group and period.

- Students may draw periodic table / structural formula of molecules in circular, spiral and any other geometrical shape using advance software and Technology.

SUGGESTED READINGS

BOOKS

- Selected Topics in Inorganic Chemistry by Wahid U Malik, GD Tuli & RD Madan, S Chand Publishing , ISBN: 81-219-0600-8.
- Concise Inorganic Chemistry by J.D. Lee, Wiley's Publications, ISBN: 9788126548750, 9788126548750.

E-RESOURCES

- https://ncert.nic.in/ncerts/l/lech109.pdf
- https://ncert.nic.in/ncerts/l/jesc105.pdf

KNOW MORE

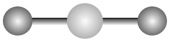
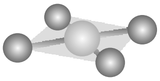
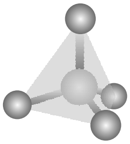
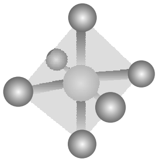
First Ionization Energies of Various Elements (kJ mol^{-1})

Group 1	Group 2	Group 13	Group 14	Group 15	Group 16	Group 17	Group Zero (18)
H 1312.0							He 2372.1
Li 520.1	Be 899.3	B 800.6	C 1086.2	N 1402.1	O 1313.7	F 1680.8	Ne 2080.4
Na 495.2	Mg 737.6	Al 577.4	Si 786.4	P 1011.7	S 999.4	Cl 1255.0	Ar 1520.3
K 418.7	Ca 589.8	Ga 579.0	Ge 760.4	As 946.1	Se 940.9	Br 1142.8	Kr 1350.6
Rb 403.0	Sr 549.3	In 558.2	Sn 708.5	Sb 88.37	Te 869.6	I 1008.8	Xe 1170.2
Cs 375.7	Ba 502.6	Ti 589.2	Pb 715.6	Bi 703.2	Po 813.5	At 916.7	Rn 1037.0

Polarizing Power of Cations

Li^+	Be^{2+}	Al^{3+}	O^{2-}	F^-
Na^+	Mg^{2+}	high	S^{2-}	Cl^-
K^+	Ca^{2+}		Se^{2-}	Br^-
Rb^+	Sr^{2+}		high	I^-
Cs^+	Ba^{2+}	Polarizability of Anions		

Coordination numbers and shapes of some complex ions

Coordination Number	Shape		Examples
2	Linear		$[CuCl_2]^-$, $[Ag(NH_3)_2]^+$, $[AuCl_2]^-$
4	Square planar		$[Ni(CN)_4]^{2-}$, $[PdCl_4]^{2-}$, $[Pt(NH_3)_4]^{2+}$, $[Cu(NH_3)_4]^{2+}$
4	Tetrahedral		$[Cu(CN)_4]^{3-}$, $[Zn(NH_3)_4]^{2+}$, $[CdCl_4]^{2-}$, $[MnCl_4]^{2-}$
6	Octahedral		$[Ti(H_2O)_6]^{3+}$, $[V(CN)_6]^{4-}$, $[Cr(NH_3)_4Cl_2]^+$, $[Mn(H_2O)_6]^{2+}$, $[FeCl_6]^{3-}$, $[Co(en)_3]^{3+}$

6

Stereochemistry and Organic Reactions

UNIT SPECIFIC

This unit discusses the topics: Representations of 3 dimensional structures. Structural isomers and stereoisomers. Configurations, symmetry and chirality. Enantiomers, diastereomers and optical activity. Absolute configurations and conformational analysis. Isomerism in transitional metal compounds.

RATIONALE

We are living in the wonderful world of molecules. Every second we are interacting with plentiful variety of natural organic and inorganic matter. Matter can vibrate, rotate, spin, etc. These all movements can be visualized and understood by the study of Stereochemistry. **Stereochemistry** is the study of spatial arrangement of atoms in molecules in 3-D space. Learning and understanding of these are highly essential, to analyze and interpret the valuable properties of everything around and inside us!

Let's get started to explore the 3D world from microscopic point of view!

PRE-REQUISITES

Chemistry : Isomerism of molecules, structure of organic compounds, IUPAC nomenclature

Maths : Basic Algebra, Geometry, Symmetry

LEARNING OUTCOMES

After this Unit, students must be able to:

U6-O1: Represent organic molecules in different 3D projection formulae.
U6-O2: Predict the geometrical and optical isomers on the basis of structure of organic molecules.
U6-O3: Differentiate between enantiomers, diastereomers, meso compounds and recemic mixture.
U6-O4: Assign R/S absolute configuration to organic compounds, corelate stability of different conformation with energy diagram.
U6-O5: Identify structural and stereiosomerism exhibited by transtion metal complexes.

MAPPING OF UNIT WISE LEARNING OUTCOMES WITH THE COURSE OUTCOMES

Outcome	EXPECTED MAPPING WITH COURSE OUTCOMES (1- Weak Correlation; 2- Medium correlation; 3- Strong Correlation)				
	CO-1	CO-2	CO-3	CO-4	CO-5
U6-O1					3

Outcome	EXPECTED MAPPING WITH COURSE OUTCOMES (1- Weak Correlation; 2- Medium correlation; 3- Strong Correlation)				
	CO-1	CO-2	CO-3	CO-4	CO-5
U6-O2					3
U6-O3					3
U6-O4					3
U6-O5					3

6.1 INTRODUCTION

In previous chapters we may learn about structure, geometry, energy and properties of atoms and molecules. Now think about orientation and representation of these molecules in 3D structure. Even minor difference in orientation can able to change entire characteristic of molecule drastically. Let us explore it step by step.

Stereochemistry is a branch of chemistry. Prefix "stereo-" means "three-dimensionality. It involves the study of the relative 3D spatial arrangement of atoms and forms the structure of organic molecules.

Organic molecules are not normally presented in such a straight-forward way. A variety of notations can be used to represent structure and orientation of organic molecules in space. There are two main categories of molecules, those that are in a straight-chain, or acyclic, form, and those that are in a ring, or cyclic, form. Information related to its classification is given below:

1. **Straight-Chain Structures**
   - Wedge-Dash Notation
   - Sawhorse Projections
   - Newman Projections
   - Fischer Projections
2. **Cyclic Structures**
   - Wedge-Dash Notation
   - Chair Conformations
   - Haworth Projections

6.1.1 Three-Dimensional Representations

Representations of three dimensional structures of Organic molecules are

1. Straight-Chain Structures:

(a) Wedge-Dash Notation

The most commonly-used notation for straight-chain molecules in organic chemistry is the **Wedge-Dash Notation.**

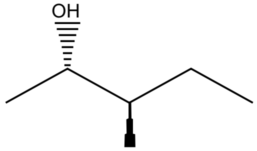


Fig. 6.1: Representation of Wedge-Dash Notation

1. In this notation, two bonds are drawn in the plane of the page (sticks), one bond is drawn coming toward you, out of the page (wedged), and one bond is drawn going away from you,behind the page (dashed).
2. **Solid Wedge**: A bond represented by a solid wedge shows that the groups or substituents arefacing out of the plane of paper towards the observer.
3. **Light Wedge**: A light wedge or dashed wedge shows that the substituents or groups are facing inside of the plane or below the plane.

(b) Newman Projections

Newman Projections are used mainly for determining conformational relationships.

1. The front carbon of this bond is represented by a dot, and the back carbon is represented by a largecircle.
2. The three remaining bonds are drawn as sticks coming off the dot (or circle), separated by one another by 120 degrees.
3. It will be drawn such that the groups on the front carbon are staggered (60degrees apart) or eclipsed (directly overlapping) with the groups on the back carbon.

   Example - Ethane, C_2H_6.

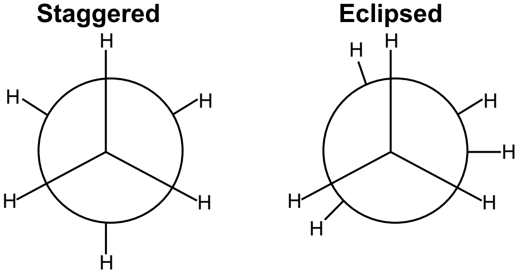


Fig. 6.2: Newman projection staggered and eclipsed forms

(c) Sawhorse Projections

1. **Sawhorse Projections** are very similar to Newman Projections.
2. Difference is only that a carbon-carbon bond is compressed in a Newman Projection, but it is fully drawn out in a Sawhorse Projection.
3. Both the front and back carbons are drawn using sticks at120 degree angles.
4. Front carbon may be staggered (60 degrees apart) or eclipsed (directly overlapping) with the groups on the back carbon.

   Example – Ethane. The structure on the left is staggered, and the structure on the right is eclipsed.

   Sawhorse Projections are useful for determining enantiomeric or diasteromeric relationships betweentwo molecules, because the mirror image or superimposibility relationships are clearer.

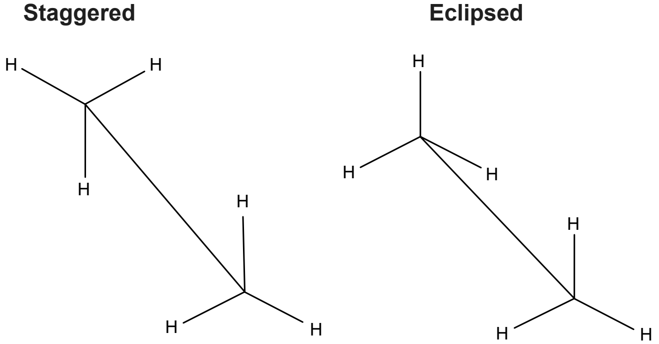


Fig. 6.3: Sawhorse projection formulas of ethane

(d) Fischer Projections

Fischer projection method is a two dimensional representation of a three-dimensional organic molecule by projection. Each place where the horizontal and vertical lines cross represents a carbon. The vertical lines are actually oriented away from you and the horizontal lines are oriented toward you.

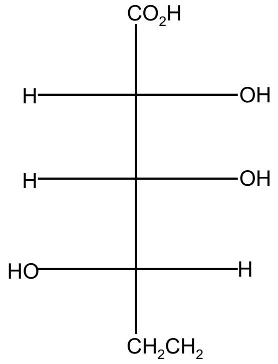


Fig. 6.4: Representation of Fischer Projection

2. Cyclic Structures

Cyclic, or ring, structures can also be drawn in a variety of ways and sizes. Commonly these are Cyclopropane (three carbons), Cyclopentane (five carbons) and Cyclohexane (six carbons).

Cyclic Wedge-Dash Notation

- As with straight chains, cyclic Wedge-Dash Notation has two bonds drawn in the plane of the page (sticks).
- One bond drawn coming toward you, out of the page and above the ring (wedged), and one bond drawn going away from you, behind the page and below the ring (dashed).
- It is important to note that groups with the same orientation (both wedged or both dashed) are cis to one another, and groups with opposite orientations (one wedged and one dashed) are trans to one another.

In the structure, the methyl group is behind the page. Since there must be four bonds to each carbon, and two sticks and one dash have already been drawn in, the remaining hydrogen must be wedged.

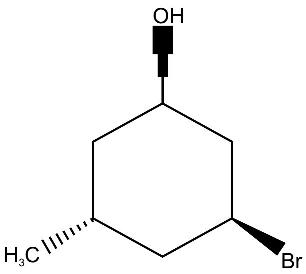


Fig. 6.5: Representation of Cyclic Wedge-Dash Notation

Haworth Projections

Haworth Projections are commonly used for cyclic sugars.

1. It is useful for being able to clearly determine whether groups are above or below the ring.

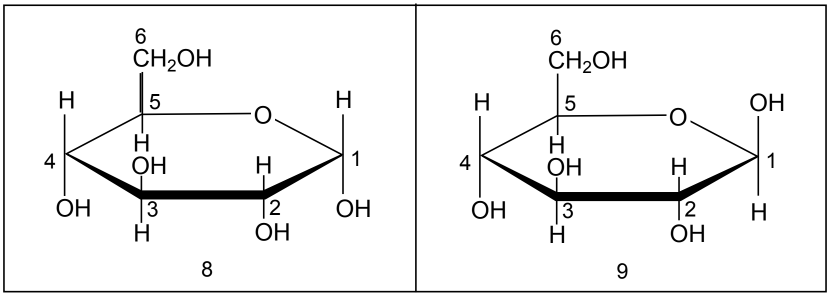


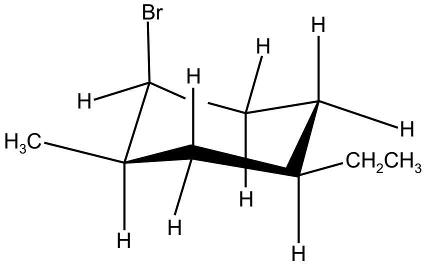
Fig. 6.6: Representation of Haworth Projections

2. Haworth Projections are similar to the cyclic Wedge-Dash notation.
3. It is important to note that two groups that are both oriented up or both oriented down are cis to one another. Two groups that are oriented one up and one down are trans to one another.

Chair Conformations

Chair conformations are the most accurate representations of orientation in 3 D space. They appropriately reflect the angles between the carbons in the ring and the positions of the groups on each carbonin the ring.

Chairs show the cyclohexane ring in its true, non-planar, orientation.



Stereo-chemistry

Fig. 6.7: Representation of Chair Conformations

Historical Timeline

Period	Scientist	Contribution
1848	Louis Pasteur	Shown that Tartaric acid has optical activity and that this depends on molecular asymmetry
1874	Jacobus H. van't Hoff and Joseph-Achille Le Bel	Both had independently explained in how a molecule with a carbon atom bonded to four different groups has two mirror-image forms.
1878	Viktor Meyer	Term stereochemistry originated for the study of stereoisomers
1975	John Cornforth and Vladimir Prelog	Nobel Prize for work on stereochemistry and stereoisomerism of alkaloids, enzymes, antibiotics, and other natural compounds.

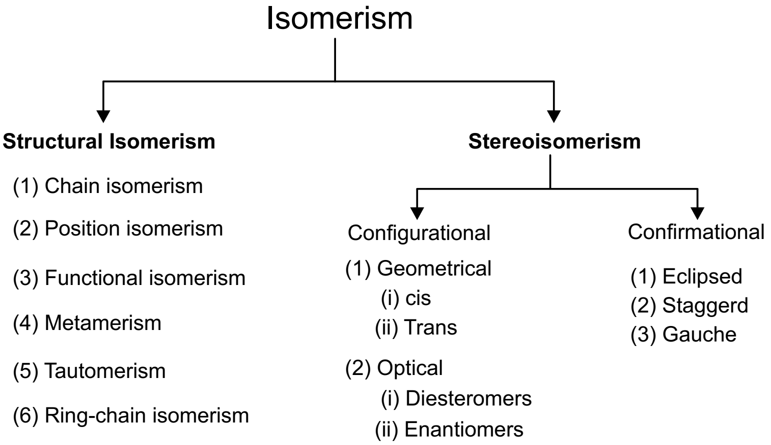
Interesting Facts

- The importance of chiral drugs in the drug development is significant. In pharmaceutical industries, 56% of the drugs currently in use are chiral molecules and 88% of the last ones are marketed as racemates (or racemic mixtures), consisting of an equimolar mixture of two enantiomers.
- Our ability to taste and smell is regulated by chiral molecules in our mouths and noses that act as receptors to "sense" foreign substances. We can anticipate, then, that enantiomers may interact differently with the receptor molecules and induce different sensations

6.2 ISOMERISM

Isomers are molecules with the same molecular formula but different structural or spatial arrangements of the atoms within the molecule. This phenomenon is known as isomerism.

Isomerism can be split into two broad groups – structural isomerism and stereo isomerism



6.2.1 Structural Isomerism

1. **Chain Isomerism:** Chain isomers are molecules with the same molecular formula, but different arrangements of the carbon‘skeleton’.

C_5H_{12} :

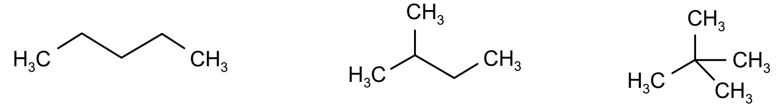


Fig. 6.8: Chain isomerism

2. **Position Isomerism:** Position isomers are based on the movement of a ‘functional group’ in the molecule. A functional groupin organic chemistry is the part of a molecule that gives it its reactivity.

$C_5H_{11}OH$:

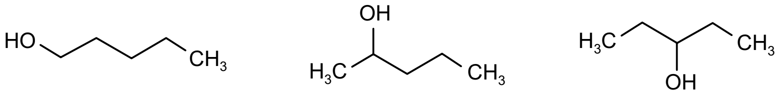
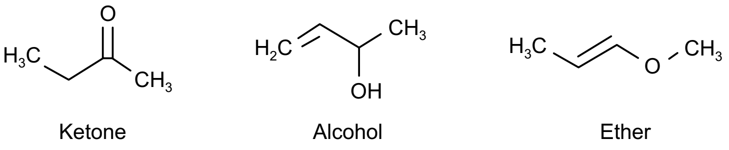


Fig. 6.9: Position isomerism

3. **Functional Isomerism :** Also referred to as functional group isomers, these are isomers where the molecular formula remains thesame, but the type of functional group in the atom is changed.

C_4H_8O :



Ketone Alcohol Ether

Fig. 6.10: Functional Isomers

4. **Metamerism :** This form of isomerism is rare and is limited to molecules having a divalent atom like O or S and alkyl groups around it. The main examples come from ethers and thioethers.

$C_4H_{10}O$:

Fig. 6.11: Metamerism

5. **Tautomerism :** This isomerism is due to spontaneous inter conversion of two isomeric forms with different functional groups. The prerequisites for this is the presence of the C=O, C=N or N=O in the usual cases and an alpha H atom. The most usual is the 'keto-enol' tautomerism, but there can be others like nitro-aci andamine-imine forms.

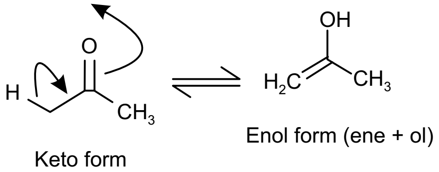


Fig. 6.12: Tautomerism

6. **Ring-Chain isomerism:** Here one isomer is an open chain molecule and the other acyclic molecule.

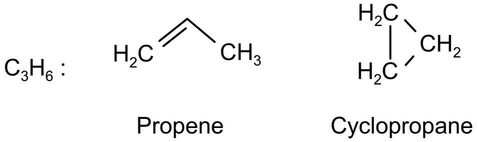


Fig. 6.13: Ring-chain isomerism

6.2.2 Stereoisomerism

Stereoisomerism is the arrangement of atoms in molecules whose connectivity remains the same but their arrangement in space is different in each isomer.

There are two main types of stereoisomerism:

- Geometric isomerism
- Optical isomerism.

Geometrical Isomerism

The isomers which possess the same structural formula but differ in spatial arrangement of groupsor atoms around the double bond are known as geometrical isomers and the phenomenon is known as geometrical isomerism.

In this system, the two atoms or groups attached to each of doubly bonded carbon atom. When the similar groups lie on the same side, it is the 'Cis isomer'.When the similar groups,lie on opposite sides, it is the 'Trans isomer'.

$$\begin{array}{c} \mathrm{H - C - COOH} \\ \| \\ \mathrm{H - C - COOH} \end{array} \qquad \qquad \begin{array}{c} \mathrm{H - C - COOH} \\ \| \\ \mathrm{HOOC - C - H} \end{array}$$

Maleic acid (Cis) Fumaric acid (trans)

Fig. 6.14: Cis -Trans isomers

Geometrical isomerism is possible only when each of the doubly bonded carbon atom has two different groups.

6.2.3 Optical Isomerism

Compounds having similar physical and chemical properties but differing only in their behavior towards plane polarized light are called optical isomers and this phenomenon is known as optical isomerism.

- Optical isomers which rotates the plane of polarised light to right (clockwise) is known as dextrorotatory isomer (*d*-form).
- Optical isomers which rotates the plane of polarised light to left (anticlockwise) is known as laevorotatory (*l*-form).
- Equimolar mixture of d and *l*-form will be optically inactive and is termed as **racemic mixture**.

Chiral Centre and Chirality- When four different groups are attached to Carbon, then Carbon is called chiral carbon. Optically active compounds have a chiral centre. Chirality is a geometric property of some molecules and ions. A chiral molecule/ion is non-superposable on its mirror image. The presence of an asymmetric carbon atom is one of the several structural features that induce chirality in organic and inorganic molecules.

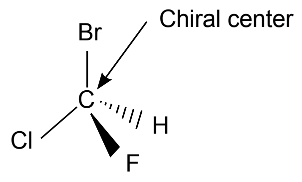


Fig. 6.15: Chiral center in Carbon

Condition for optical activity

Necessary conditions to show optical activity of any molecule are -

- The compound must contain an asymmetrical carbon atom.
- The molecule must contain a chiral axis.
- The molecule must possess a chiral plane.
- The molecule does not possess any elements of symmetry.

To make above points more clear let us discuss about elements of symmetry of any molecules in brief. Symmetry elements are of three types-

(a) **Plane of Symmetry:** A plane which divides an object into two symmetrical halves issaid to be plane of symmetry. An object lacking plane of symmetry is called dissymmetric. In order to exhibit optical activity molecule must lack plane of symmetry.

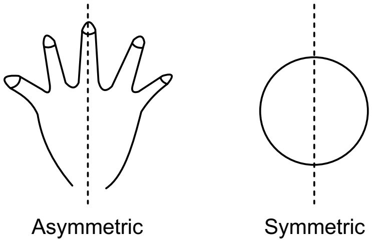


Fig. 6.16 Plane of Symmetry

(b) **Centre of Symmetry:** It is a point within a molecule through which if straight lines ; drawn, they meet identical atoms or groups in both direction from that point.

Optically active compound must not have center of symmetry. A chiral object can be defined as one that is not superimposable on its mirror image. Thus, necessary condition for a molecule to be optically active is that geometric structure of molecule should not superimpose on its mirror image.

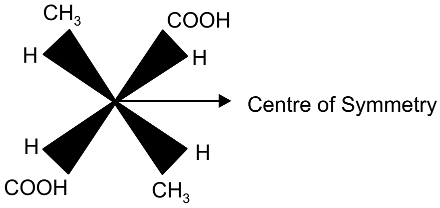


Fig. 6.17: Centre of Symmetry

(c) **Alternating axis of symmetry**: An axis of symmetry is an imaginary axis around which by rotating through a minimum angle of rotation, the original compound is obtained.

A molecule is said to possess an n-fold alternating axis of symmetry if, when it is rotated through an angle of $360^0/n$ about it axis and then reflected across a plane perpendicular to the axis, an identical structure is obtained.

Optical Isomerism in organic compounds

Calculation of number of optical isomers

1. If molecule does not contain plane of symmetry, then

   Number of optically active form = 2^n

   Number of *meso* form = 0

   n = number of Chiral center

1. **Compound containing one chiral carbon atom**

Ex. Lactic Acid

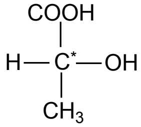


Fig. 6.18: Lactic Acid

Lactic acid contains one symmetric carbon.

It can form three isomeric forms. Out of which two forms are optically active and third one will be optically inactive:

(*i*) **dextro-rotatory (d form) or (+) lactic acid:** It rotates plane of polarised light to right.

(*ii*) **laevo rotatory (l form) or (-) lactic acid:** It rotates plane of polarised light to left.

(*iii*) **Racemic (dl form) or (±) lactic acid:** It is equimolar mixture of *d* and *l*-forms. It is optically inactive. The inactivity is due to external compensation.

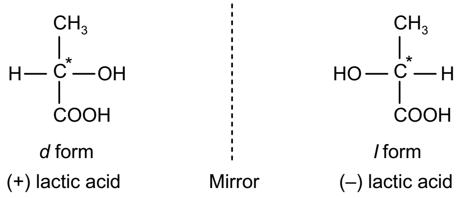


Fig. 6.19: Two Enantiomers of Lactic Acid

2. **Compound containing two chiral carbon atom**

Optical isomerism in tartaric acid: Tartaric acid has two asymmetric carbon atoms.

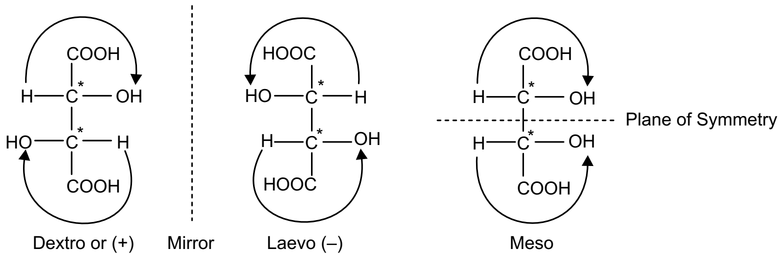


Fig. 6.20: Isomerism in Tartaric Acid

There are four forms of tartaric acid :

(*i*) **Dextro-tartaric acid (*d*-form) :** This rotates plane of polarised light to right. Both asymmetric carbon reinforce each other and cause the rotation of polarised light to same direction.

(*ii*) **Laevo-tartaric acid (*l*-form) :** This rotates plane of polarised light to left. Both asymmetric carbon reinforce each other and cause the rotation of polarised light to same direction.

(*iii*) **Meso-tartaric acid :** It possess a plane of symmetry and as a result it is optically inactive. Oneof the asymmetric carbon turns the plane of polarised light to right while other to left to the same extentso that rotation due to upper half of molecule is compensated by lower half of molecule. This is known as internal compensation of optical activity.

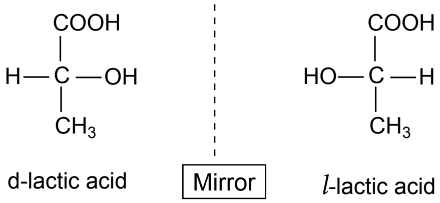
(*iv*) **Racemic tartaric acid :** It is equimolar mixture of *d* and *l*-forms. The rotation of equal number of molecules of *d*-form is compensated by *l*-form. This is known as external compensation of optical activity.

6.3 ENANTIOMERS AND DIASTEREOMERS

Enantiomers: Pair of stereoisomers which are non-superimposable mirror images of each other is called enantiomers.

Diastereomers : Pair of stereoisomers which are not mirror images of each other is called diastereomers. For any compound to show diastereomerism there should be at least two stereocentres.

Example- d- and *l*-lactic acids are an example of enantiomers, as they are mirror image of each other.



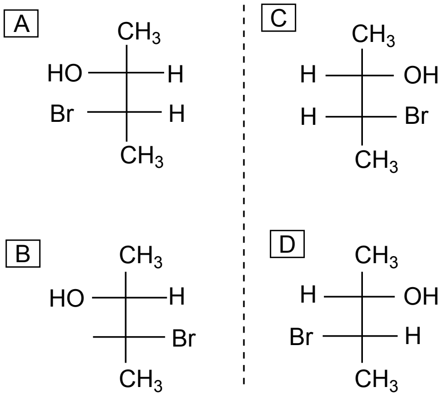


Fig. 6.21 : Enantiomers and diastereomers in **3-bromo-2-butanol**

Figure shows the 4 isomers of 3-bromo-2-butanol, which has two chiral carbon atoms.

Notice that (A) is the mirror image of (B), (C) is the mirror image of (D).

Thus the four isomers are two pairs of enantiomers. Now compare (A) with (C).

They are neither superimposable nor are they mirror images.

They are called diastereomers. (A) and (D) are also diastereomers, as are (B) and (C), and (B) and (D).

6.3.1 Difference between Enantiomers and Diastereomers:

Enantiomers	Diastereomers
They are non superimposable mirror images of each other.	They are non superimposable and non mirror images of each other.
If a compound has two chiral C atoms, then enantiomers differ in configuration at both chiral C atoms.	If a compound has two chiral C atoms, then diastereomers differ in configuration at only one chiral C atom.
All enantiomers are optically active Enantiomers generally have identical physical properties (Melting point, boiling point, density etc.) and chemical properties. They differ only in the direction of rotation on Plane Polarized Light, giving rise to d and l compounds.	Few diastereomers are optically active. Few diastereomers are optically inactive. Two diastereomers will have different melting points, boiling points, and solubilities. They will also have different reactivities toward most reagents

6.3.2 Application in Daily Life

- Biology is very sensitive to chirality and the activity depends on which enantiomer is used. Example- (R)-(+)-enantiomer of the dichlorprop is famous herbicide in killing the weeds, while the (S)-(-)-enantiomer is inactive as an herbicide.
- D-alanine and L-alanine are examples of enantiomers or mirror images. Only the L-forms of amino acids are used to make proteins.

USE OF ICT

https://phet.colorado.edu/en/search?q=stereo+chemistry

6.4 CONFIGURATION

Arrangement in space of the atoms or groups that characterizes a stereoisomer is Called its configuration. A stereoisomer should be recognized by its configuration. Method used for naming configuration is Absolute Configuration method.

6.4.1 Absolute Configuration

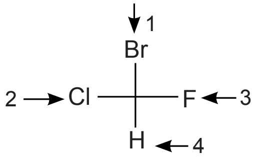
(R, S nomenclature) This system was given by Cahn-Ingold-Prelog. Absolute configuration uses a set of rules to describe the relative positions of bonds on chiral centers.

Enantiomers are two different compounds so we need to distinguished by name R and S. 'R' stands for Rectus means right or clock wise direction. 'S' stands for Sinister means left or anticlockwise direction.

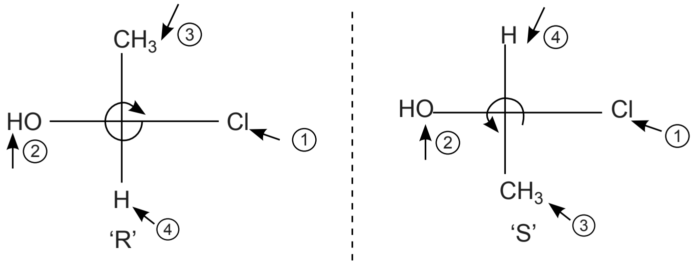
R and S configuration is decided by certain sets of rules. These are:

1. Assign priorities of all four groups attached to the chiral center. Priority decided by atomic weight of first atom of the group.
    - Is the highest priority group while 4 is the lowest priority group. Hydrogen is the lowest possible priority substituent so always assigned 4.

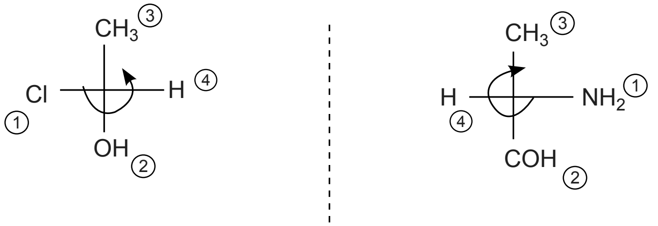
Ex.



- If atomic weight of first atom is same the priority is decided by atomic weight of next atom.
- **Ex. —CH_2Cl > —CH_2OH > –CH_2NH_2> —CH_2 CH_2Cl** like that..
- Atoms participating in double or triple bonds are considered to be bonded to an equivalent number of similar atoms by single bonds.
- Ex . —CH=CH_2 < —CH=NH
- Now, if first three groups rotate in clockwise direction then configuration is 'R' and if first three groups rotate in anticlockwise direction then configuration is 'S', Provided that the group with lowest priority (4th group) is on vertical line.



- If the group with lowest priority 4th is on horizontal line in Fischer structure then we take opposite configuration of correct answer.



Now configuration is 'R'

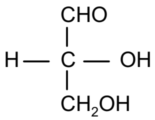
Now configuration is 'S'

Priority order

I, Br, Cl, SO_3, H, F, OR, OH, NO_2, NR_2, NHR, NH_2, COOR, COOH, $CONH_2$, $COCH_3$, CHO, CH_2OH, CN, $-CH = CH_2$, –C=CH, C, CR_3, CH_2R, CH_3, D, H

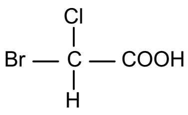
Examples: Assign R or S configuration to each of the following:

(a)



$$\begin{array}{c} CHO \\ | \\ H - C - OH \\ | \\ CH_2OH \end{array}$$

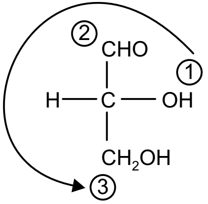
(b)



$$\begin{array}{c} Cl \\ | \\ Br - C - COOH \\ | \\ H \end{array}$$

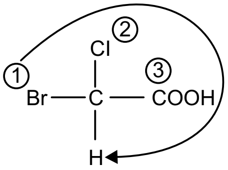
Solutions:

(*a*)



Here 'H' is on horizontal plane and priority order is in anticlockwise direction so, it is specified as 'S'.

(*b*)



'H' is on vertical plane and priority order is in clockwise direction, so it is specified as 'S'.

6.5 CONFORMATIONS

Different spatial arrangement of atoms that result from the free rotation of groups about C—C bond axis are called conformations.

(*a*) ***Conformation of Ethane:*** Of the infinite number of possible arrangements of ethane, two conformations represent the extremes. These are called eclipsed and staggered conformation.

In eclipsed conformation hydrogens of one carbon atom are directly behind the other while in staggered conformation, hydrogens of two carbon atoms are staggered with respect to one another.

Any other rearrangement which will be between these two extreme positions is known as Gauche or skew.

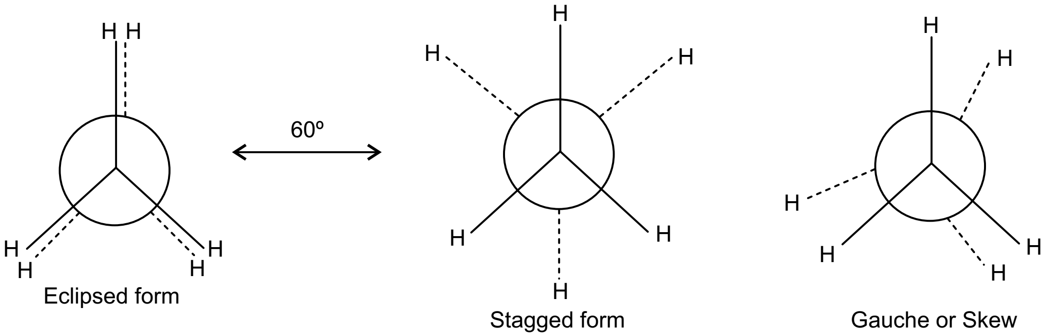


Fig. 6.22: Confirmations of Ethane

Eclipsed form is least stable because hydrogens and bonding pairs of electrons are as near as possible. Thus there is maximum repulsion and potential energy is high.

Staggered form is most stable because hydrogens and bonding pairs of electrons are at maximum distance. Thus there is minimum repulsion and potential energy is low.

(b) **Conformation of butane:** In ethane and propane all eclipsed conformations are equivalent and similarly all staggered conformations are equivalent, but in butane two distinct eclipsed and staggered conformations are possible.

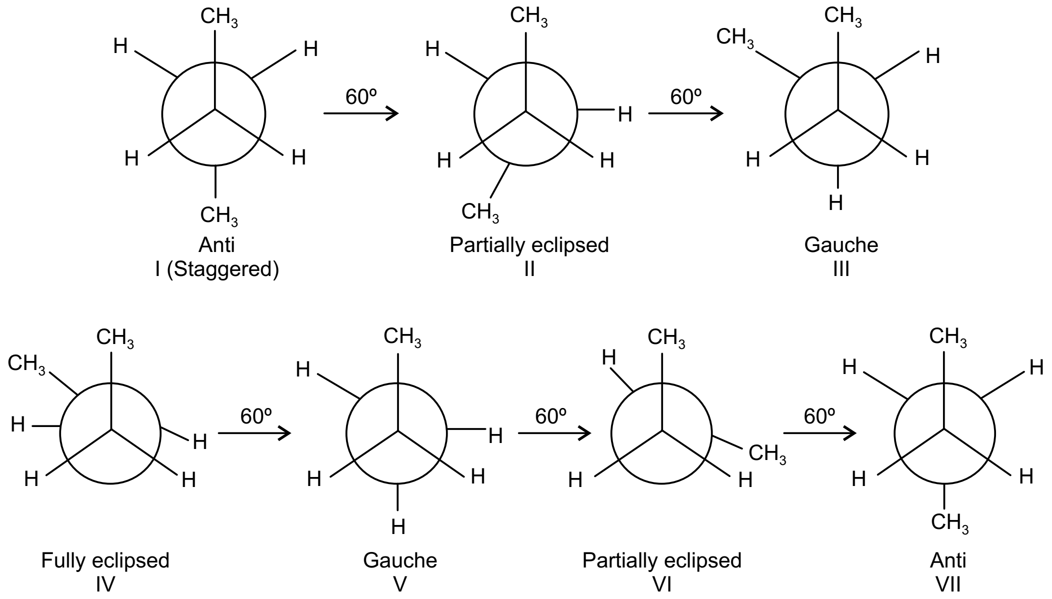


Fig. 6.23: Conformation of n-butane

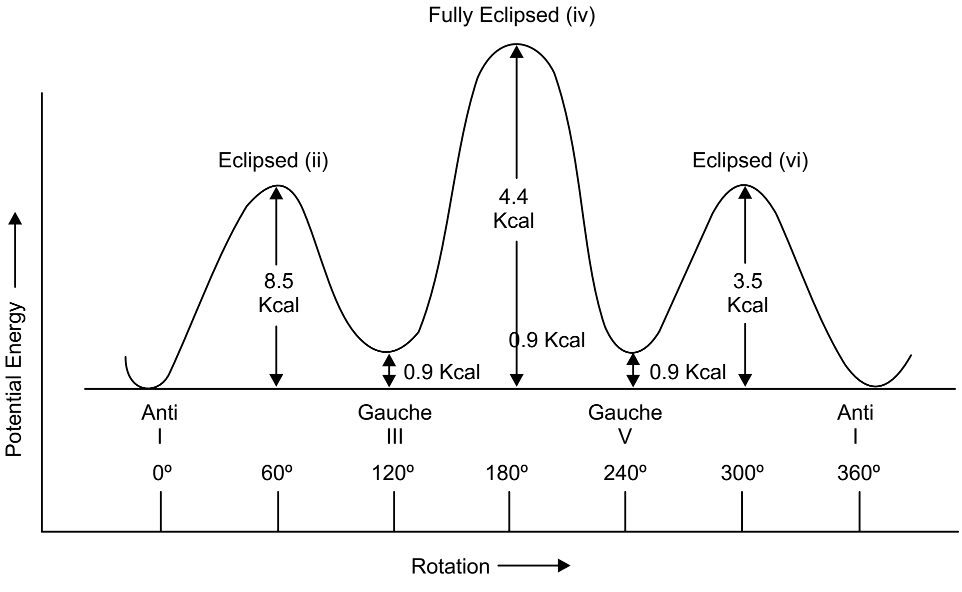


Fig. 6.24: Energy charges during rotation around the central C-C bind in n-butane

INTERESTING FACTS

- Enantiomer ratio is extremely important because while one enantiomer is beneficial to the body, the other enantiomer can be highly toxic to the body. A well-known example of enantiomer related toxicity is the R- and S-enantiomers of thalidomide.

- Introduced in late 1950's (and banned in 1961), thalidomide was prescribed to treat morning sickness in pregnant women. What followed was the biggest man-made medical disaster ever, where over 10,000 children were born with a range of severe and debilitating malformations.

6.6 ISOMERISM IN TRANSITION METAL COMPOUNDS

Phenomenon of isomers in organic molecules we have already learnt at the start of this chapter. Now applying same concept in metal complexes.

Isomers - Two or more compounds with the same formula but different arrangements of the atoms are called isomers. The existence of coordination compounds with the same formula but a different arrangement of the ligands was crucial in the development of coordination chemistry. Isomerism is divided in to two types. Each of which can be further subdivided.

1. **Structural Isomerism:** Structural isomerism occurs when the bonds are different. Isomers are distinct compounds that can have different physical properties such as colour, crystal structure, and melting point.
   - (a) Coordination isomerism
   - (b) Ionisation isomerism
   - (c) Hydrate isomerism
   - (d) Linkage isomerism
2. **Stereoisomerism:** Stereoisomers occur when the ligands have the same bonds, but the bonds are in different orientations relative to one another.
   - (a) Geometrical isomerism
   - (b) Optical isomerism

Let us learn it gradually-

1. **Structural Isomers :** There are several types of this isomerism frequently encountered in coordination chemistry and thefollowing represents some of them.

   (a) Coordination isomerism: In coordination isomerism, both positive and negative ions of a saltare complex ions and the two isomers differ in the distribution of ligands between the cationand the anion.

   Example - $[Co(NH_3)_6][Cr(CN)_6]$ and $[Cr(NH_3)_6][Co(CN)_6]$.

   where compounds containing complex anionic and cationic parts can be thought of as occurring

   by interchange of some ligands from the cationic part to the anionic part. one isomer $[Co(NH_3)_6]\ [Cr(C_2O_4)_3]$

   another isomer $[Co(C_2O_4)_3]\ [Cr(NH_3)_6]$

   (b) Ionisation isomers: In ionisation isomerism, the isomers result in different ions in solution although they have the same composition. This type of isomerism occurs when the center ionof the complex is also a potential ligand. For example, pentaaminebromidocobalt(III) sulphate $[Co(NH_3)5Br]SO_4$ is violet and in solution gives a precipitate with barium chloride, confirming the presence of sulphate ion. Pentaaminesulphatecobalt(III) bromide

$[Co(NH_3)5SO_4]Br$, on the other hand, is red and tests negative for sulphate ion in solution. It gives a precipitate of silverbromide (AgBr) with silver nitrate ($AgNO_3$).

Example - one isomer $[PtBr(NH_3)_3]NO_2^- > NO_2^-$ anions in solution

another isomer $[Pt(NO)(NH_3)_3]Br^- > Br^-$ anions in solution

(c) Hydrate isomerism: In solvate or hydrate isomerism, the isomers have the same compositionbut differ with respect to the number of solvent ligand molecules as well as the counter ion inthe crystal lattice.

Example - the best known example of this occurs for chromium chloride "$CrCl_3.6H_2O$" which may contain 4, 5, or 6 coordinated water molecules.

$[CrCl_2(H_2O)_4]Cl.2H_2O$ bright-green $[CrCl(H_2O)_5]Cl_2.H_2O$ grey-green $[Cr(H_2O)_6]Cl_3$ violet

These isomers have very different chemical properties and on reaction with $AgNO_3$ to test forCl^- ions, would find 1, 2, and 3 Cl^- ions in solution respectively.

(d) Linkage isomerism: Linkage isomerism occurs with ambidentate ligands that can bind inmore than one place.

Example - NO_2 can bind to a metal at either the N atom or an O atom occurs with ambidentate ligands. These ligands are capable of coordinating in more than one way. In the monodentateligands SCN^- / NCS^- and NO^- / ONO^-.

For example: $[Co(ONO)(NH_3)_5]Cl$ the nitrito isomer - O attached $[Co(NO_2)(NH_3)_5]Cl$ the nitro isomer - N attached.

2. **Stereoisomers :** In metal complexes, Stereoisomers have the same atoms, same sets of bonds, but differ in the relativeorientation of these bonds.

(a) Geometric isomers: Metal complexes that differ only in which ligands are adjacent to one another (**cis**) or directly across from one another (**trans**) in the coordination sphere of the metal. The expected number of geometric isomers are as follows:

Square Planar:

Compound type	No. of isomers
Ma_2b_2	2 (cis- and trans-)
Mabcd	3 (use cis- and trans- relations)

Here a, b, c, and d refer to monodentate ligands.

A number of examples of these types have been isolated and characterized and they show very different chemical and biological properties. Thus for **example, cis-$PtCl_2(NH_3)_2$ is an anti-cancer agent (cisplatin) whereas the trans-isomer is inactive against cancer (it is toxic), and so not useful in Chemotherapy.**

cis- and trans- isomers of $[PtCl_2(NH_3)_2]$ refer to the position of 2 groups relative to each other. In the cis- isomer they are "nextto each other" *i.e.* at 90 degrees in relation to the central metal ion, whereas in the trans- isomer they are"opposite to each other", *i.e.* at 180 degrees relative to the central metal ion.

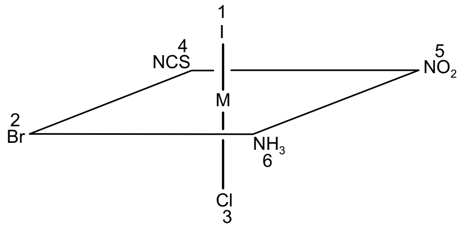
Octahedral:

Compound type	**No. of isomers**
Ma_4b_2	2 (cis- and trans-)
Ma_3b_3	2 (fac- and mer-)
MAA_2b_2	3 (2*cis- and 1 trans-)

here a, and b, represent monodentate ligands and AA is a bidentate ligand.

(b) **Optical Isomerism:** Optical isomers are related as non-superimposable mirror images and differ in the direction with which they rotate plane-polarised light. These isomers are referred to as enantiomers or enantiomorphs of each other and their non-superimposable structures are described as being asymmetric.

Priorities are assigned for mononuclear coordination systems based on the standard sequence rulesdeveloped for enantiomeric carbon compounds by Cahn, Ingold and Prelog (CIP rules). These rules usethe coordinating atom to arrange the ligands into a priority order such that the highest atomic number gives the highest priority number (smallest CIP number). For example the hypothetical complex [Co ClBr I NH_3 NO_2 SCN]$^{2-}$ would assign the I as 1, Br as 2, Cl as 3, SCN as 4, NO_2 as 5 and NH_3 as 6.



Here is one isomer where the I and Cl, and Br and NO_2 were found to be trans- to each other.

The reference axis for an octahedral centre is that axis containing the ligating atom of CIP priority 1 and the trans ligating atom of lowest possible priority (highest numerical value). The atoms in the coordination plane perpendicular to the reference axis are viewed from the ligand having that highest priority (CIP priority 1) and the clockwise and anticlockwise sequences of priority numbers are compared.

Optical isomers are possible for both tetrahedral and octahedral complexes, but not square planar.

6.7 USES OF COORDINATION COMPOUNDS

1. **Dyes and Pigments:** Coordination compounds have been used from the earliest times as dyes and pigments. Example - Madder dye which is complex of Hydroxyanthraquinone is red in colour, used by the ancient Greeks. A more modern example is the pigmentcopper phthalocyanine, which is blue.
2. **Analytical Chemistry:** Many complex compounds are being used as analytical reagent for detection and identification purpose.

(a) **Colour Tests:** Since many complexes are highly coloured they can be used as colourimetric reagents *e.g.* formation of red 2,2'-bipyridyl and l,l0-phenanthroline complexes as a test for Fe(II).

(b) **Gravimetric Analysis**: Here chelating ligands are often used to form insoluble complexes *e.g.* $Ni(DMG)_2$ and $Al(oxine)_3$.

(c) EDTA and other complexing agents have been used to speed the elimination of harmful radioactive and other toxic elements from the body. (*e.g.* Pb^{2+}). In these cases soluble metal chelate complexes are formed.

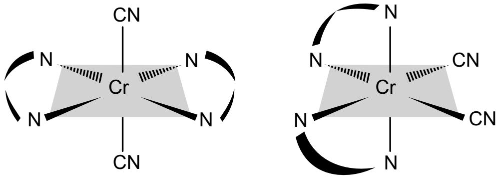
3. **Extraction of Metals:** Sometimes certain metals can be leached from their ores by formation of stable complexes *e.g.* Ag and Au as complexes of cyanide ion.
4. **Bio-Inorganic Chemistry:** Naturally occurring complexes include haemoglobin, chlorophyll, vitamin B_{12} etc.
5. **Chemo-therapy:** An example here is the use of cis-$PtCl_2(NH_3)_2$ as an anti-tumour drug.

SUMMARY

- **Three-Dimensional Representations:** Representation of 3D structures of Organic molecules are Wedge-Dash Notation, Newman Projections, Sawhorse Projections, Fischer Projections and Haworth Projections
- **Isomerism :** isomers are molecules with the same molecular formula (i.e. the same number of atoms of each element), but different structural or spatial arrangements of the atoms within the molecule.
- **Structural isomerism :** Isomers can be split into two broad groups – structural (or constitutional) isomers, and stereoisomers.
- **Chain Isomers :** Chain isomers are molecules with the same molecular formula, but different arrangements of the carbon 'skeleton'.
- **Position Isomers :** Position isomers are based on the movement of a 'functional group' in the molecule. A functional group in organic chemistry is the part of a molecule that gives it its reactivity.
- **Functional Isomers :**Also referred to as functional group isomers, these are isomers where the molecular formula remains the same, but the type of functional group in the atom is changed.
- **Metamerism :** This form of isomerism is rare and is limited to molecules having a divalent atom like O or S and alkyl groups around it. The main examples come from ethers and thioethers.
- **Tautomerism :** Due to spontaneous inter conversion of two isomeric forms with different functional groups. The prerequisites for this is the presence of the C=O, C=N or N=O in the usual cases and an alpha H atom. The most usual is the 'keto-enol' tautomerism, but there can be others like nitro-aci and amine-imine forms.
- **Ring-Chain isomerism :** Here one isomer is an open chain molecule and the other a cyclic molecule.
- **Enantiomers :** Pair of stereoisomers which are non-superimposable mirror images of each other are called enantiomers.
- **Diastereomers:** Stereoisomers which are not mirror images of each other are called diastereomers.
- **Configuration :** Method used for naming configuration is Absolute Configuration method.
- **Conformation :** Different spatial arrangement of atoms that result from the free rotation of groups about C—C bond axis are called conformations.

SUBJECTIVE QUESTIONS

1. What are optically active compounds? What are the necessary conditions for the compoundto be optically active?
2. Draw all the possible geometrical isomers for the complex [Cr(en) (CN)]$^+$.



trans cis

Two geometrical isomers are possible: trans and cis.

3. (i) Give examples for four different types of structural isomers ?

   Explain optical isomerism with examples and in case of [$CoCl_2(en)_2$]$^+$ why trans form is optically inactive than cis form ?
4. Draw the structure of the smallest alkane (with a general molecular formula of C_nH_{2n+2}) whichhas optical isomers.
5. What do you understand by optical activity? The optical activity is associated with the presence of an assymetric carbon atom in it. Justify this statement with suitable example.
6. What are enantiomers? Describe properties of enantiomers.
7. What you mean by conformational analysis? Describe the confirmation of cyclohexane.
8. Describe with the help of suitable example of relative and absolute configuration methods for representing the configuration of optically active compounds.
9. Explain the difference between optical isomerism and geometrical isomerism.

OBJECTIVE QUESTIONS

1. Which of the following compounds will exhibit cis-trans isomerism?

(a) 2-butene	(b) 2-butyne
(c) 2-butanol	(d) butanal [**Ans.** (a)]

Feedback: The compounds with each doubly bonded carbon attached to two different groups exhibit geometrical isomerism, due to restricted rotation of double bond. However, even though there is restricted rotation for triple bond, alkynes do not exhibit geometrical isomerism, since the triply bonded carbons are attached to one group each only.

2. Find the number of stereoisomers for $CH_3 – CHOH – CH = CH – CH_3$.

(a) 1	(b) 2
(c) 3	(d) 4 [**Ans.** (d)]

Feedback: The number of stereoisomers for $CH_3 – CHOH – CH = CH – CH_3$ is four. This is calculated by the formula 2^n

3. Which of the following compound would show optical isomerism?

(a) $CH_3 - CH(OH)\ COOH$ (b) $H_2N\ CH(CH_3)_2$

(c) $(CH_3)_2\ CHCHO$ (d) $H_2N\ CH_2\ COOH$ [**Ans.** (a)]

Feedback: $CH_3 - CH(OH)\ COOH$ will show optical isomerism as it possess chiral carbon.

4. Which of the following groups has the highest priority according to the Cahn-Ingold-Prelog sequence rules?

(a) CH_3 (b) CH_2Cl

(c) CH_2OH (d) CHO [**Ans.** (b)]

Feedback: According to the Cahn-Ingold-Prelog sequence rules.

5. Which of the following notations is not used to distinguish between pairs of enantiomers?

(a) R and S (b) E and Z

(c) + and - (d) D and L [**Ans.** (b)]

Feedback: All four of these notations are used to distinguish between isomers, but only three are used specifically in the context of enantiomers. The fourth - E and Z - is used to differentiate between geometric isomers, not enantiomers.

6. Select the correct statement from the following option.

(a) Meso compound possess both plane of symmetry and centre of symmetry

(b) Meso compound possess either plane or centre of symmetry

(c) Meso compound does not possess either plane or centre of symmetry

(d) Meso compounds are externally compensated form [**Ans.** (b)]

Feedback: Meso compound possess either plane or centre of symmetry. They do not possess both plane of symmetry and centre of symmetry and also they are internally compensated form.

7. How many optical isomers are possible in a compound with one chiral carbon?

(a) 5 (b) 4

(c) 2 (d) 3 [**Ans.** (d)]

Feedback: A compound with one chiral carbon has three optical isomers (+), (-) and (±).

ACTIVITY

- Identical Twins are mirror images! Can you make an analogy with enantiomers?
- Students to design an alternative Experiment (as group or individual basis) and present as group with individual participation as well.

SUGGESTED READINGS

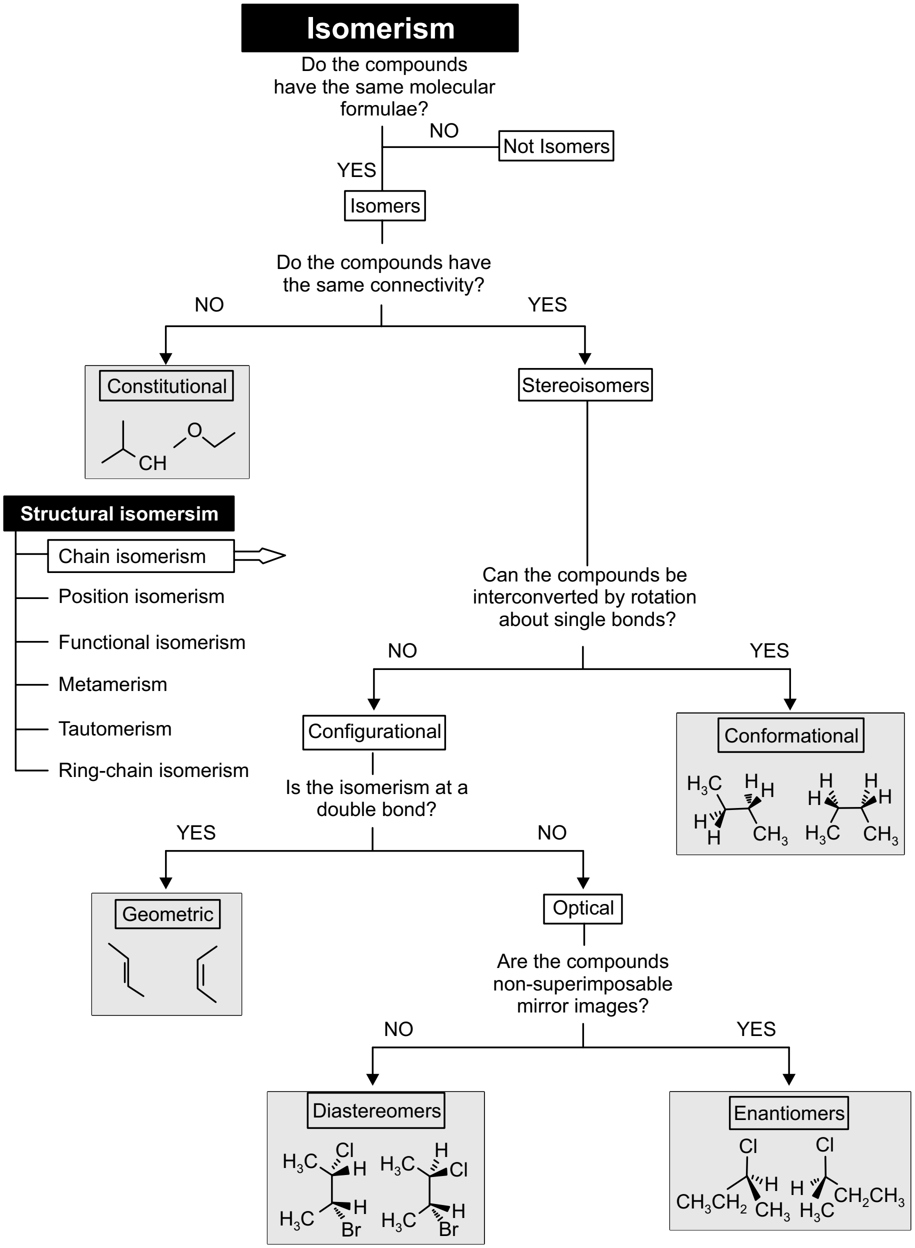
BOOKS

- Organic Chemistry by A. Bahal and B.S. Bahal, S Chand & Company Publications ISBN No. 9789352-531967.
- Organic Chemistry, Reaction and Reagents by O. P. Agrawal GOEL Publishing house.
- Advanced Organic Chemistry Part A: Structure and Mechanisms by Carey, Francis A., Sundberg, Richard J., Springer Publication house, ISBN 978-0-387-44899-2

E-RESOURCES

- https://nptel.ac.in/courses/104/105/104105086/
- https://onlinecourses.nptel.ac.in/noc19_cy25/preview

KNOW MORE



FORMULA FOR CALCULATION OF OPTICAL AND GEOMETRICAL ISOMERS

Optical Isomers

1. **If molecule does not contain plane of symmetry and contain even number of chiral center, then**

   Number of optically active form = 2^{n-1}

   Number of *meso* form = $2^{n/2-1}$

   Total isomer = $2^{n-1 + 2^{n/2-1}}$

2. **If molecule does not contain plane of symmetry and contain odd number of chiral center, then**

   Number of optically active form = $2^{(n-1)} - 2^{(n-1)/2}$

   Number of *meso* form = $2^{(n-1)/2}$

   Total isomer = 2^{n-1}

Geometrical isomers

1. When a compound has n double bonds and ends of polyene are different, the number of geometrical isomers = 2^n

   Ex. $C_6H_5 - CH = CH - CH = CH - CH = CH - CH = CH\text{-}Cl$

2. Given compound has 4 double bonds and two ends are different, so no. of geometrical isomers

   $= 2^n = 2^4 = 16$

7

Organic Reactions Synthesis of Drug Molecules

UNIT SPECIFIC

This unit discusses the topics: Introduction to reactions involving substitution, addition, elimination, oxidation and reduction, cyclization and ring openings reactions. Synthesis of commonly used drug molecules.

RATIONALE

Chemical change is the key to understanding chemistry. The goal of chemists is to know how and why a substance changes in the presence of another substance or even by itself. Chemical changes are happening everywhere outside and even inside us! There are millions of chemical substances and a huge number of possible chemical reactions. In this unit, we will study organic reactions and drug molecules.

PRE-REQUISITES

Chemistry – Basic knowledge of chemical equations and synthesis process

Physics – Knowledge of electronic transformation

LEARNING OUTCOMES

At the end of this unit, students must able to -

U7-O1: Categorize a given organic reaction into substitution, addition and elimination Reactions.

U7-O2: Predict the products of simple oxidation and reduction reactions.

U7-O3: Apply theories of cyclization and ring openings for preparation of simple organic compounds.

U7-O4: Synthesize some commonly used drug molecules.

MAPPING OF UNIT WISE LEARNING OUTCOMES WITH THE COURSE OUTCOMES

Outcome	EXPECTED MAPPING WITH COURSE OUTCOMES (1- Weak Correlation; 2- Medium correlation; 3- Strong Correlation)				
	CO-1	CO-2	CO-3	CO-4	CO-5
U7-O1					3
U7-O2					3
U7-O3					3
U7-O4					3

7.1 INTRODUCTION

Organic chemistry was first defined as a branch of modern science in the early 1800's by Jon Jacob Berzelius. He classified chemical compounds into two main groups: organic if they originated in living or once-living matter and inorganic if they came from "mineral" or non-living matter. Let us learn more through historical timeline represented as in table as below-

Duration	Scientist	Contribution
1856	William Henry Perkin	Attempting to synthesize quinine, and had a successful career in **dye synthesis**.
1862	Emil Erlenmeyer	Was the first to suggest the possibility of **double and triple bonds** between two carbons.
1865	August Kekulé	First to draw structures of organic compounds using lines for bonds - **Structure of benzene**.
1870	Vladimir V. Markovnikov	**Markonikov's rule** stating that in an addition of H-X to an alkene
1877	Charles Friedel, James Crafts	**Friedel-Crafts reaction** involving alkylation and acylation reactions of aromatic rings.
1895	Paul Walden	Stereochemistry concept of the **Walden inversion**.
1900	F. A. Victor Grignard	The discovery that magnesium reacts with organohalides to form **Grignard reagents** .
1931	Erich Hückel	**Hückel's rule** that states that a planar ring with 4n + 2 p electrons for aromaticity.
1954	Vladimir Prelog	**Reactivity to organic structure** with regard to stereoisomerism.
1991	Sumio Iijima	synthesized **carbon nanotubes**
2004	Andre Geim, K. Novoselov	**Graphene** and its two dimensional properties.

Modes of reactions are different according to its mechanism. It may be divided into numerous varieties like – Substitution, Addition, Elimination, Oxidation, Reduction, Rearrangement etc. Let us learn one by one.

7.2 SUBSTITUTION REACTION

Substitution reaction: Substitution reaction are those reaction in which an atom, ion, or group of a molecule is replaced by another atom, ion, or group.

Example - CH_3Cl reacted with a hydroxy ion (OH^-) will produce CH_3OH and chlorine.

$$CH_3\mathbf{Cl} + OH^- \longrightarrow CH_3\mathbf{OH} + Cl^-$$

7.2.1 Components of a Substitution Reaction

An electron-rich species donates a pair of electrons to an electron-poor species and forms a new product and a new base. Therefore, a substitution reaction contains four components.

Nucleophile: the electron-rich species donating a pair of electrons to carbon.

Ex. Cl^-, Br^-, I^-, OH^-, RO^-, CN^-, H_2O, and NH_3.

Electrophile: the electron-deficient species accepting a pair of electrons.

Ex. H_3O^+, NO_2^+, and SO_3.

Product: the species that is formed from a substitution reaction

Leaving group: the group that leaves the compound

7.2.2 Types of Substitution Reaction

Substitution reaction is further classified into three types-

(*i*) ***Free radical substitution reaction*** - Free Radical substitution takes place when an atom or group of atoms in a molecule is replaced by a free radical. Examples of free radicals are $^\cdot$Br, $^\cdot$Cl, $^\cdot$I and $^\cdot$OH.

(*ii*) ***Electrophilic substitution reaction*** - When the substituent is electrophile and accepts an electron pair for bonding with the compound is called electrophilic substitution.

Electrophilic Substitution is of two types

(a) Electrophilic aliphatic substitution

(b) Electrophilic aromatic substitution.

(*iii*) ***Nucleophilic Substitution Reaction :*** When nucleophile provides an electron pair for bonding with the compound being transformed, it is called nucleophilic substitution.

They are represented by SN (S stands for substitution and N stands for Nucleophilic) and are more common in aliphatic compounds. For *e.g.* →

$$\mathbf{R{-}X + KOH \longrightarrow ROH + KX}$$

SN reaction may follow two mechanisms.

1. **Unimolecular mechanism:** It proceeds via unimolecular mechanism are represented by S_N1.
2. **Bimolecular Mechanism:** It proceeds through bimolecularmechanism are represented as S_N2.

Table 7.1: Difference between S_N1 and S_N2 reactions

S.N.	Parameter	S_N1	S_N2
1.	Alkyl halide structure	tertiary > secondary >>>> primary > methyl	methyl > primary > secondary >>>> tertiary
2.	Nucleophile	poor nucleophile (often the solvent)	high concentration of a strong nucleophile
3.	Mechanism	2-step	1-step
4.	Rate limiting step	carbocation formation	bimolecular transition state
5.	Rate law	rate = k[R-X]	rate = k[R-X][Nu]
6.	Stereo-chemistry	mixed configuration	inversion of configuration
7.	Solvent	polar protic	polar aprotic

S_N2 reactions are favored by strong nucleophile and presence of simple and fewer alkyl groups. Thus presence of bulky groups hinders S_N2 reaction and facilitates the S_N1 reaction.

The hydrolysis of 2° alkyl halides may take place by any one of S_N1 and S_N2 mechanism.

7.2.3 Applications of Radical Substitution

- Halogenation Reaction
- Wohl-Ziegler reaction
- Aldol Condensation
- Hunsdiecker reaction
- Cannizzarro Reaction

7.3 ADDITION REACTION

Reaction in which two or more molecules combine to form a larger molecule. Addition Reaction is shown by unsaturated hydrocarbons which contain double or triple bonds.

Molecules containing carbon—hetero double bonds like carbonyl (C=O) groups, or imine (C=N) groups, can undergo addition,

Example:

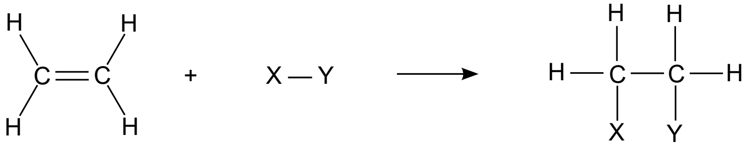


Fig. 7.1: Addition reaction of alkenes

7.3.1 Electrophilic Addition Reaction

The π bond is localized above and below the C-C σ bonds in alkenes and alkynes. The π electrons are quite far away from the nuclei and are therefore loosely bonded. During Electrophilic addition, the pi electrons attack an electrophile, forming a carbocation (the carbon atom with only 3 bonds and a positive charge), on the most stable carbon. After this, the nucleophile attacks the carbocation to form the product.

Example –Addition HX in alkenes and alkynes

Examples of electrophilic additions of alkenes and alkynes are:

- **Hydrohalogenation Reaction:** Addition of HX (Follows- Markownikoff's Rule)

  $CH_3 - CH = CH_2 + HX \longrightarrow CH_3\text{–}CHX\text{–}CH_3$

- **Hydration reactions:** Acid catalysed addition of water H_2O (Follows - Markownikoff's Rule)

  $CH_3 - CH = CH_2 + H_2O \xrightarrow{H^+} CH_3\text{–}CH(OH)\text{–}CH_3$

- **Halogen addition reactions: X_2**

  $CH_3 - CH = CH_2 + X_2 \longrightarrow CH_3 - CHX\text{–}CH_2X$

7.3.2 Nucleophilic Addition Reaction

An addition reaction where a chemical compound with an electrophilic double or triple bond reacts with a nucleophile and double or triple bond is broken. It is common in aldehyde and ketones.

Example - Addition to Carbonyl groups

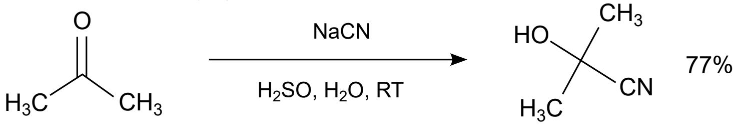


Fig. 7.2: Addition to Carbonyl groups

Other Examples of Nucleophilic addition reactions:

- Addition of Alcohol to aldehydes and ketones to form hemiacetals and acetals.
- Addition of Hydride during the reduction of aldehydes and ketones to form 1^0 and 2^0 alcohols respectively.

7.3.3 Free-radical Addition

It is an addition reaction in organic chemistry which involves free radicals. The addition may occur between a radical and a non-radical, or between two radicals.

Reaction has three basic steps

- Step I- Initiation by a radical initiator: A radical is created from a non-radical precursor.
- Step II- Chain propagation: A radical reacts with a non-radical to produce a new radical species
- Step III- Chain termination: Two radicals react with each other to create a non-radical species

Organic Chemistry-I

Example-

- Anti-Markownikoff's reaction of HBr to an alkene in the presence of organic peroxides. This reaction proceeds via the attack of bromine free radical generated by combination of HBr and organic peroxides.

$$CH_3 - CH = CH_2 + HBr \xrightarrow{\text{Peroxide}} CH_3{-}CH_2{-}CH_2Br$$

7.4 ELIMINATION REACTION

Elimination reaction involves the loss of two atom or groups of atoms from the same or adjacent atoms of a substance leading to the formation of a multiple bond.

It is almost opposite of addition reaction. After elimination of group product form an unsaturated linkage.

$$RCH_2CH_2X \longrightarrow RCH{=}CH_2 + HX$$

7.4.1 Types of Elimination Reaction Mechanisms

Reaction follows two mechanisms these are E1 and E2 types.

E1 type It is two-step removal mechanism process, also known as unimolecular elimination reaction. Formation of an intermediate.

Example – $(CH_3)_2{-}\ CHOH \xrightarrow{\text{Acid Catalysed}} CH_3{-}CH{=}CH_2 + H_2O$

E2 type It is one step removal mechanism process, also known as bimolecular elimination reaction.

Example - $CH_3{-}CH_2{-}Br \xrightarrow{\text{Base}} CH_2{=}CH_2 + HBr$

Table 7.2 Difference between E1 and E2 reactions

S. No.	Properties	E1 Reaction	E2 Reaction
1.	Substrate	Encountered in Secondary and Tertiary Substrate	Encountered in Primary Substrate
2.	Rate law	Unimolecular as it depends on concentration of substrate only	Bimolecular as it depends on concentration of both substrate and base
3.	Big Barrier	Formation of carbocation $3^{0} > 2^{0} >> 1^{0}$	None
4.	Requirement of strong base	Not required	Strong base is required

7.5 OXIDATION AND REDUCTION REACTIONS

You are already aware that when a compound or element is oxidized it loses electrons, and when it is reduced it gains electrons. But, here we are talking about the oxidation and reduction of organic compounds. We are mainly concerned with the number of carbon-heteroatom bonds in the compound compared to the number of carbon-hydrogen bonds.

Heteroatom in organic chemistry generally refers to ***oxygen, nitrogen, sulfur, or a halogen.***

7.5.1 Oxidation

Oxidation of an organic compound results an increase in the number of carbon-heteroatom bonds, and/or a decrease in the number of carbon-hydrogen bonds.

Simply we can say ***Dehydrogenation = oxidation***

Example - oxidation of an alcohol to a ketone or aldehyde

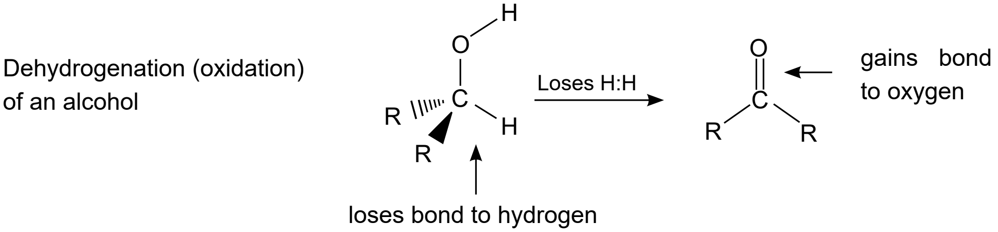


Fig. 7.3: Oxidation

7.5.2 Explanation

Oxygen is more electronegative than carbon, so when a carbon atom gains a bond to a heteroatom, it loses electron density and is thus being oxidized.

Thus a carbon atom loses a bond to hydrogen and gains a bond to a heteroatom (or to another carbon atom), it is considered to be an oxidative process because hydrogen, of all the elements, is the least electronegative. Thus, in the process of dehydrogenation the carbon atom undergoes an overall loss of electron density - and loss of electrons is oxidation.

7.5.3 Reduction

Reduction of an organic compound results in a decrease in the number of carbon-heteroatom bonds, and/or an increase in the number of carbon-hydrogen bonds.

Hydrogenation = Reduction

Example –

- Hydrogenation of an alkene to an alkane
- Hydrogenation of a ketone to an alcohol

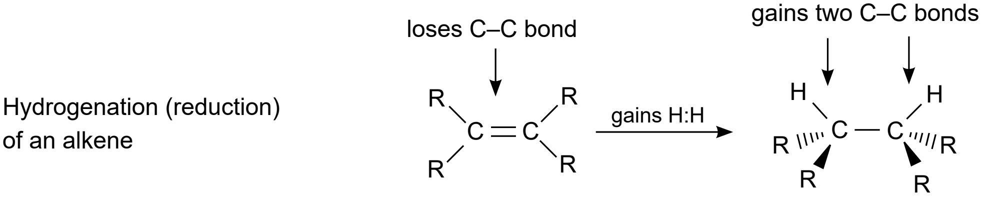


Fig. 7.4: Reduction

7.5.4 Explanation

Hydrogenation results in *higher* electron density on a carbon atom(s), and thus we consider process to be one of reduction of the organic molecule. Hydrogen is less electronegative than carbon, so when a carbon gains a bond to a hydrogen, it is gaining electron density, and thus being reduced.

Notice that neither hydrogenation nor dehydrogenation involves the gain or loss of an oxygen *atom*.

7.5.5 Common Oxidation and Reduction Reactions

A. Oxidation Reactions

Primary alcohols can be oxidised to aldehydes using mild oxidising agents like Collin's reagent and to carboxylic acids by using Acidified dichromate or alkaline $KMnO_4$

$$\underset{\text{(Primary Alcohol)}}{R{-}CH_2{-}OH} \xrightarrow{\text{Collin's Reagent}} \underset{\text{(Aldehyde)}}{R{-}CHO}$$

$$\underset{\text{(Primary Alcohol)}}{R{-}CH_2{-}OH} \xrightarrow{\text{Acidified Dichromate OR alk. } KMnO_4} \underset{\text{(Carboxylic Acid)}}{R{-}COOH}$$

Secondary alcohols can be oxidised to Ketones using Acidified dichromate or alkaline $KMnO_4$

$$\underset{\text{(Secondary Alcohol)}}{R{-}CH(OH){-}R'} \xrightarrow{\text{Acidified Dichromate OR alk. } KMnO_4} \underset{\text{(Ketone)}}{R{-}CO{-}R'}$$

B. Reduction reactions

When aldehyde and ketones are treated with molecular hydrogen in presence of metallic catalyst like Ni/ Pd/ Pt, they give rise to primary and secondary alcohols respectively.

Organo-metallic Chemistry

Reactions

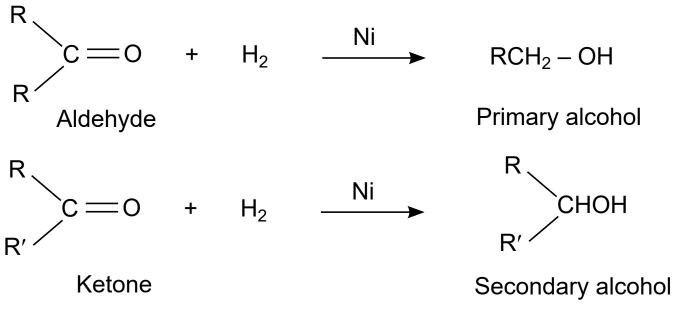


Fig. 7.5: Reduction reactions in aldehyde and ketones

7.6 CYCLIZATION AND RING OPENING

We have observed that organic reactions proceed either change of polarity of solvent or by the presence of radicals but there is a small group of reactions which not influenced by these. They are generally influenced by heat or light. These reactions are known as electro-cyclic reaction where ring opening and closing may take place in single or more molecules.

7.6.1 Cyclization Reaction

During ring closing or cyclization reaction followed through σ bond formation. These reactions are mainly concerned with electronic rearrangements involved in bond breaking and making proceed simultaneously in a one step process.

The transition state is cyclic and the reaction are attended by a high degree of stereo selectivity.

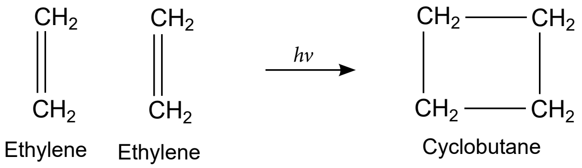
7.6.2 Types of Cyclization Reaction

Cycloaddition Reaction: Reaction in which two unsaturated molecules combine to forms cyclic compound, with π electrons being used to forms new bonds is known as Cycloaddition reaction.

Cycloaddition reaction may again be of two types depending upon the number of π electrons in two components. It is of two types-

1. (2+2) Cycloaddition
2. (4+2) Cycloaddition

1. **(2+2) Cycloaddition:** When both of the reactant have 2π electrons each.
   Example-formation of cyclobutane from ethylene



2. **(4+2) Cycloaddition;** When one of the reactant has 4π electrons and another one of the reactant has 2π electrons. **Diels Alder reaction is a** commonly known reaction of this type**.**

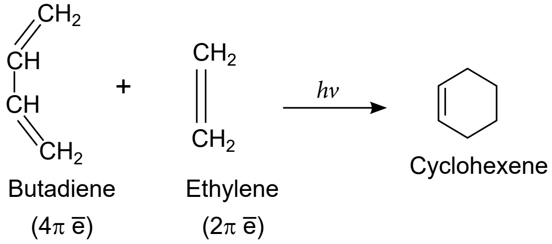


Fig. 7.6: Diels Alder reaction

7.6.3 Ring opening Reaction

An electrocyclic ring-opening reaction is a reaction in which a σ bond of a cyclic reactant is cleaved to form a conjugated product with one more π bond will form.

Example – Formation of 1-3 butadiene by heating of cyclobutene

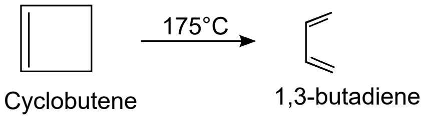


Fig. 7.7: Ring opening Reaction

7.7 SYNTHESIS OF COMMONLY USED DRUG MOLECULES

Synthesis of drug molecules is an intersection discipline of organic chemistry and pharmaceutical chemistry. In more detail we can say it's a study of synthetic organic chemistry, and pharmacology and various other biological specialties. It involved with design and chemical synthesis of drug molecule. Let us discuss few of them in brief-

7.7.1 ASPIRIN

Aspirin is prepared by chemical synthesis from salicylic acid, through acetylation with acetic anhydride.

Chemicals Required – Salicylic acid + Acetic anhydride + Sulphuric acid.

Method - Place 2.0 g of salicylic acid in a 125 mL Erlenmeyer flask. Add 5 mL of acetic anhydride, followed by 5 drops of conc. H_2SO_4 (use a dropper, H_2SO_4 is highly corrosive) and swirl the flask gently until the salicylic acid formed. After completion of reaction recrystallize it for purification.

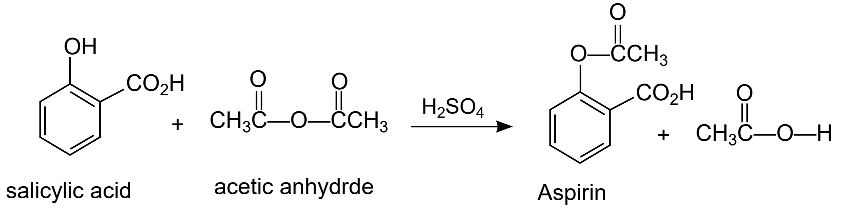


Fig. 7.8: Synthesis of Aspirin

Properties

- The molecular weight of aspirin is 180.16g/mol.
- Aspirin is an oral non-steroidal anti-inflammatory drug.
- It is rapidly absorbed from the stomach and the small intestine.
- Aspirin exhibits analgesic, fever-reducing, and anti-inflammatory action.
- It also reduces aggregation of thrombocytes.

7.7.2 Paracetamol

Paracetamol is made by reacting 4-aminophenol with acetic anhydride.

Chemicals Required – 4-aminophenol + acetic anhydride + sulphuric acid.

Method - Take 6 g of 4-aminophenol and 6.5 mL of acetic anhydride add 3-4 drops of sulphuric acid. Mixed thoroughly in dried and cleaned 100 mL flask. Warm the reaction mixture on water bath with temperature 60°C for about 20-25 min. After completion of reaction pour into ice cold water. The paracetamol is then isolated and purified.

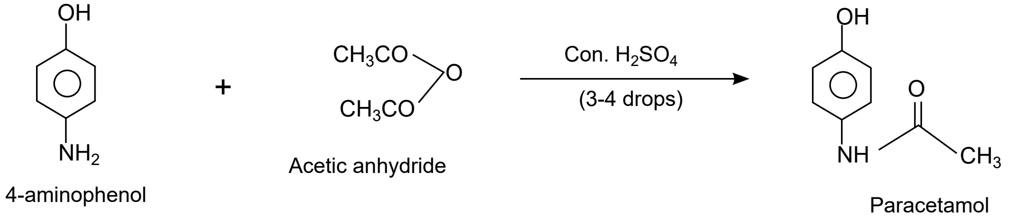


Fig. 7.9: Synthesis of Paracetamol

Properties

- General Formula is $C_8H_9NO_2$
- Molar mass of Paracetamol molecule is151.165 g mol^{-1}
- Paracetamol has analgesic and antipyretic properties.
- Medication of Paracetamol used to treat fever and mild to moderate pain.

7.7.3 IBUPROFEN

Ibubrofen is **synthesized** from the starting materials isobutylbenzene and acetic anhydride through a Friedel-Crafts acylation, carbonyl reduction, chloride substitution, and Grignard reaction.

Chemicals Required – isobutylbenzene + acetic anhydride + hydroiodic acid + phosphorus

Method- It is prepared in 3 steps-

(*i*) Acylation of isobutylbenzol by acetyl chloride to give iso-butylbenzophenone.

(*ii*) Iso-butyl benzophenone is reacted with sodium cyanide to produce oxynitrile.

(*iii*) On reaction of oxynitrile with hydroiodic acid in the presence of phosphorus to give ibuprofen, which subsequently undergoes phases of dehydration, reduction and hydrolysis

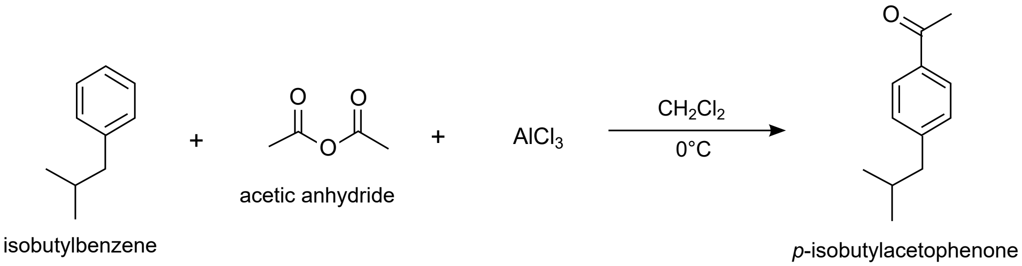


Fig. 7.10: Synthesis of IBUPROFEN

Properties

- Molecular weight of Ibrufen is 206.28 g mol^{-1}
- It works by reducing hormones that cause pain and swelling in the body.
- Effective for relieving headache, dental pain, pain due to menstrual cramps, reducing fever and relieving pain due to minor injuries.

SUMMARY

- **Substitution reaction:** Substitution reaction are those reaction in which an atom, ion, or group of a molecule is replaced by another atom, ion, or group.
- **Addition reaction:** Reaction in which two or more molecules combine to form a larger molecule. Addition Reaction is shown by unsaturated hydrocarbons which contain double or triple bonds.
- **Elimination reaction:** Elimination reaction involves the loss of two atom or groups of atoms from the same or adjacent atoms of a substance leading to the formation of a multiple bond.
- **Oxidation, reduction reaction** -Reaction concerned with the number of carbon-heteroatom bonds in the compound compared to the number of carbon-hydrogen bonds.

- **Cyclization reaction**: During ring closing or cyclization reaction followed through σ bond formation.
- **Ring opening Reaction**- An electrocyclic ring-opening reaction is a reaction in which a σ bond of a cyclic reactant is cleaved to form a conjugated product with one more π bond will form.
- **Synthesis of commonly used Drug molecules** - Aspirin, Paracetamol and ibuprofen.

EXERCISE

SUBJECTIVE QUESTIONS

1. If an atom or group is being replaced by other atoms or group which type of reaction will be it ? Write details of it with suitable example.
2. Define nucleophile and electrophile. What are the role of it in chemical reactions?
3. How any one may identify Substitution Reaction? Write its characteristics, types and examples in details.
4. Differentiate between
   - S_N^1 and S_N^2 Reaction
   - E_1 and E_2 Reaction
   - Addition and Elimination Reaction
5. Define oxidation and reduction reactions in organic reactions. How it is different from general reaction of redox. Justify this statement with suitable example.
6. Write chemical reaction for synthesis of paracetamol along with its medicinal properties.
7. Write short notes on
   - Cyclization reaction
   - Aspirin
   - Ibobrufan

OBJECTIVE QUESTIONS

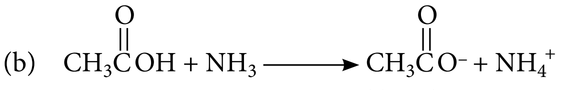
1. Which of the following cannot react as a nucleophile?

   (a) CH_3NH_2
   (b) $(CH_3)_2NH$
   (c) $(CH_3)_3N$
   (d) $(CH_3)_4N^+$ **[Ans. (d)]**

   Feedback : Nucleophile are negatively charged or neutral groups

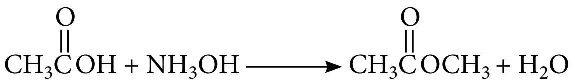
2. Which of the following reactions is an elimination reaction?

   (a) $(CH_3)_3CCl \longrightarrow (CH_3)_2C{=}CH_2 + HCl$

   (b) $CH_3\overset{\overset{\displaystyle O}{\|}}{C}OH + NH_3 \longrightarrow CH_3\overset{\overset{\displaystyle O}{\|}}{C}O^- + NH_4^+$

   (c) $CH_3{-}CH_2{-}CH_2{-}OH \xrightarrow{\text{Mild Acid/Base}} CH_3{-}CH_2{-}COH$

(d) 

$CH_3COOH + NH_3OH \longrightarrow CH_3COOCH_3 + H_2O$ [**Ans. (a)**]

Feedback: Formation of unsaturated center is key feature of elimination reaction.

3. Nitration of benzene is an example of –

(a) Substitution reaction (b) Addition reaction

(c) Elimination reaction (d) Cyclization reaction [**Ans.** (a)]

Feedback: H is being substituted by $-NO_2^+$ ion.

4. Example of chlorine Free radical is –

(a) Cl_2 (b) $^{\cdot}Cl$ (d) Cl [**Ans. (b)**]

Feedback : Rest are molecule, ion or element.

5. **$R—X + KOH \longrightarrow ROH + KX$ is an**

(a) Substitution reaction (b) Elimination reaction

(c) Addition reaction (d) Cyclization reaction [**Ans.** (a)]

Feedback : X^- is replaced by OH^- here

6. Find out oxidation-reduction reactions-

(a) Alcohol to a ketone or aldehyde (b) Anti-Markovnikov reaction

(c) Base catalyzed elimination of HCl from alkyl chloride

(d) Alcohol in acetalisation to an acetal [**Ans. (a)**]

Feedback : Rest are the examples of elimination and addition reactions

7. Raw materials required for ASPIRIN –

(a) 4-aminophenol + acetic anhydride + sulphuric acid

(b) Salicylic acid + Acetic anhydride + Sulphuric acid

(c) isobutylbenzene + acetic anhydride + hydroiodic acid

(d) 4-aminophenol + acetic Acid + Hydrocloric acid [**Ans (b)**]

Feedback : ASPIRIN synthesized with Salicylic acid and Acetic anhydride in presence of catalyst Sulphuric acid.

PRACTICAL

Experiment

(Student to Record the Experiment as per Template given in Annexure – 4)

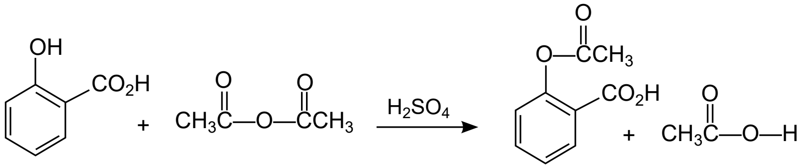
Aim: Synthesis of Aspirin drug

Requirement:

- **Chemicals:** Salicylic acid, acetic anhydride, phosphoric acid

- **Glassware:** Buchner funnel, beaker, flask.

Theory: Aspirin is prepared by chemical synthesis from salicylic acid, through acetylation with acetic anhydride.



Procedure:

1. Weigh out 3.0 g of salicylic acid and place it in a 250 mL Erlenmeyer flask. Add acetic anhydride in the flask.
2. Carefully add 5 to 10 drops of 85% phosphoric acid, a catalyst, to the flask and swirl to mix everything thoroughly. Heat the mixture for about 10 min. and warm upto70-80 oC.
3. Next add 20 mL of distilled water and cool in an ice bath. Filter and dry the product.
4. Filter the solid aspirin through a piece of pre-weighed filter paper using a Buchner funnel and the aspirator. Wash the crystals with 2-3 mL of chilled water. The liquid is mostly water and can be washed down the sink. Allow the air to be drawn through the solid and filter paper for 15 minutes. Be sure to record the filter paper weight in your notebook.

Precaution:

- Don't let the acetic anhydride contact your skin and don't get the vapours in your eyes.
- Be sure to do this in the hood and wear your goggles.

Result: Crude yield, appearance - characteristics of drug.

Discussion: The Experiment, Observations and Result(s) to be discussed while correlating with theory and real life/industrial applications.

Case study: Corona pandemic case study on

- Life cycle of drug
- Relevance of medicine
- High price selling of medicine
- Ethical awareness
- Use of medicines after Expiry dates

Interesting Facts

- The first synthetic drug, **chloral hydrate**, was discovered in 1869 and introduced as a sedative hypnotic; it is still available today in some countries.
- In twentieth century the scientific understanding of polymers and enzymes, which led to the controversial and crucial understanding the petroleum was a biological by-product of life.
- Whether a perfume fragrance comes from a flower or a lab, the molecules we may smell and enjoy are an example of organic chemistry.
- The cosmetics industry is a lucrative sector of organic chemistry. Chemists examine changes in the skin in response to metabolic and environmental factors, formulate products to address skin problems and enhance beauty, and analyse how cosmetics interact with the skin and other products.

SUGGESTED READINGS

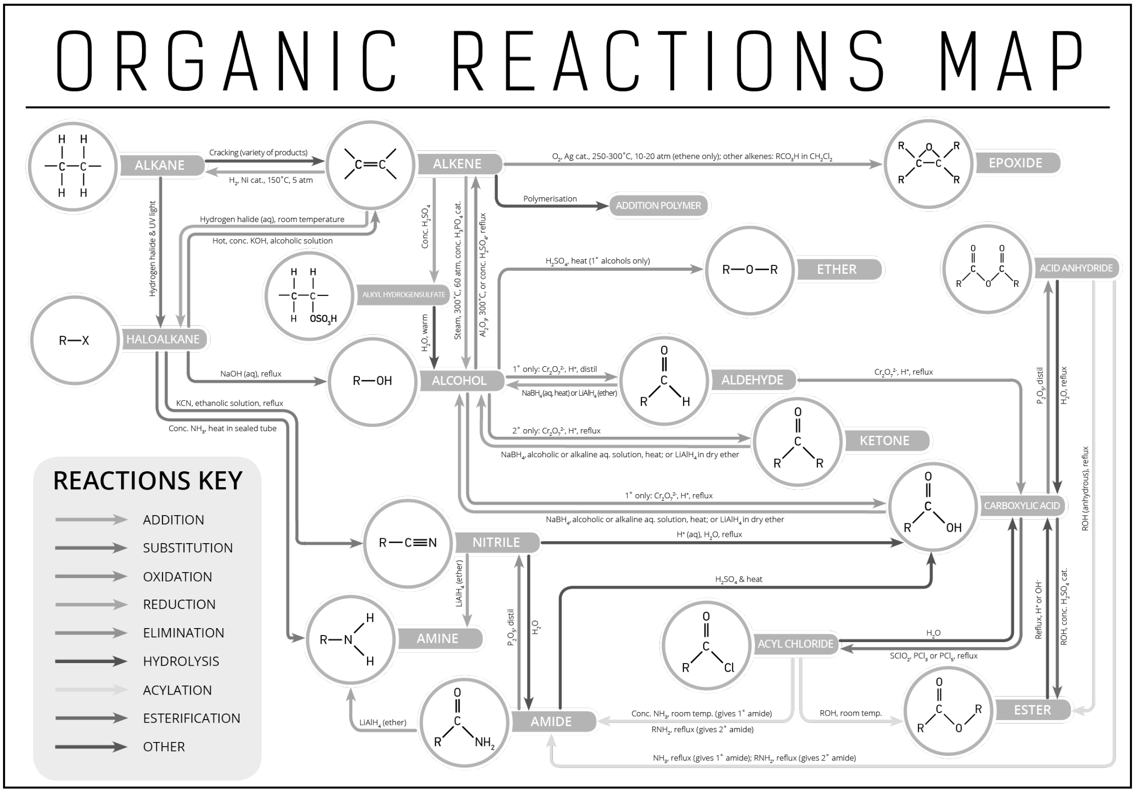
BOOKS

- Organic Chemistry by A. Bahl and B.S. Bahl, S Chand & Company Publications ISBN No. 9789352-531967.
- Organic Chemistry, Reaction and Reagents by O. P. Agrawal GOEL Publishing house ISBN No. 10- 818283483X.
- Organic Chemistry 7th Edition by R.T. Morrison and R. N. Boyd, Pearson Prentice Hall Publications ISBN 978-81317-04813.

E-RESOURCES

- https://www.jiit.ac.in/sites/default/files/VIRTUAL%20LAB%20MANUAL_18Feb.pdf
- https://www.che.iitb.ac.in/research-area/drug-delivery

KNOW MORE



Annexure - 1

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17. https://courses.lumenlearning.com/boundless-chemistry/chapter/coordination-compounds/
18. http://electron6.phys.utk.edu/phys250/modules/module%203/hydrogen_atom.htm
19. http://www.umich.edu/~chem461/QMChap7.pdf
20. http://eguruchela.com/chemistry/learning/Introduction_of_Molecular_orbital.php
    https://www.allaboutcircuits.com/textbook/semiconductors/chpt-2/band-theory-of-solids/
21. https://www.sanfoundry.com/organic-chemistry-questions-answers-hybrid-orbitals/
    https://www.varsitytutors.com/mcat_physical-help/oxidation-number
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24. https://www.chem.tamu.edu/
25. http://www.questionpapers.net.in/chemistry
26. https://www.learninsta.com/
27. https://www.quiz4engineers.online/2020/06/Molecular-Orbital-Theory.html

Annexure - 2

Attainments & Gap Analysis

Attainments of the Program Outcomes will be compiled in the Table below to make a Gap Analysis and work out remedial measures:

Course Outcome	**Attainment of Programme Outcomes (1- Weak Correlation; 2- Medium correlation; 3- Strong Correlation)**											
	PO-1	**PO-2**	**PO-3**	**PO-4**	**PO-5**	**PO-6**	**PO-7**	**PO-8**	**PO-9**	**PO-10**	**PO-11**	**PO-12**
CO-1												
CO-2												
CO-3												
CO-4												
CO-5												

Annexure - 3

Experiments as per AICTE Model Curriculum

Some of the experiments prescribed by AICTE Model Curriculum are included in different units. The experiments, which could not be included in between the units are given below:

General Instructions

- Student to Record the Experiment as per Template given in Annexure – 4.
- Refer to the MSDS data of each chemical being used for the safety and environment friendly approach to conduct the experiment.
- Discussion - The Experiment, Observations and Result(s) to be discussed while correlating with theory and real life/industrial applications.

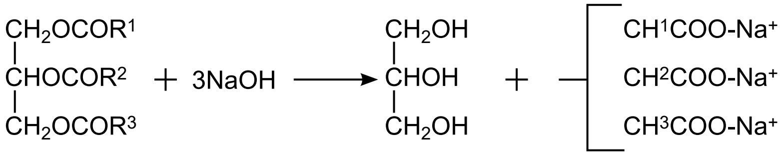
Experiment - 1

Aim: Determination of saponification value of oil.

Requirements:

- **Chemicals:** Standard Hydrochloric acid (N/2), Base solution, Phenolphthalein
- **Glassware:** Water condenser, water bath, conical flask or round bottom flask, Burette

Theory: The saponification value of an oil is determined by refluxing a known quantity of the sample with a known excess of standard NaOH/KOH / Base solution and determining the alkali consumed by titrating the unreacted alkali.



$$\begin{array}{l} CH_2OCOR^1 \\ | \\ CHOCOR^2 \\ | \\ CH_2OCOR^3 \end{array} + 3NaOH \longrightarrow \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + \left[\begin{array}{l} CH^1COO\text{-}Na^+ \\ CH^2COO\text{-}Na^+ \\ CH^3COO\text{-}Na^+ \end{array} \right.$$

A triglyceride + sodium hydroxide → glycerol + sodium carboxylates

Where R^1, R^2 and R^3 are long chain alkyl groups. The unreacted NaOH is titrated back with standard acid using phenolphthalein as indicator.

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

$$\text{Saponification Value} = = \frac{\text{Volume in mL of } \frac{N}{2} \text{ NaoH consumed}}{\text{Wt. of oil taken in grams}} \times 100$$

Procedure

1. Weigh accurately about 5 g of the oil sample and transfer it into a 250 or 500 mL flask.
2. Add base solution and alcohol or ethyl methyl ketone as solvent into the flask.
3. Add the same amount of solvent and alcoholic base to another flask for blank determination.
4. Fit the two flasks with water condensers and reflux the contents on a water bath for a minimum period of 1 hour.

5. Cool the contents slightly, disconnect the condenser and rinse it with small amount of distilled water in to the flask.
6. Add 10-12 drops of phenolphthalein indicator and titrate the contents of the flask with a standard solution of HCl (N/2) until the pink colour has just disappeared.

Precautions

1. The glass apparatus required for the experiment should be cleaned properly before the start of the experiment.
2. The alcoholic solution of base should be freshly prepared.
3. The blank determination and the test with the oil sample should be performed under the similar conditions to get the accurate result.

Observations and Calculations

- Weight of the sample taken = X g
- Volume of alcoholic NaOH added to both the flasks = 50 mL
- Volume of N/2 HCl used in the sample determination = V_1 mL
- Volume of N/2 HCl used in the blank determination = V_2 mL

Result: Saponification Value and correlation with structure of oil

Experiment - 2

Aim: Synthesis of a polymer – Bakelite as an Example

Requirements:

- **Chemicals:** Glacial acetic acid ,40% Formaldehyde solution, Phenol ,Conc. HCl .
- **Glassware:** Glass rod, Beaker, Conical flask, Glass funnel, Filter paper.

Theory: Bakelite thermosetting polymer are obtained by reacting phenol C_6H_5OH and Formaldehyde CH_2O. Formaldehyde forms $-CH_2-$ bridges between two phenol molecules, producing chains. Linear chains are obtained when the reaction ratio is 1:1.

The first step is preparation of a low molecular weight, generally linear pre-polymer. Adding more formaldehyde, the polymer cross-links and hardens, becoming a rigid, non-deformable mass.

Procedure:

1. Place 5 mL of glacial acetic acid and 2.5 mL of 40% formaldehyde solution in a 500 mL beaker and add 2 g of phenol.
2. Wrap a cloth or towel loosely around the beaker.
3. Pass dry HCl (or less preferably a few mL of con. HCl) in to the mixture carefully.
4. Within 5 min, large mass of pink plastic is formed. (If conc. HCl is used slight heating is required).
5. The residue obtained is washed several times with distilled water, and filtered product dried and yield is calculated.

Precaution:

1. The reaction is sometimes vigorous and it is better to be a few feet away from the beaker while adding the HCl and until the reaction is complete.
2. The experiment should be preferably carried out in fume cupboard.

Result: Crude yield, appearance- characteristics of polymers

Experiment - 3

Aim: Determination of the partition coefficient of a substance between two immiscible liquids.

Requirements:

- **Chemicals :** Hypo Solutions (N/10 and N/100), Saturated solution of Iodine in CCl_4 Starch indicator solution
- **Glassware :** Shaker machine, Four glass- stoppered reagent bottles of about 250 mL capacity, Separating funnel.

Theory: Iodine distributes itself in two miscible solvents as water and carbon tetra chloride and same molecular state of I_2 in both of these solvents.

If C_1 and C_2 are concentrations of Iodine in water and carbon tetra chloride layers in contact with each other and forming the heterogeneous equilibrium, then the ratio of these concentrations ; i.e. $= \frac{C_1}{C_2}$ would be constant at fixed temperature.

$$K = \text{Distribution or partition coefficient } = \frac{C_1}{C_2} = \frac{\text{Concentration of } l_2 \text{ in water layer}}{\text{Concentration of } l_2 \text{ in } CCl_4 \text{ layer}}$$

Procedure

1. Take clean and dry stoppered reagent bottles and label them as 1, 2, 3 and 4. Fill 10,20,30 and 40 mL of the solution in different glass bottles.
2. Add 40, 30, 20 and 10 mL of CCl_4 in each bottle respectively. Then add 50 mL of distilled water in each bottle.
3. Stopper these bottles and shake each bottle vigorously for about 20 minutes.
4. Allow to stand till two separated layers are formed distinctly.
5. Pour the content of each bottle separately in to a separating funnel and collect carbon tetra chloride and water layer of each bottle in separate beaker.
6. Pipette out CCl_4 layer from the separated layers. Add about 1 g of KI, 5 drops of starch solution and titrate against N/10 hypo solution.
7. Disappearance of the blue colour marks the end point. Repeat to get two concordant readings. Repeat this process with CCl_4 layer of other bottles in the same way.
8. Pipette out aqueous layer into titration flask and titrate against N/100 hypo solution as given in step 7.
9. Carry similar titration for upper and lower layers respectively in other bottles.

Precautions:

1. Do not use rubber stopper as Iodine solution in CCl_4 can react with it.
2. The reagent bottles should be thoroughly cleaned and dried.
3. The stopper are kept properly pressed during shaking of bottles
4. Loosen the stopper after shaking for releasing the pressure if any developed during the process of shaking the contents in the bottles.
5. Use only the fresh starch solution as indicator in hypo solutions.

Observations & Calculations:

Room temperature = °C

Vol. of water layer used in each titration = mL

Vol. of CCl_4 layer used in each titration = mL

S. No.	Percentage of Iodine (V/V)	Titration with water layer				Titration with CCl_4 layer			
		Initial Reading	Final Reading	Vol. of Hypo Solution used V_1 mL	Normality of Hypo Solution	Initial Reading	Final Reading	Vol. of Hypo Solution used V_1 mL	Normality of Hypo Solution
1	10%				N/100				N/10
2	20%				N/100				N/10
3	30%				N/100				N/10
4	40%				N/100				N/10

$$\text{Concentration of water layer} = \frac{\text{Normality of hypo used with water layer X } V_1}{\text{Volume of water layer used}} \text{ g eq. L}^{-1}$$

$$\text{Concentration of layer} = \frac{\text{Normality of hypo used with } CCl_4 \text{ layer X } V_2}{\text{Volume of } CCl_4 \text{ layer used}} \text{ g eq. L}^{-1}$$

Result: The partition coefficient of Iodine between water and carbon tetra chloride is ……at ……°C.

Experiment - 4

Aim: To determine the value of rate - constant (K) for the hydrolysis of ethyl acetate catalysed by hydrochloric acid.

Requirements:

- **Chemicals:** NaOH Solutions (N/10), HCl ,Ethyl acetate.
- **Glassware:** Conical flasks - Six of 50 mL and one 250 mL, Cork, Stop watch.

Theory: The hydrolysis of ethyl acetate catalysed by dilute HCl is a reaction of first order as the concentration of water is in large excess and does not change significantly during the progress of the reaction. It is thus pseudo unimolecular reaction.

$$CH_3COOC_2H_5 + H_2O \longrightarrow CH_3COOH + C_2H_5OH$$

Formula used:

$$K = \frac{2.303}{t} \log_{10} \frac{V_\infty - V_o}{V_\infty - V_t}$$

The value of K is determined for the different sets of values corresponding to different intervals of time.

Procedure:

(i) Take HCl in a clean dry 250 mL conical flask, cork and set it in a water – bath to maintain temperature and add half –test –tube of ethyl acetate in conical flask .

(ii) In the mean time, fit the burette properly and fill it with 0.1 N NaOH solution. Also add about 15 g of the ice in each of the six 50 mL conical flask.

(iii) Pipette out 5 mL of the ester from the conical flask and add it to the flask containing 100 mL of 0.5 N HCl.

(iv) Shake the contents, pipette out 10 mL of the reaction mixture and transfer it at once to first conical flask containing ice or chilled water. Titrate this against 0.1 N NaOH solution taken in the burette and adding a drop of phenolphthalein as indicator to the titration flask. Appearance of light pink colour, marks the end point.

(V) Also note the time of the draining out 10 mL of the mixture solution into the titration flask in the above case and if this is 10 seconds, then in the subsequent estimations, the mixture solution should be added to the chilled water or ice 5 second earlier than the time interval of 10 minutes.

(vi) Pipette out 10 mL of mixture solution and add it to the conical flask containing ice/chilled water after 10 minutes as suggested above. Titrate against 0.1 N NaOH. This gives V_t after 10 minutes.

(vii) Repeat the above procedure after every 10 minutes so as to get six readings. Pipette out 10 mL of the reaction mixture and titrate against 0.1 N NaOH.

Precautions:

(1) During the progress of the hydrolysis of ester, the conical flask should be kept stoppered after pipetting out the solution of the reaction mixture.

(2) Sufficient amount of pounded ice or chilled water should be taken in the flask

Observations and Calculations

$$K = \frac{2.303}{t} \log \frac{a}{a-x} = \frac{V_\infty - V_o}{V_\infty - V_t} \text{ min}^{-1}$$

When time = 10 min $^{-1}$

V_o, V_t, and V_∞ are the volumes of NaOH solution used for the titration of same volume of the reaction mixture after times 0, t and ∞ respectively.

Similarly, calculate the value of rate constant K at other interval of time. The mean value of K obtained from the different sets of the reading gives the value of the rate constant, K.

Result: Since the values of K are …….the hydrolysis of ethyl acetate catalysed by acid is a pseudo first order reaction.

Experiment - 5

Aim: Study of oxidation of iodide ions by hydrogen peroxide as an iodine clock reaction.

Requirements:

- **Apparatus:** Burette, 5 mL pipette, 250 mL measuring jar, 500 mL conical flask, stop watch.
- **Chemicals:** 0.1M H_2O_2, 1.0M KI, 2M H_2SO_4, 0.025M hypo solution, starch solution.

Theory: The reaction can be represented as

$H_2O_2 + 2H^+ + 2I^- \xrightarrow{\qquad} I_2 + 2H_2O$ (Main Reaction)

$I_2 + 2S_2O_3^- \xrightarrow{\qquad} 2I^- + S_4O_6$ (Monitor Reaction)

I_2 + starch $\xrightarrow{\qquad}$ blue colour

Procedure:

1. Place about 150mL of distilled water in a 500mL conical flask, and add about 20mL of 1M KI, 10mL of 2M H_2SO_4 and 1mL of starch solution into it.
2. Add from the burette exactly 5mL 0.025M hypo solution. Keep it in a water bath to attain room temperature. Keep 0.1M H_2O_2 in another water bath.
3. Add 5mL of 0.1M H_2O_2 solution with a pipette and start the stop watch half way through the addition. Shake the solution and stand it in water bath. Note the time for appearance of blue colour.
4. Repeat this procedure for 5 or 6 additions of hypo solution. Calculate the values of concentrations hydrogen peroxide (a-x) at the measured time intervals taking into account increase in volume of solution is due to additions of hypo solution.
5. Concentration of H^+ ions and iodide ions also change but their initial values being high the proportionate change may be small and can be neglected.
6. Initial concentration of hydrogen peroxide can be worked out in terms of equivalent volume of hypo solution. For this purpose measure out, 10mL of hydrogen peroxide solution, add carefully drop wise 10 mL of concentrated sulphuric acid and 8 g of KI dissolved in minimum quantity of water. I_2 liberated is titrated against 0.025M hypo solution and tabulate the results.

Observation and Calculation

Volume of hypo added corresponding to time t

$[H_2O_2]_0 \ \alpha \ V\infty [V_t = 0]$

$[H_2O_2]_t \ \alpha \ V\infty - V_t$

Graph: Plot a graph by taking V_t Vs time a parabolic curve is obtained and slopes of the tangents to this curve at various times t represent the rate of reaction at these moments plot another graph log ($V\infty - V_t$) Vs time. A straight line is obtained and the slope of this will be equal to the order of reaction.

Result: change of colour …….., rate at which reactions take place**…..**

Experiment - 6

Aim: Determination of the molal freezing point depression constant, K_f.

Requirement: Non-ionisable liquid, Ex. Acetone, benzene or cyclohexane.

Theory: Several important properties of solutions depend on the number of solute particles in the solution and not on the nature of the solute particles. These properties are called Colligative Properties. Freezing point depression is an example of it. The addition of a solute to a solvent will decrease the freezing point (temperature) of the solvent.

The decrease in freezing point, ΔT_f, when a nonvolatile, nonionizing solute is dissolved in a solvent is proportional to the molal concentration, m, of the solute present in the solution.

$\Delta T_f \ \alpha \ m$

$\Delta T_f = K_f m$

Procedure:

a. Calculate actual molalities of the given solutions using the mass measurements and the molar mass of the solute.
b. Plot $-\Delta T_f$ against molality ($-\Delta T_f$ is a positive quantity because ΔT_f is negative) for four data points (concentrations of 0, ~0.5, ~0.10, and ~0.15 mol kg^{-1}).

c. Fit the best straight line to four points and determine the equation for the line with the proper units.
d. Compare this with equation and report experimentally-determined K_f for liquid.
e. Compare the value with the reported literature values.

Observation and Calculation:

Notice that the freezing point of a substance or a mixture is the temperature at which the solid and liquid phases are in equilibrium at one atm of pressure.

K_f is a constant for a given solvent. K_f is called the molal freezing point depression constant and represents how many degrees the freezing point of the solvent will change when 1.00 mole of a non-volatile nonionizing solute dissolves in one kilogram of solvent.

Result: Molal freezing point depression constant is …..

Annexure - 4

Suggestive Outlines to Report Experiments

- Aim
- Relevance
- Requirements for Experiment
- Procedure, Observations and Inference [Step-wise and using minimal quantities of chemicals (0.5 g or less)]

Step No.	Procedure	Observation	Inference
1.			
2.			
3.			

- Video/animation
- Observations & Calculations
- Conclusions
- Validation of the topics in Experiments with Theory
- Result & Discussion
- Use of ICT (Excel for graph plotting, Literature survey through internet, etc.)
- Viva-Voce Questions (To be discussed)
- Environment Friendly Approach: 3 R's –
  - o What all can you reuse?
  - o How can you reduce the waste?
  - o How can you recycle the waste?
  - o Any other..

Lab Safety

Safety symbols of the chemicals being used, first aid measures in case of accidents.

e-Resource for Lab Safety

https://myeclass.academy/course/view.php?id=2536
https://www.youtube.com/watch?v=gi3DeFY0cfw
https://ehs.ucsc.edu/programs/research-safety/safe-lab-practices.html
https://www.youtube.com/watch?v=8queMM7VVfw

Appendices

Rubrics for Assessments

A: Indicative guidelines for evaluation of assessments based on theory :

Different assessment may be given to the students wherein each question is tagged to different levels of difficulties and Revised Bloom's Taxonomy.

Revised Bloom's Taxonomy

Category I Questions	Category II Questions Higher Order Thinking Skills
Bloom's Level 1: Remember Bloom's Level 2: Understand Bloom's Level 3: Apply	Bloom's Level 4: Analyse Bloom's Level 5: Evaluate Bloom's Level 6: Create

Difficulty Levels: LOD1: Easy, LOD2: Moderate, LOD3: Difficult

Use of LMS or other ICT based assessment tools is encouraged for continuous assessment with the help of different types of objective and subjective questions

B: Indicative guidelines for evaluation of practical (as per AICTE Curriculum), may be modified as applicable to different practical.

Criteria and Level	Developing	Competent	Proficient
Truthfulness in recording of observations			
Keen observer			
Curiosity			
Viva-Voce			
Lab Safety and discipline			
Use of ICT			
Reporting / Writing of Practical			
Accuracy of Result			
Interpretation and analysis			
Environmental friendly practices			
Any Other:			

C: Indicative guidelines for evaluation of group presentation for new practical/ projects/ activities:

Criteria and Level	Developing	Competent	Proficient
Content			
Research/Survey			
Use of latest Technology			
Stays on Topic			
Preparedness			
Confidence of Presentation			
ICT usage including ppt making skill			
Time management			
Group Efforts			
Individual Efforts			
Truthfulness in recording of observations			
Curiosity			
Any Other			