DIRECTORATE OF DISTANCE & CONTINUING EDUCATION

MANONMANIAM SUNDARANAR UNIVERSITY

TIRUNELVELI- 627 012

OPEN AND DISTANCE LEARNING (ODL) PROGRAMMES

(FOR THOSE WHO JOINED THE PROGRAMMES FROM THE ACADEMIC YEAR 2023–2024)

B. Sc. Chemistry Course material

Foundation Course

JFCH11 Foundation Course in Chemistry

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Foundation Course

Course Code JFCH11 **Foundation Course in Chemistry**

Unit I

Structure of atom and periodic classification of Elements and properties

Atom structure-Fundamental particles-Atomic mass- Atomic number – Isotopes –Isobars – Isotones – Orbitals-Quantum number and their significance. Shapes of s,p and d orbitals-Rules governing electronic configuration in various its atomic orbitals.

Periodic table-periodic laws (Mendeleev and Mosley)- Classification of elements into s,p, d and f-blocks .Metals-Non metals-Periodic properties-Concept,Variation and factors affecting various periodic properties-Inert pair effect.

Unit II

Chemical Bonding

Definition- Types of chemical bond-Ionic bond- Ion polarization - Dipole moment and Percentage of ionic character-Covalent bond-Definition –Postulates of Valence bond theory and Concept of hybridization (sp, sp^2 ,sp^3 , sp^3d, sp^3d^2, dsp^2, d^2sp^3) –Magnetic properties – Paramagnetic – Diamagnetic-Ferromagnetic. Co-ordinate covalent bond-Definition – Examples-Co-ordination compounds (basic concepts only).

Unit III

Nomenclature and Isomerism in Organic compounds

Carbon compounds- Uniqueness of carbons- Classification of hydrocarbons - IUPAC Nomenclature of Organic compounds

Isomerism: Structural and Stereoisomerism

Structural Isomerism: Chain isomerism, Functional isomerism, Positional isomerism and Meta isomerism.

Stereoisomerism: Geometrical and Optical isomerism-Chiral molecule- Enantiomers-Diastereomers- Meso compounds-Racemic mixture.

Unit IV

States of Matter

Gaseous state: Kinetic theory of gases- Ideal and Non-ideal gases- Ideal gas equation-Deviation of ideal gas from ideal behavior -vander Waal's equation and Liquification of gases.

Liquids : Intermolecularforces, Vapour pressure and Boiling point of liquid - Surface tension – Viscosity- Factors affecting surface tension and viscosity.

Solids: Definition - Characteristics of solids- Amorphous and Crystalline solids - Space lattice and unit cells - Close packed structure of solids-Radius ratio rule.

Unit V

Introduction to Spectroscopy

Electromagnetic radiation- General characteristics of Wave – Wavelength – Frequency – Amplitude – Wave number - Electromagnetic spectrum- Absorption and Emission spectrum-Quantization of Energy level - Selection rule - Intensity of the Spectral lines –Width of Spectral lines. Types of spectroscopy: Microwave spectroscopy, Infrared spectroscopy, UV-Visible spectroscopy, Nuclear Magnetic Resonance spectroscopy, Electron spin resonance spectroscopy.

Recommended Text

1.B.R Puri, L.R.Sharma, K.C. Kalia, Principles of Inorganic chemistry, Milestone Publishers and Distributors, New Delhi, 2012.

2. B.R. Puri and L.R.Sharma, 38th edition, Vishal Publishing company, Jalendar 2002.

3. K.S, Tewari, S.N. Mehrothra and N.K.Vishnoi, Text book of Organic Chemistry, 2nd edition Vikas publishing House, New Delhi, 1998.

Recommended Books

1. R.D. Madan, Sathya Prakash, Mordern Inorganic chemistry 2nd edition, S.Chand and company, New Delhi, 2003.

2. B.S.Bhal, Arun Bhal, Advanced Organic chemistry, 3rd edition, S.Chand and company, New Delhi, 2003.

3. U.N.Dash, O.P.Dharmarha, P.L.Soni, Textbook of Physical Chemistry, Sultan Chand & sons, New Delhi, 2016.

4. Y.R.Sharma Organic spectroscopy Principles and Chemical applications, S.Chand&Company PVT Ltd ,2002.

5. C.N.Banwell, Fundamentals of spectroscopy Tata McGraw Hill, 1983.

UNIT I - STRUCTURE OF ATOMS AND PERIODIC CLASSIFICATION OF ELEMENTS AND PROPERTIES

Atomic structure is the structure of an atom that consists of a nucleus at the center containing neutrons and protons, while electrons are revolving around the nucleus. As atoms are made up of a very tiny, positively charged nucleus that is surrounded by a cloud of negatively charged electrons. The earliest concept of atoms was given by Indian philosopher Maharshi Kanad who proposed that matter is made up of very small indestructible particles called 'Parmanu'. A Greek philosopher named Democritus also initially claimed that matter is formed of atoms, and is credited with developing the concepts of atomic structure and quantum mechanics. Later in the 1800s, John Dalton a British Scientist put out the first atomic structure scientific theory.

Atomic Models

Many scientists used atomic models to understand the structure of the atom in the early centuries. Each of these models had advantages and disadvantages of its own and played a significant role in the development of the modern atomic model. Scientists like John Dalton, J.J. Thomson, Ernest Rutherford, and Niels Bohr made the most noteworthy contributions to science.

This section of the article discusses the following theories regarding atomic structure:

- Dalton's Atomic Theory
- Thomson's Atomic Model
- Rutherford's Atomic Model
- Bohr's Atomic Model
- Quantum Mechanical Model

Postulates of Dalton's Atomic Theory

- *Every matter that exists is made of atoms.*
- *Atoms are indivisible.*
- *A particular element has only one type of atom in it.*
- *Atoms of different elements differ in size and mass.*
- *An atom has a constant mass that varies for every element.*
- *During a chemical reaction, atoms undergo rearrangement.*
- *Atoms can neither be created nor destroyed but can only be transformed from one form to another.*

The existence of atoms has been proposed since the time of early Indian and Greek philosophers (400 B.C.) who were of the view that atoms are the fundamental building blocks of matter. According to them, the continued subdivisions of matter would ultimately yield atoms which would not be further divisible. The word 'atom' has been derived from the Greek word 'a-tomio' which means 'uncutable' or 'non-divisible'. These earlier ideas were mere speculations and there was no way to test them experimentally. These ideas remained dormant for a very long time and were revived again by scientists in the nineteenth century. The atomic theory of matter was first proposed on a firm scientific basis by John Dalton, a British school teacher in 1808. His theory, called Dalton's atomic theory, regarded the atom as the ultimate particle of matter (Unit 1). In this unit we start with the experimental observations made by scientists towards the end of nineteenth and beginning of twentieth century. These established that atoms can be further divided into subatomic particles, i.e., electrons, protons and neutrons— a concept very different from that of Dalton. The major problems before the scientists at that time were:

- to account for the stability of atom after the discovery of sub-atomic particles,
- to compare the behaviour of one element from other in terms of both physical and chemical properties,

to explain the formation of different kinds of molecules by the combination of different atoms and,

- to understand the origin and nature of the characteristics of electromagnetic radiation absorbed or emitted by atoms.

2.1 SUB-ATOMIC PARTICLES

Dalton's atomic theory was able to explain the law of conservation of mass, law of constant composition and law of multiple proportion very successfully. However, it failed to explain the results of many experiments, for example, it was known that substances like glass or ebonite when rubbed with silk or fur generate electricity. Many different kinds of sub-atomic particles were discovered in the twentieth century. However, in this section we will talk about only two particles, namely electron and proton. Discovery of Electron In 1830, Michael Faraday showed that if electricity is passed through a solution of an electrolyte, chemical reactions occurred at the electrodes, which resulted in the liberation and deposition of matter at the electrodes.

He formulated certain laws which you will study in class XII. These results suggested the particulate nature of electricity. An insight into the structure of atom was obtained from the experiments on electrical discharge through gases. Before we discuss these results we need to keep in mind a basic rule regarding the behaviour of charged particles : "Like charges repel each other and unlike charges attract each other". In mid 1850s many scientists mainly Faraday began to study electrical discharge in partially evacuated tubes, known as cathode ray discharge tubes. A cathode ray tube is made of glass containing two thin pieces of metal, called electrodes, sealed in it. The electrical discharge through the gases could be observed only at very low pressures and at very high voltages. The pressure of different gases could be adjusted by evacuation. When sufficiently high voltage is applied across the electrodes, current starts flowing through a stream of particles moving in the tube from the negative electrode (cathode) to the positive electrode (anode). These were called cathode rays or cathode ray particles. The flow of current from cathode to anode was further checked by making a hole in the anode and coating the tube behind anode with phosphorescent material zinc sulphide. When these rays, after passing through anode, strike the zinc sulphide coating, a bright spot on the coating is developed(same thing happens in a television set) . A cathode ray discharge tube .A cathode ray discharge tube with perforated anode The results of these experiments are summarised below.

(i) The cathode rays start from cathode and move towards the anode.

(ii) (ii) These rays themselves are not visible but their behaviour can be observed with the help of certain kind of materials (fluorescent or phosphorescent) which glow when hit by them. Television picture tubes are cathode ray tubes and television pictures result due to fluorescence on the television screen coated with certain fluorescent or phosphorescent materials.

Charge to Mass Ratio of Electron

In 1897, British physicist J.J. Thomson measured the ratio of electrical charge (e) to the mass of electron (me) by using cathode ray tube and applying electrical and magnetic field perpendicular to each other as well as to the path of electrons (Fig. 2.2). Thomson argued that the amount of deviation of the particles from their path in the presence of electrical or magnetic field depends upon:

(i) the magnitude of the negative charge on the particle, greater the magnitude of the charge on the particle, greater is the interaction with the electric or magnetic field and thus greater is the deflection. Fig. 2.2 The apparatus to determine the charge to the mass ratio of electron

(ii) (ii) the mass of the particle — lighter the particle, greater the deflection.

(iii) (iii) the strength of the electrical or magnetic field — the deflection of electrons from its original path increases with the increase in the voltage across the electrodes, or the strength of the magnetic field. When only electric field is applied, the electrons deviate from their path and hit the cathode ray tube at point A. Similarly when only magnetic field is applied, electron strikes the cathode ray tube at point C. By carefully balancing the electrical and magnetic field strength, it is possible to bring back the electron to the path followed as in the absence of electric or magnetic field and they hit the screen at point B. By carrying out accurate measurements on the amount of deflections observed by the electrons on the electric field strength or magnetic field strength, Thomson was able to determine the value of e/me as: e/m = 1.758820 × 1011 C kg–1 Where me is the mass of the electron in kg and e is the magnitude of the charge on the electron in coulomb (C). Since electrons are negatively charged, the charge of the electron.

Atomic orbitals

which are mathematical functions, describe the wave behavior of electrons (or electron pairs) in an atom. Atomic orbitals have different shapes according to their type. The different shapes of atomic orbitals describe that there is either the highest or zero probability of finding an electron around the nucleus in some directions. There are four types of orbitals, each with a different shape and represented by the letters s, p, d, and f. The s and p orbitals are taken into account because they are the most abundant in chemical and biological chemistry. An **s-orbital** has a spherical nucleus in the center, a **p-orbital** is dumbbell-shaped, and four of the five **d orbitals** are cloverleaf shaped. The fifth d orbital is fashioned like a long dumbbell with a doughnut in the center. The orbitals of an atom are organized into layers or electron shells.

Orbital Wave Function

The quantum atomic model predicts that an atom can have a huge variety of orbitals. These orbitals can be grouped according to their size, geometry, or inclination. A reduced orbital size increases the probability of obtaining an electron close to the nucleus. The mathematical function used to represent an electron's coordinates is called the **orbital wave function**. The probability of discovering an electron is represented by the square of the orbital wave function.

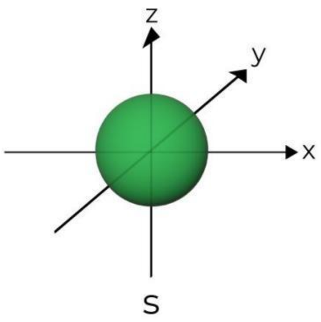
Shapes of Atomic Orbitals

The atomic orbitals' shapes vary. That is to say, the probability distributions of the electrons they describe surrounding the nucleus are different. The fact that the electrons in different orbitals are likely to be located in different areas around the parent nucleus and hence experience the latter's attraction with varied strengths is one of the reasons why orbitals range in energy. It is astonishing that all orbitals in a given shell of the hydrogen atom have the same energy while having varied forms. This is due to the elimination of various energy-related contributions.

Shape of s-orbital

- The s orbital boundary surface diagram resembles a sphere with the nucleus at its center, which can be shown in two dimensions as a circle.

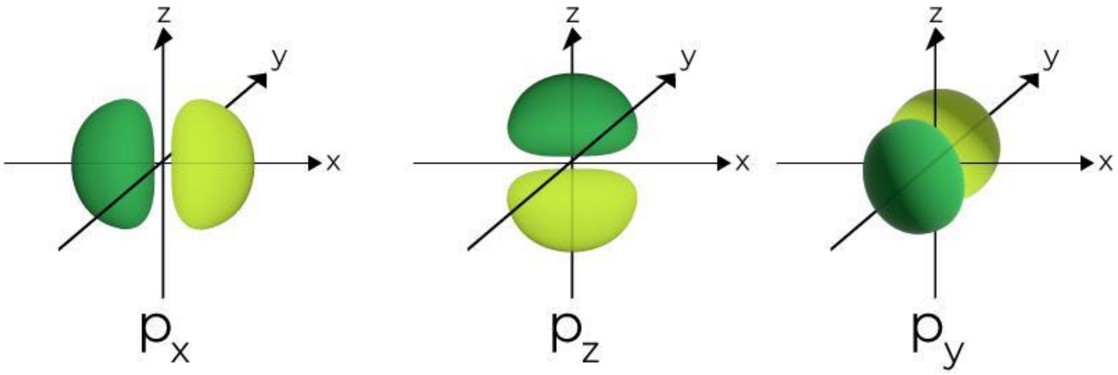
- s-orbitals are spherically symmetric, which means that the probability of finding an electron at a given distance is the same in all directions.
- The size of the s orbital is likewise shown to increase as the value of the primary quantum number (n) increases; hence, 4s > 3s > 2s > 1s.
- The nodal point is a location where there is no chance of locating the electron. Nodes are classified into two types: radial nodes and angular nodes. The distance from the nucleus is calculated by the radial nodes, while the orientation is determined by the angular nodes.



Shape of s-orbital

Shape of p-Orbital

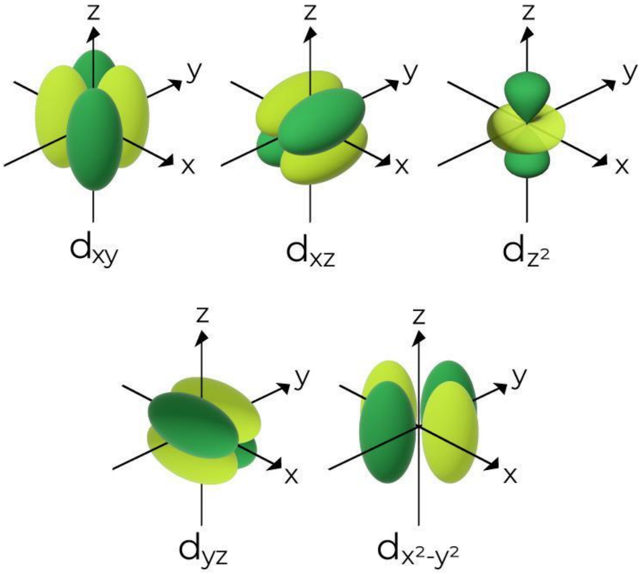
- The p orbitals are formed like dumbbells.
- The p orbital node is located at the nucleus's center.
- Because of the presence of three orbitals, the p orbital can occupy a maximum of six electrons.
- Each p orbital is made up of two parts known as lobes that are located on either side of the plane that runs across the nucleus.
- Each p orbital has parts known as lobes on either side of the plane that runs across the nucleus. At the plane where the two lobes intersect, the likelihood of finding an electron is nil.
- The three orbitals are known as degenerate orbitals because they have the same size, shape, and energy.
- The sole difference between the orbitals is the orientation of the lobes. Because the lobes are orientated along the x, y, or z-axis, they are given the names 2_{px}, 2_{py}, and 2_{pz}. The formula n –2 is used to calculate the number of nodes.
- Similarly to s orbitals, the size and energy of p orbitals rise as the primary quantum number increases (4p > 3p > 2p).



Shape of p-orbital

Shape of d-Orbital

- For d orbitals, the magnetic orbital quantum number is given as (-2,-1,0, 1,2). As a result, we can claim there are five d-orbitals.
- These orbitals are denoted by the symbols d_{xy}, d_{yz}, d_{xz}, $d_{x}{}^{2}–y^{2}$, and $d_{z}{}^{2}$.
- The forms of the first four d orbitals are similar to each other, which differs from the $d_{z}{}^{2}$ orbital, but the energy of all five d orbitals is the same.

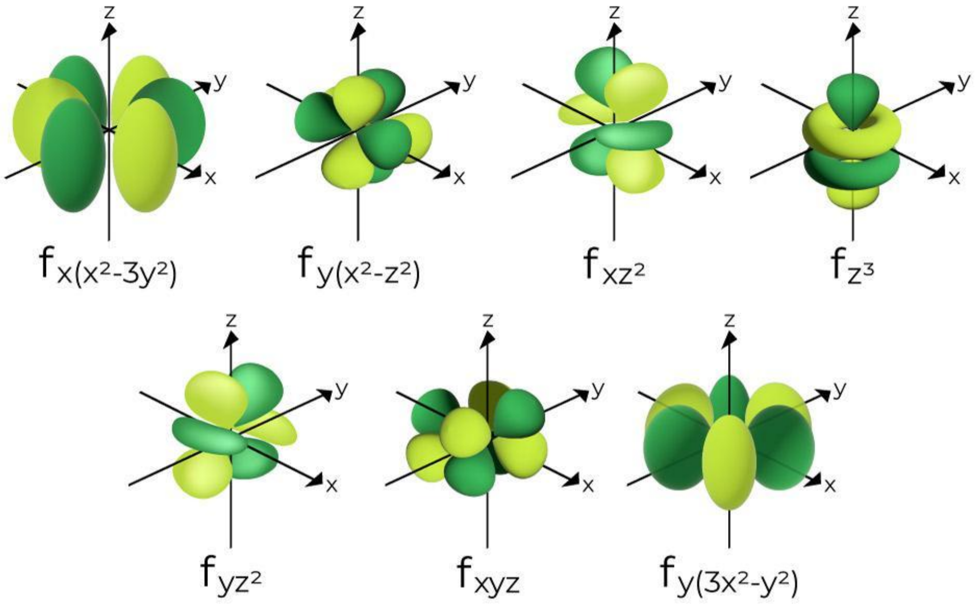


Shape of d-orbital

Shape of f-Orbital

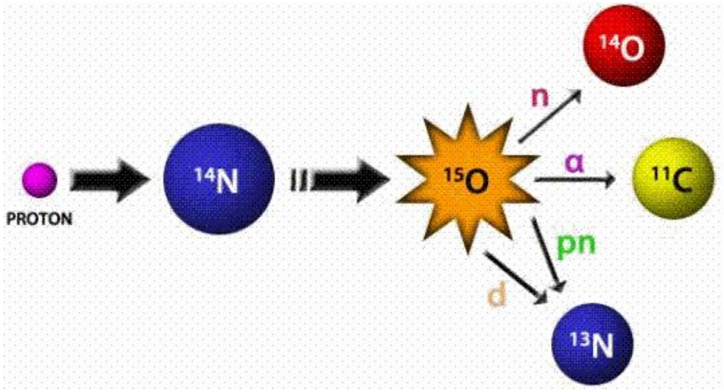
- The form of the f orbital is dispersed. Because the value of l=3 for the f orbital, the minimal value of the primary quantum number n is 4.
- The equivalent ml values for the f orbital are (-3,–2, –1, 0, +1, +2, +3).

- As a result, there are seven f orbitals for l = 3.



Shape of f-orbital

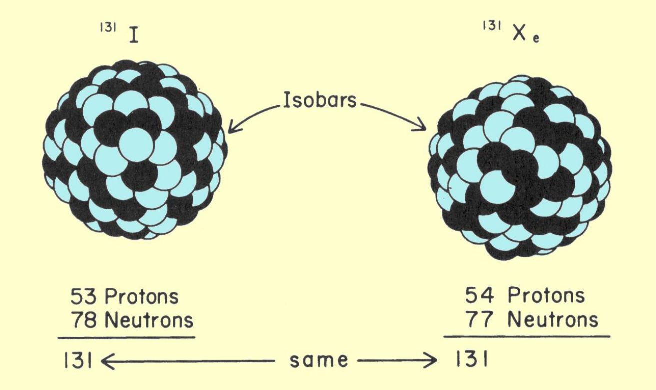
Isotopes are atoms having same atomic number(Protons) but different mass number.i.e., the number of neutrons are different. Hence the atomic weights of the isotopes of an element are different. Isotopes of the same element have the same chemical properties because they have the same number and arrangement of electrons. However, isotopes may not have the same nuclear and physical properties. The relative abundance of different isotopes differs from element to element.



Isobars are atoms of different elements which have the same mass number but different atomic numbers. These have different number of protons, different number of electrons and different number of neutrons. The chemical properties of isobars are widely different because they have different number and arrangement of electrons. Their physical properties may be identical.

Isotones are the nuclei which have the same number of neutrons. Both the atomic number Z and the mass number A are different but the value (A – Z) [= No. of neutrons] is the same. The numbers of naturally occurring isotones provide useful evidence concerning the stability of particular neutron configurations.

For example, the relatively large number (six and seven, respectively) of naturally occurring 50– and 82–neutron isotones suggests that these nuclear configurations are especially stable. On the other hand, from the fact that most atoms with odd numbers of neutrons are an isotonic, one may conclude that odd–neutron configurations are relatively unstable.



Electronic configuration

It is defined as the distribution of electrons into the orbitals of an atom. Every neutral atom consists of a fixed number of electrons which is equal to the number of protons and is called the atomic number. Apart from electrons and protons, an atom also has neutrons which may or may not be equal to the number of the protons. In an atom, the protons and the neutrons lie in the nucleus and have almost negligible role in governing any chemical reaction. However, the electrons are the ones which lie outside the nucleus of the atom and their precise distribution inside an atom play a very important role in governing the chemical reactions that the atom involves in. Electronic configuration of an atom defines the precise distribution of electrons in an atom and this distribution helps in understanding the reasons for the chemical reactions that the atom or its corresponding molecules get involved in.

Principal quantum number, n: It can be visualized to be the quantum number assigned to the shells or orbits in which the electrons lie and this is similar to the orbit/shell that was discussed by Bohr in his atomic model.Every shell has a fixed number of atomic orbitals and as the value of n increases, the number of allowed atomic orbitals also increases accordingly. Every shell is designated a value which is basically the principal quantum number. So, for the 1st shell n=1, for the 2nd shell n=2, for the 3rd shell n=3 and so on.n = 1 2 3 4…Shell= K L M N…

Azimuthal quantum number, l: It is the quantum number which is assigned to the subshells. However, they are basically the orbital angular momentum or subsidiary quantum number. Every shall has a fixed number of subshells/sublevels. The number of subshells is equal to the value of the principal quantum number i.e. n. So, for $n=1$ i.e. 1st shell, there can be only one subshell, and the corresponding value for $l=0$. For $n=2$ i.e., 2nd shell, there can be 2 subshells, and their value corresponds to $l=0$ and 1. For $n=3$, i.e. 3rd subshell, there can be 3 subshells and their values correspond to $l=0$, 1 and 2; and so on. So, we can say that every subshell is assigned an Azimuthal quantum number, and for every subshell we have a corresponding symbol in order to designate the subshell.Value of l = 0 1 2 3 4…Symbol/notation for subshell = s p d f g…So, the notation for different subshells go this way: nlSubshell Notation101s20,12s, 2p30,1,23s, 3p, 3dSo the 1st shell has just one subshell i.e. 1s.

The 2nd shell has 2 subshells 2s and 2p. The 3rd shell has 3 subshells i.e. 3s, 3p, and 3d and so on.

Magnetic orbital quantum number, m: It is basically the quantum number assigned to different atomic orbitals present in a subshell. Every atomic orbital has a particular spatial orientation with respect to the standard set of coordinate axes and this differentiates atomic orbitals within a subshell and every atomic orbital in a subshell is designated with a magnetic quantum number. For a sub-shell defined by value ‘l’, there can be $2l+1$ values of ‘m’ i.e. the total no. of orbitals in that subshell can be $2l+1$ and their corresponding values of m goes this way: $-l$ to $+l$.

So, 1st shell, $n=1$ has 1 subshell i.e. 1s and it can have just one atomic orbital ($2*0+1=1$ so only 1 orbital) and the corresponding magnetic quantum number, ‘m’ for the single orbital is 0 itself. 2nd shell, $n=2$ and has 2 subshells i.e. 2s and 2p. 2s subshell can have only one atomic orbital ($2*0+1=1$ so only 1 orbital) and the corresponding value for ‘m’ is 0. However, 2p subshell can have 3 atomic orbitals which are designated as 2px, 2py and 2pz ($2*1+1=3$ so 3 orbitals) and the corresponding values of ‘m’ are -1,0,+1.

Aufbau principle

Aufbau is a German word that means building up. This principle tells the sequence in which various orbitals are filled with electrons. According to the Aufbau principle “**In the ground state of the atoms, the orbitals are filled with electrons in order of increasing energies.**”

Electrons enter the orbitals according to the following $(n + l)$ rules.

Orbitals are filled in order of increasing value of $(n + l)$

Example: Consider 3d and 4s orbitals

For 3d, n= 3 and = 2. Hence (n + l) =3+2= 5

For 4s, n = 4 and = 0. Hence (n + l)= 4 +0= 4

As the value of (n + l) for 4s orbital is less than that of 3d orbital, 4s orbital is filled before 3d orbital.

Therefore, 3d orbital is filled up before 4p orbital. The order of energy of different orbitals in an atom is given below.

1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d< 5p < 6s < 4f < 5d and so on

The sequence given above can be represented by a diagram as shown Fig. 3.25 Order of filling of atomic orbitals.

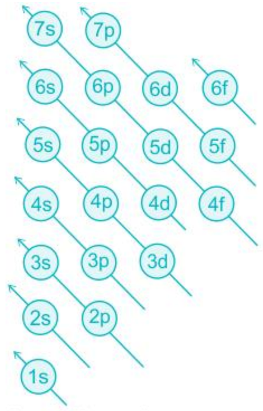
Pauli's Exclusion Principle

This principle limits the number of electrons that can occupy any orbital of an atom.

Statement: "**Two electrons in an atom cannot have the same set of all four quantum numbers."**

Or

"Only two electrons may exist in the same orbital with three quantum numbers same i.e. the fourth quantum number is different and these electrons must have opposite spin."

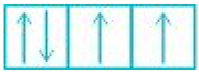
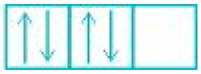


Order of filling of atomic orbitals

Hund's rule of maximum multiplicity

Statement: **When several orbitals of equal energy (degenerate orbitals) are available, the electrons first fill all the orbitals singly before pairing in any of these orbitals.**

The Configuration of four electrons occupying p-orbitals is

 and not as 

Completely filled or half filled orbitals give extra stability

Periodic Trends of Properties of Elements

In Periodic Table Modern periodic law is the base of periodic trends of properties of elements in the modern periodic table. Following properties of elements show a very clear periodic trend in the periodic table –

- Atomic Radius
- Ionisation energy
- Electron affinity
- Electronegativity
- Valence electrons
- Valency
- Metallic character of the elements
- Non – metallic character of the elements
- Reactivity of elements
- Melting and boiling points of elements

Now, understand the trends of properties in detail by knowing the reason for the variation of properties. Atomic Radius Atomic radius is the distance between the centre of the nucleus of an atom to its outermost shell. The periodic trend of atomic radius across a period – As we move from left to right in a period, atomic radius gradually decreases. Reason – As we move left to right in a period the atomic number of the elements increases so nuclear charge.

Ionisation Energy Ionisation energy is the amount of energy required to remove one electron from an atom. First ionisation energy is the amount of energy required to remove one outermost electron from an atom. The periodic trend of ionisation energy across a period – As we move from left to right in a period, ionisation energy gradually increases. **Reason** – As we move left to right in a period atomic size or atomic radius decreases while nuclear charge increases.

Electron Affinity The amount of energy required to add an electron to an atom is called the electron affinity of that atom. In other words, electron affinity is the change in energy when an electron is added to the atom and a neutral atom changes into a negative ion. The periodic trend of electron affinity across a period – As we move from left to right in a period, electron affinity gradually increases. **Reason** – As we move left to right in a period atomic size or atomic radius decreases while nuclear charge increases.

Electronegativity Electronegativity is a measure of the ability of an atom or molecule to attract pairs of electrons in the context of a chemical bond. Across A Period – As we move left to right across a period, electronegativity increases in the periodic table. Fluorine is the most electronegative element**.** **Reason** – As the nuclear charge increases of an atom, its electron loving character also increases.

Valence Electrons Electrons present in the outermost shell of an atom are called valence electrons of that atom. **Across A Period** – As we move left to right across a period in the periodic table, the number of valence electrons increases.

Valency Valency is the combining capacity of an atom. **Across a Period** – on moving left to right across a period in the periodic table, first valency increases then decrease.

Unit II - Chemical Bonding and Molecular Structure

1. CHEMICAL BOND:

Chemical bonding is the creation of a chemical compound by forming a chemical link between two or more atoms, molecules, or ions. The atoms in the resulting molecule are held together by chemical bonds.

Types of chemical bonds include:

a. Ionic Bonds

b. Covalent Bonds

c. Hydrogen Bonds

d. Polar Bonds

Modes of Chemical Composition:

1. When one or more electrons are completely transferred from one atom to another. Electrovalency is the name given to this process, and the chemical bond generated is known as an electrovalent bond or an ionic bond.

2. Through the sharing of electrons. This can happen in one of two ways:

(a) A covalent bond is created when the two joining atoms provide equal amounts of shared electrons.

(b) A coordinate bond, also known as a dative bond, is produced when theseelectrons are contributed totally by one of the atoms but shared by both.

3. LEWIS SYMBOLS:

In 1916, Kossel and Lewis were successful in providing a successful explanation for why atoms unite to form molecules based on the concept of an electrical configuration of noble gases. Noble gas atoms have little or no inclination to mix with other noble gas atoms or atoms of other elements. This implies that the electronic arrangements of these atoms must be stable.

Lewis used simple symbols to represent an atom's valence shell electrons. The outer shell electrons are depicted as dots around the atom symbol. Lewis symbols or electron dot symbols are the names given to these symbols.

4. IONIC BOND:

Ionic bonding is a sort of chemical bonding that occurs when electrons are transferred from one atom or molecule to another. One atom loses an electron in this process, which is then gained by another atom. When an electron transfer occurs, one of the atoms gains a negative charge and is referred to as an anion.

The cation is the other atom that gets a positive charge. The difference in charge between the two atoms strengthens the ionic link; the higher the charge differential between the cation and the anion, the stronger the ionic bond.

Explanation of Ionic Bond: Atoms are electrically neutral. Therefore, they possess an equal number of protons and electrons. On losing an electron, an atom becomes positively

A A e

On the other hand, in case of atoms gaining the electron, the number of electrons exceeds the number of protons and thus the atom becomes negatively charged.

B e B

The oppositely charged particles formed above attract each other by electrostaticforces of attraction. The bond thus formed is known as electrovalent or ionic bond.

Electrovalency:

The electrovalency of an element is defined as the number of electrons lost orgained during the development of an electrovalent connection.

For example, sodium and calcium both lost one electron and had valencies of one and two, respectively. Chlorine and oxygen gain one and two electrons, respectively, and have an electrovalency of one and two. In other words, valency isthe same as the ion's charge.

Factors governing the formation of ionic bonds:

(i) Ionisation Enthalpy (Ionization Energy): The amount of energy necessary to remove one electron from the outermost shell of an isolated atom in gaseous phase and convert it to a gaseous positive ion is known as ionisation enthalpy.

(ii) Electron Gain Enthalpy (Electron Affinity): The enthalpy change that occurs when an extra electron is added to an isolated atom in the gaseous phase to form a gaseous negative ion is known as electron affinity.

(iii) Lattice Enthalpy (Lattice Energy): In the production of ionic compounds, positively and negatively charged ions combine to form the compound.

Characteristics of Ionic Compounds:

1) Crystalline in nature: Ionic compounds form crystalline structures, but the size of the crystalline structure is determined by the size of the anions and cations. Because the number of cations equals the number of anions that combine to form ionic compounds, the crystal structure of ionic compounds is uncharged.

2) Ionic compounds are stiff and brittle because the ions are bound together by strong electrostatic forces. Because these compounds are held together by strong forces, breaking them requires a lot of force. Ionic compounds are fragile by nature.

3) Boiling and melting points are also high.

Ionic compounds are hard to break because they are kept together by strong electrostatic forces. High melting and boiling temperatures are required to break such strong forces and overcome the force of attraction between them.

4) High Fusion and Vaporization Enthalpies: Ionic chemicals have higher Fusion and Vaporization Enthalpies than other molecular molecules. Their enthalpies are ten to one hundred times higher than those of molecular molecules.

5) Solubility: Ionic compounds can be dissolved in polar solvents such as water. In Non-Polar Covalent solvents, they are less soluble.

6) Good conductors of electricity in aqueous or molten form: Ionic compounds act as a good conductor of electricity when they are in aqueous or molten form because ionic compounds are tightly packed, which prevents ions from moving, making them a poor conductor of electricity. However, when they are in aqueous or molten form, ions are free to move, making them a good conductor of electricity.

7) Acts as insulators: When molten or watery, ionic compounds act as good conductors of electricity; otherwise, they act as insulators.

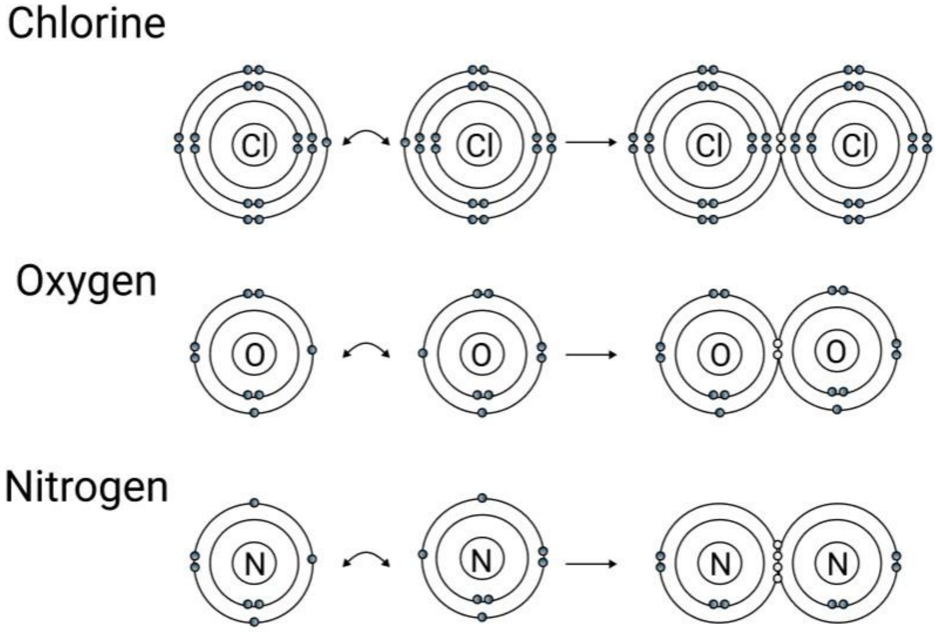
5. COVALENT BOND:

In nature, covalent bonds can be either polar or nonpolar. Electrons are shared unequally in Polar

Covalent chemical bonding because the more electronegative atom pulls the electron pair closer to itself and away from the less electronegative atom. A polar molecule like water is an example.

The irregular spacing of electrons between the atoms causes a charge difference in different parts of the atom. The molecule's one end is partially positively charged, while the other end is partially negatively charged.

Example:



Conditions for writing the Lewis dot structures:

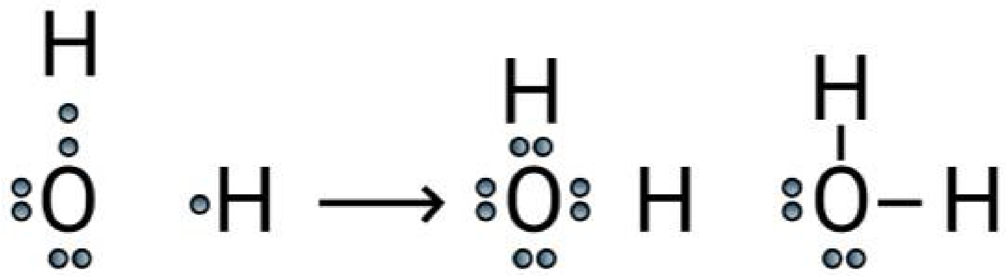
- Sharing of an electron pair between the atoms results in the formation ofcovalent bonds.
- During bond formation, each bond consists of two electrons which arecontributed by each one of the combining atoms.
- By the mutual sharing of electrons, each atom attains octet configuration inits valence shell.

The octet rule is used to write electron dot structures of covalent compounds. Except for the hydrogen atom, all of the atoms in the molecule will have eight electrons in their valence shell according to this law. Because only two electrons complete the first shell of hydrogen to achieve the helium configuration, it will have only two electrons.

To achieve a stable octet, elements in group 17 like Cl would share one electron; elements in group

16 like O and S would share two electrons; elements in group 15would share three electrons, and so on.

For Example, the oxygen atom which has six electrons in its valence shell completes its octet by sharing its two electrons with two hydrogen atoms to form a water molecule.



Lewis Structure of Water Molecule

1. FORMAL CHARGE:

A charge on an individual atom(s) in a polyatomic molecule is known as formal charge. It's a deceptive charge that's linked to only one atom in the structure. We term it fake because a molecule or compounds true charge is distributed across the species' structure. Formal charge is caused by flaws in the configuration of an atom involved in the synthesis of a compound. Calculation is required for formal charge,as we will see later. From here, we'll go through things like the formal charge formula and how to compute formal charge, among other things. The formal charge is a crucial part in chemistry.

Formal Charge Formula:

Now that we know what formal charge is, we will move onto the formal chargeformula. Mathematically, the formal charge formula stands as follows:

Formal Charge = Valence Electrons - 0.5 Bonding Electrons - NonbondingElectrons

We half the value of bonding electrons because the bond exists between two electrons.

Now that we know the formal charge formula, we can move onto an example andunderstand how to calculate formal charge of a polyatomic molecule.

Example:

How To Calculate Formal Charge Of SO_2 ?

Here we will understand how to calculate the formal charge of SO_2 . For calculating the formal charge of SO_2 , we have to unlock its Lewis structure. Therefore, the first step of calculating formal charge is drawing the Lewis structure. The Lewis structure of SO_2 is as follows:

Numbers 1,2,3,4 Indicate The Index of the Oxygen Atom.

Atom	**Valence electrons in the free state**	**No. of non-bonding electrons in Lewis structure**	**No. of pairsof bonding electrons in Lewis structure**	**Formal Charge**
Sulphur (S)	6	0	12	6 – 0 – 12/2 = 0
Oxygen (O) –1	6	4	4	6 – 4 – 4/2 = 0
Oxygen (O) –2	6	6	2	6 – 6 – 2/2 = -1
Oxygen (O) –3	6	4	4	6 – 4 – 4/2 = 0
Oxygen (O) - 4	6	6	2	6 – 6 – 2/2 = -1

1. VALENCE SHELL ELECTRON PAIR REPULSION THEORY:

VSEPR (pronounced "vesper") stands for valence shell electron pair repulsion model, which is a model for predicting the geometry of molecules. VSEPR models examine the bonding and molecular geometry of organic compounds and polyatomic ions in particular. It is applicable to practically all compounds with a non-metal centre atom.

Because Lewis structures are limited to two dimensions, they can only tell you the number and type of links between atoms. The VSEPR model accurately predictsthe 3-D shape of molecules and ions, but it fails to provide any detailed information on link length or bond structure.

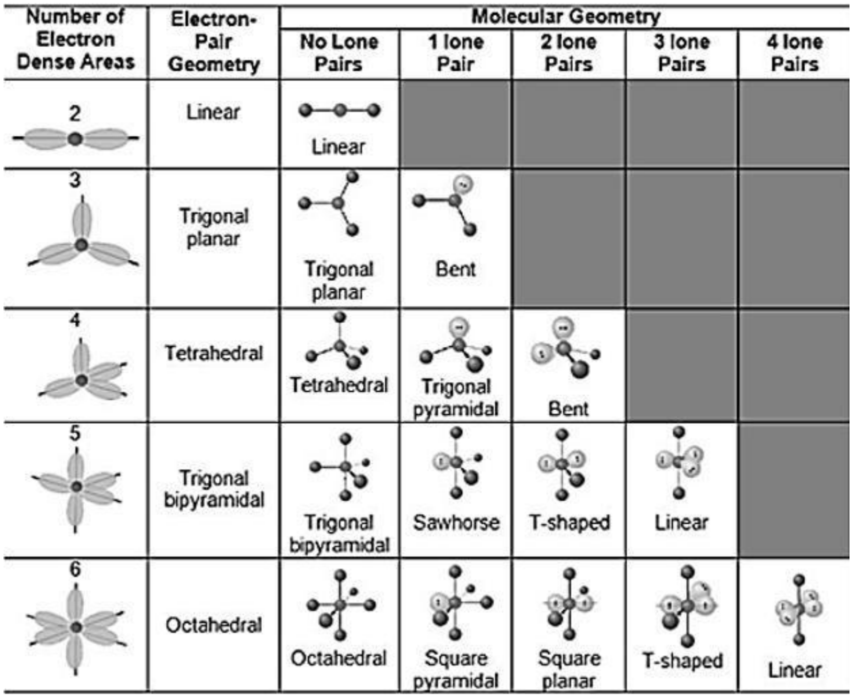
The following terms are commonly used in discussing the shapes of molecules:

- VSEPR models are based on the idea that electrons revolving around a core atom will arrange themselves to minimise repulsion, dictating the molecule'sshape.
- As long as the central atom is not a metal, it can predict the form of practically all compounds with a central atom. Each form is given a name as well as an idealised bond angle.
- Lone pair: a pair of valence electrons that are not shared with another atom.

- Bond angle: the angle formed by a bonded atom, the centre atom, and another bonded atom

- Molecular geometry: a polyatomic ion or molecule's 3-D arrangement of bound atoms.
- Electron pair geometry is the 3-D arrangement of electron pairs around apolyatomic ion or molecule's core atom.

The major distinction between molecular geometry and electron pair geometry is that molecular geometry excludes unpaired electrons, whereas electron pair geometry includes both bound and unpaired atoms. The molecule and electron pair geometries will be the same if there are no unpaired electrons in the chemicalunder consideration.



Number of Electron Dense Areas	Electron-Pair Geometry	Molecular Geometry				
		No Lone Pairs	1 lone Pair	2 lone Pairs	3 lone Pairs	4 lone Pairs
2	Linear	Linear				
3	Trigonal planar	Trigonal planar	Bent			
4	Tetrahedral	Tetrahedral	Trigonal pyramidal	Bent		
5	Trigonal bipyramidal	Trigonal bipyramidal	Sawhorse	T-shaped	Linear	
6	Octahedral	Octahedral	Square pyramidal	Square planar	T-shaped	Linear

Calculating the total number of electron pairs, bond pairs, and lone pairs, as well as estimating molecule and ion shapes:

1. Total no. of electron pairs around the central atom =1 (No. of valenceelectrons of central atom + No. of atoms linked to central atom by single bonds)

   For negative ions, add the number of electrons equal to the units of negativecharge on the ion to the valence electrons of the central atom.

   For positive ions, subtract the number of electrons equal to the units of positivecharge on the ion from the valence electrons of the central atom.

2. No. of bond pairs (shared pairs) = No. of atoms linked to the central atom bysingle bonds.
3. No. of lone pairs = Total no. of electron pairs – No. of shared pairs.

HYBRIDISATION:

Hybridisation is defined as the mixing of atomic orbitals belonging to the same atom but with slightly varying energies, resulting in an energy redistribution between them and the production of new orbitals with identical energies and shapes. Hybrid orbitals are the novel orbitals that result from this process.

Hybridisation: Some Important Points:

(i) Only orbitals with comparable energies and belonging to the same atom or ion can be hybridised.

(ii) The number of hybrid orbitals created equals the total number of atomicorbitals combined.

(iii) Hybridization does not require the participation of all half-filled orbitals. Similarly, only half-filled orbitals are not required to participate in hybridisation. Even orbitals that are totally filled but have slightly varying energy can participate.

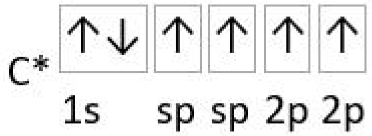
(iv) Hybridisation does not happen in isolated atoms; it only happens when bonds are formed.

(V) The type of hybridisation indicates the molecule's geometry. The type ofhybridisation used can be used to determine the shape of a molecule.

(vi) The hybrid orbital is larger lobe is always positive, whereas the smaller lobe on the opposite side is always negative.

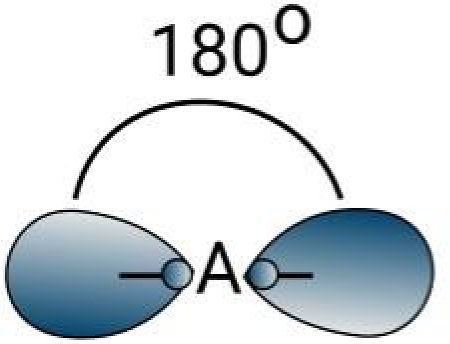
Type of Hybridisation:

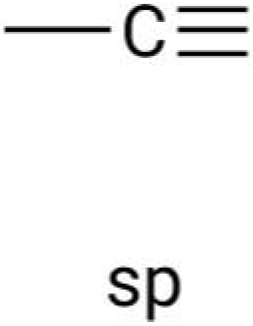
1. **Diagonal or sp hybridisation:**



The chemical bonding in compounds such as alkynes with triple bonds is explained by sp hybridization. In this model, the 2s orbital is mixed with only one of the three p orbitals,

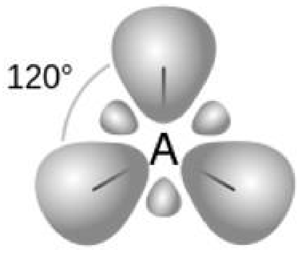
Resulting in two sp orbitals and two remaining p orbitals. The chemical bonding in acetylene (ethyne) C_2H_2 consists of sp–sp overlap between the two carbon atoms forming a **σ** bond and two additional **π** bonds formed by p–p overlap. Each carbon also bonds to hydrogen in a **σ** s–sp overlap at 180° angles.



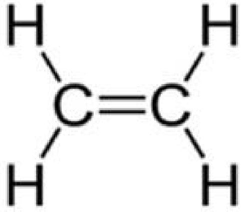


1. Diagonals of Sp_2 hybridization: Other carbon compounds and other molecules may be explained in a similar way. For example, ethanedouble bond C_2H_4 has a between the carbons.

Forming a total of three Sp_2 orbitals with one remaining p orbital. In ethylene (ethane) the two carbon atoms form a **σ** bond by overlapping one Sp_2 orbital from each carbon atom. The **π** bond between the carbon atoms perpendicular to themolecular plane is formed by 2p–2p overlap. Each carbon atom forms covalent C–H bonds with two hydrogens by s–Sp_2 overlap, all with 120° bond angles. The hydrogen–carbon bonds are all of equal strength and length, in agreement withexperimental data.



Three Sp₂ orbitals



Ethene structure

Formula	Shape (Name)	Bond Angles	Hybridization
AX_2	Linear	180	sp
AX_3	Trigonal Planar	120	sp^2
AX_4	Tetrahedral	109.5	sp^3
AX_5	Triangular Bipyrimidal	120, 90	sp^3d
AX_6	Octahedral	90	sp^3d^2
AX_2N	Bent	120	sp^2
AX_2N_2	Bent	109.5	sp^3
AX_3N	Trigonal Pyramidal	109.5	sp^3

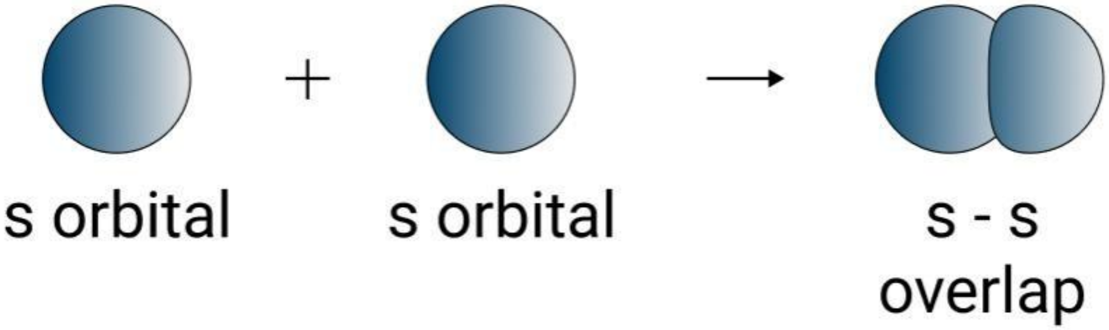
Sigma (σ) Bond:

Head-on positive (same phase) overlap of atomic orbitals along the internuclear axis forms this sort of covalent connection. Due to the direct overlapping of the participating orbitals, sigma bonds are the strongest covalent bonds. The electrons that participate in a bond are referred to as electrons.

All single bonds are, in general, sigma bonds. The following atomic orbital combinations can be used to make them.

S-S Overlapping:

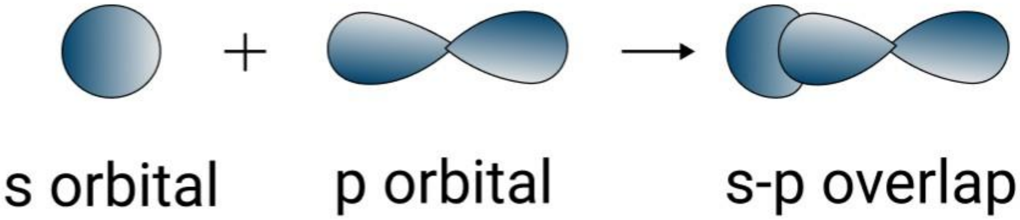
One "s" orbital from each participating atom undergoes head-on overlapping alongthe internuclear axis in this type of overlapping. Before one s orbital can overlap with another, it must be half-filled.



Above is an illustration of two s orbitals overlapping to form a sigma bond. In hydrogen molecules, where each hydrogen atom has a half-filled s orbital, this form of overlap happens.

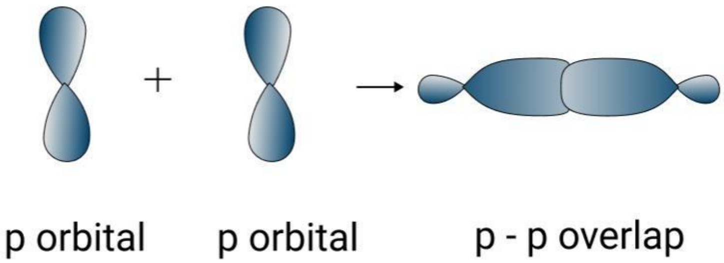
Sp Overlapping:

Here, one half filled s orbital overlaps with one half-filled p orbital along theinternuclear axis, forming a covalent bond. This condition is illustrated below.



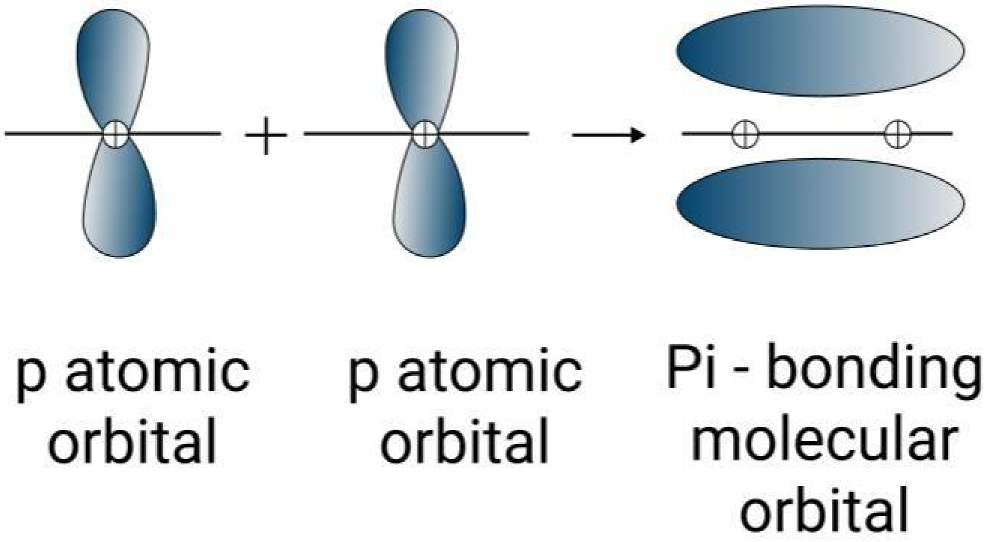
P-P overlapping:

In this condition, one half-filled p orbital from each participating atom undergoes head-on overlapping along the internuclear axis. This type of overlapping is illustrated below.



The Pi (π) Bond:

Sidewise positive (same phase) overlap of atomic orbitals in a direction perpendicular to the internuclear axis forms pi bonds. The axes of the atomic orbitals are parallel to one another during bond formation, whereas the overlapping is perpendicular to the internuclear axis. This sort of covalent bonding is depictedin the diagram below.



Due to the substantially smaller degree of overlapping, pi bonds are often weaker than sigma bonds. A typical triple bond is made up of two bonds and one sigma bond, whereas a typical double bond is made up of one sigma bond and one pi bond. It's worth noting that a sigma and pi bond combination is always stronger than a single sigma bond.

Difference between Sigma and Pi Bonds:

The key differences between sigma and pi bonds are tabulated below.

Sigma Bond	Pi Bond
The overlapping orbitals can be pure orhybrid	The overlapping orbitals must beunhybridized
These bonds are strong and have highbond energies.	These bonds are relatively weak.
Can exist independently	Must exist along with a sigma bond.
Has an impact on the shape of molecules	Has no role in determining the shapeof molecules

Bond Parameters:

- **Bond length:** The equilibrium distance between the centres of the nuclei of the two bonded atoms is called its bond length.
- Bond energy: The amount of energy required to break one mole of bonds ofa particular type so as to separate them into gaseous atoms is called bond dissociation enthalpy or simply bond enthalpy.
- Bond angle: The angle between the lines representing the directions of the bonds, i.e., the orbitals containing the bonding electrons is called the bond angle.
- Bond order: In the Lewis representation of a molecule or ion, the number of bonds present between two atoms is called bond order.

VAN DER WAALS FORCES:

Van der Waals forces are weak intermolecular forces that are dependent on the distance between atoms or molecules. These forces arise from the interactions between uncharged atoms/molecules.

For example, Van der Waals forces can arise from the fluctuation in the polarizations of two particles that are close to each other.

In the group of forces that fall under the category of ‘**weak chemical forces’**, Van der Waals forces are the weakest. They are known to rapidly vanish when the distance between the interacting molecules increases. The strengths of Van der Waals forces typically **range from 0.4 kJ.mol-1 to 4 kJ.mol-1.**

When the electron density around the nucleus of an atom undergoes a transient shift, it is common for Van der Waals forces arising. For example, when the electron density increases in one side of the nucleus, the resulting transient charge may attract or repel a neighbouring atom. The nature of these forces is dependent on the distance between the atoms:

When the distance between the atoms is greater than 0.6 nanometres, the forces areextremely weak and cannot be observed.

When the distance between the atoms ranges from 0.6 to 0.4 nanometres, the forces are attractive.

If the interatomic distance is smaller than 0.4 nanometres, the forces are repulsive in nature.

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  When the distance between the atoms ranges from 0.6 to 0.4 nanometres, theforces are attractive.

- If the interatomic distance is smaller than 0.4 nanometres, the forces arerepulsive in nature.

Types of Vander Waal's force:

1. Ion dipole attraction - This force is between an ion such as Na and a polarmolecule such as HCl.
2. Dipole dipole attraction - It is again in between two polar molecules such asHF and HCl.
3. Ion induced dipole attraction - In this case a neutral molecule is induced byan ion as a dipol.
4. Dipole - induced dipole attraction: In this case a neutral molecule is inducedas a dipole

by another dipole.

5. Induced dipole - induced dipole attraction or London dispersion force between two nonpolar molecules as in Cl_2 , He etc.

DIPOLE MOMENT:

Dipole moments in chemistry express the polar character or polarity of the molecules. The product of charge and distance of separation of atoms in a chemicalbond defines the term dipole moment. If +q amount positive charge separated by -q
amount of negative charge by the bond distance I, then dipole moment ( ) of polar
molecule Perfectly non-polar molecules like hydrogen, oxygen, and
q I.
nitrogen have zero dipole moment and the polar molecules like water, ammonia, and methane have positive values. It is a tool used to calculate the percentage ionic character, electric polarization, and residual charge on the atoms of the molecules.

Applications of Dipole Moment:

1. For predicting the nature of the molecules- molecules with zero dipole moment are non- polar while the molecule with specific dipole moment are polar in nature.
2. For determining the shape of the molecule-If a molecule has a specific dipole moment then its shape will not be symmetrical, they may be bent or angular and the molecule with zero dipole moment will be symmetrical and has linear shape.

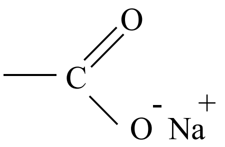
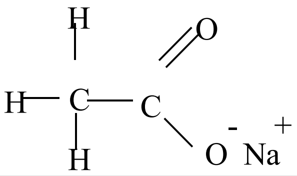
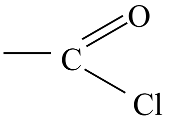
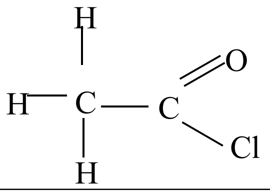
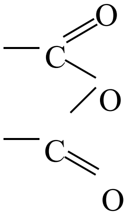
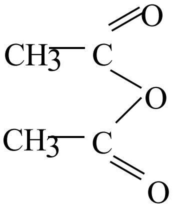
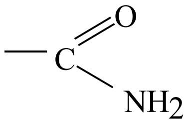
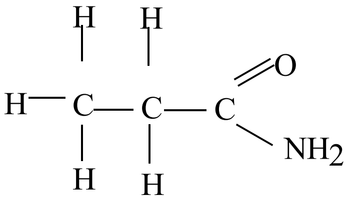
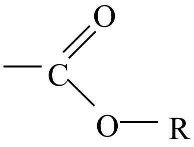
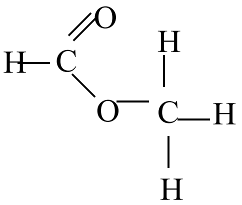
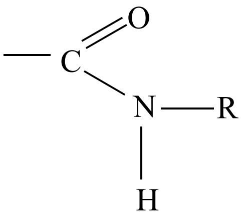
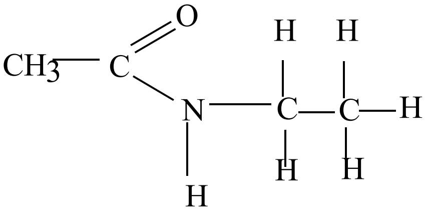
3. for comparing the polarities of the molecules- greater the dipole moment value, more will be the polarity and vice versa.

NOMENCLATURE AND ISOMERISM IN ORGANIC COMPOUNDS
NEW FUNCTIONAL GROUPS

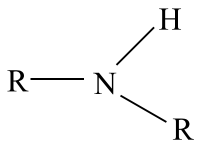
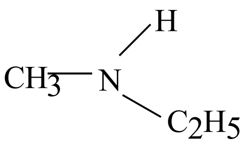
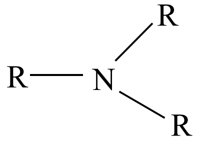
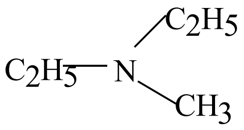
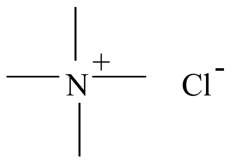
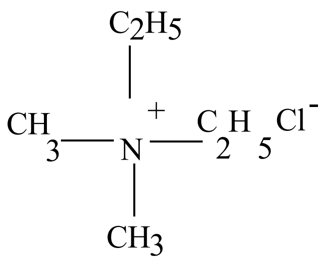
Introduction to new groups

The IUPAC method for naming organic compounds has been explained in the AS notes.

There are a number of new organic molecules in A2 Chemistry:

Type of compound	**Structure of group**	**Example**
Carboxylate salt		
Acyl choride		
acid anhydride		
amide		
ester		
N-substituted amide		

Primary amines were covered at AS-level, but there are a number of other types of amine and related molecules of which knowledge is required at A2 level:

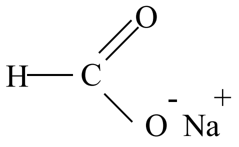
Secondary amine		
Tertiary amine		
Alkyl ammonium salt		

Nomenclature of new groups

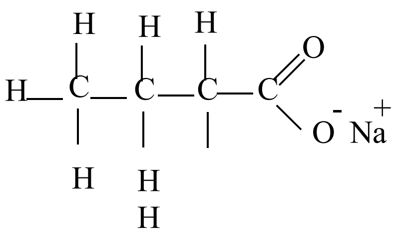
a) **carboxylate salts**

Carboxylate salts are named with the cation first and then the suffix **–anoate**

Eg



sodium methanoate

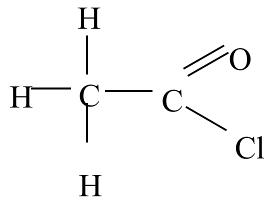


sodium butanoate

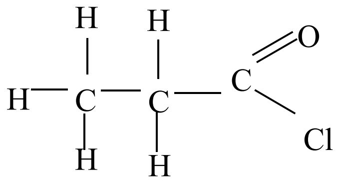
b) acyl chlorides

Acid chlorides are named using the suffix: **–anoyl chloride**

Eg



ethanoyl chloride



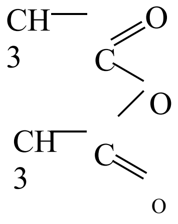
propanoyl chloride

The group is always at the end of the molecule, so numbering is not necessary.

c) acid anhydrides

If both alkyl groups are the same, acid anhydrides are named using the suffix –**anoic anhydride**

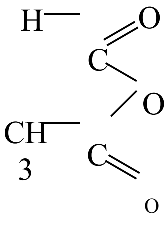
Eg



ethanoic anhydride

If the alkyl groups are different, each must be specified:

Eg

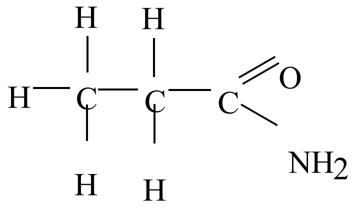


methanoic ethanoic anhydride

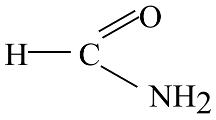
d) amides

Amides are named using the suffix –**anamide**

Eg



propanamide



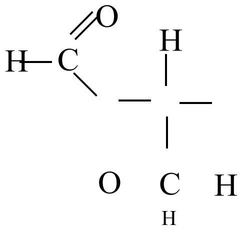
methanamide

The group is always at the end of the molecule, so numbering is not necessary.

e) esters

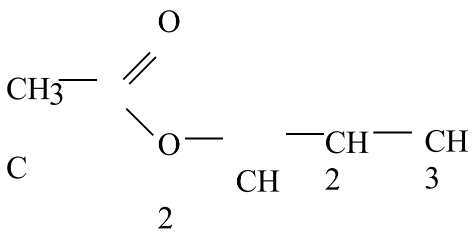
Esters are named using an **alkyl** prefix to indicate the group attached to the single O and the suffix –**anoate** to indicate the group attached to both oxygen atoms.

Eg



methyl methanoate

The methyl indicates the number of carbons in the chain attached to the single O (ie 1), and the methanoate indicates the number of carbons in the chain attached to both O atoms (ie 1).

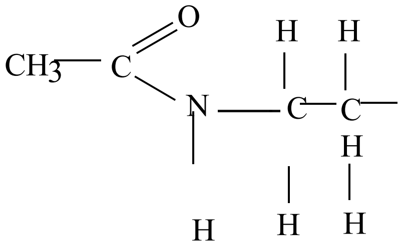


propyl ethanoate

f) N-substituted amides

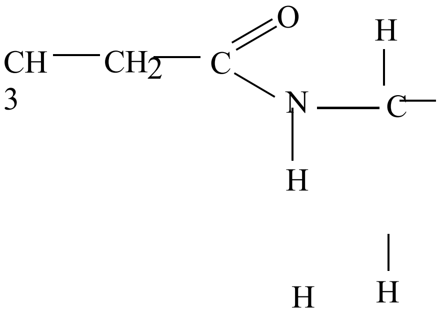
N-substituted amides are named using an N-alkyl prefix to indicate the group attached to the N only and the suffix –**anamide** to indicate the group attached to both O and N atoms.

Eg



N-ethyl ethanamide

The ethyl indicates the number of carbons in the chain attached to the N only (ie 2) and the ethanamide indicates the number of carbons in the chain attached to both N and O (ie 2)



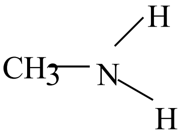
N-methyl propanamide

g) amines

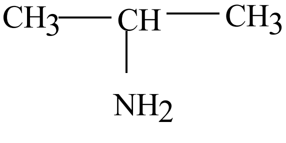
Primary amines are named using the prefix **amino-** followed by the suffix –**ane**.

If the carbon chain contains more than 2 carbon atoms, the amino should be preceded by a number to indicate the position of the amino group on the chain.

Eg



aminomethane

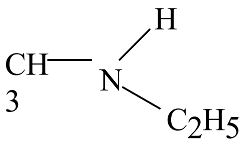


$CH_3-CH(NH_2)-CH_3$

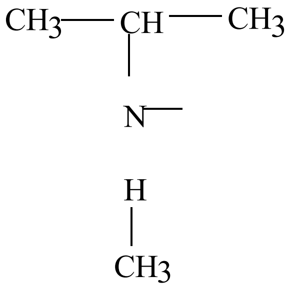
2-aminopropane

Secondary amines are named by using a N-alkyl prefix to indicate the nature of the shorter chain attached to the N atom. The longest chain is named afterwards, followed by the suffix –ane.

Eg



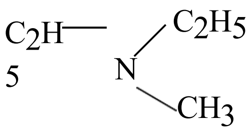
N-methylaminoethane



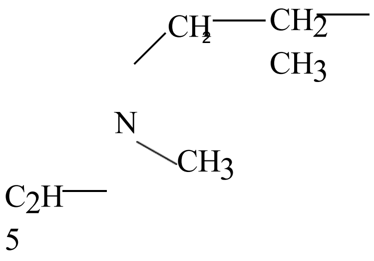
N-methyl, 2-aminopropane

Tertiary amines are named in the same way as secondary amines. The two shortest alkyl groups are indicated with a N-alkyl prefix.

Eg



N-methyl, N-ethylaminoethane

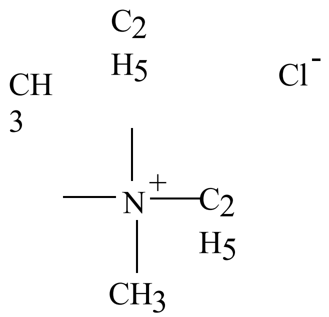


N-methyl, N-ethyl, 1-aminopropane

g) alkylammonium salts

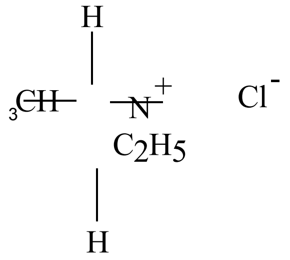
Alkylammonium salts can be primary, secondary, tertiary or quartenary depending on the number of alkyl groups attached to the nitrogen atom. They are named simply by indicating the nature and number of each alkyl group before the ending –**ammonium chloride**.

Eg



$$CH_3-\overset{\overset{C_2H_5}{|}}{\underset{\underset{CH_3}{|}}{N^+}}-C_2H_5 \quad Cl^-$$

dimethyldiethylammonium chloride



$$CH_3-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{N^+}}-C_2H_5 \quad Cl^-$$

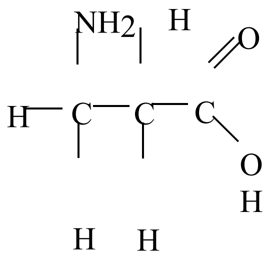
methylethylammonium chloride

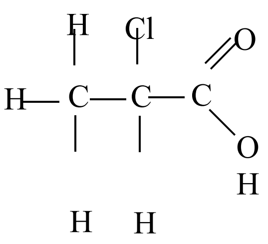
NOMENCLATURE OF COMPOUNDS CONTAINING MORE THAN ONE FUNCTIONAL GROUP

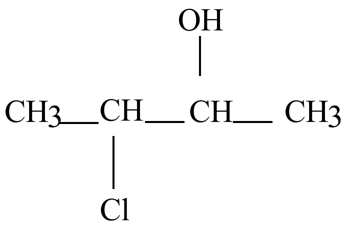
Many organic compounds contain more than one functional group. Naming more complex compounds such as these can be quite complicated, and only a few combinations need to be named at A-level.

- If one of the functional groups is an amine or a haloalkane, the molecule is named simply by adding the necessary prefix:

Eg

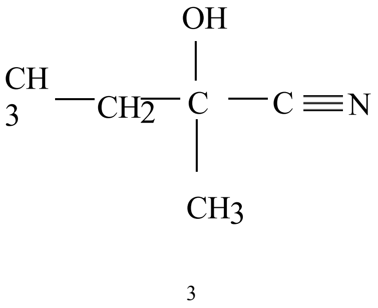

3-aminopropanoic acid

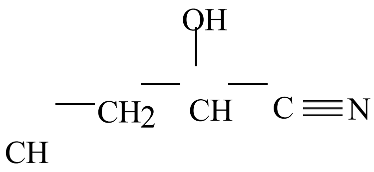

2-chloropropanoic acid

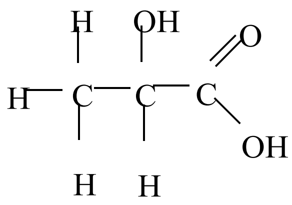

3-chlorobutan-2-ol

- If one of the functional groups is an alcohol and the other is a nitrile or anything containing a C=O bond, the alcohol group is named using a **hydroxy-** prefix.

Eg

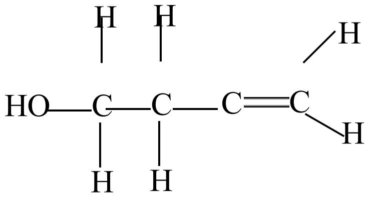

2-methyl, 2-hydroxybutanenitrile


2-hydroxybutanenitrile

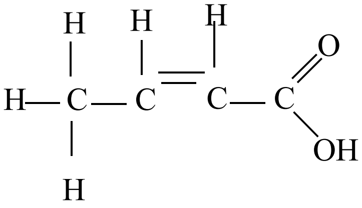

2-hydroxypropanoic acid

- If one of the functional groups is an alcohol and the other is anything other than an amine or a haloalkane, the molecule is named by replacing the –an- part of the name with –en-, including a number if the position of the alkene has to be specified.

Eg



but-1-en-4-ol



but-2-enoic acid

Many other organic molecules can be named in this way. The most important at A2 level are **hydroxynitriles** and **amino acids**.

ISOMERISM

Isomers are compounds with the same molecular formula but different structures.

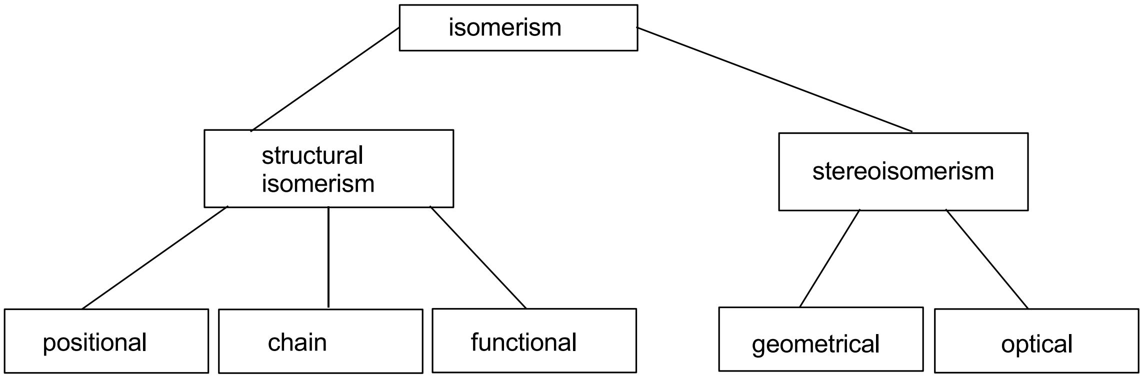
Isomerism can be divided into two types; **structural isomerism** and **stereoisomerism**.

These in turn can be further subdivided:

There are three types of structural isomerism; **positional isomerism**, **chain isomerism** and **functional isomerism**.

There are two types of stereoisomerism: **geometrical isomerism** and **optical isomerism**.

The different types of isomerism are summarised in the following diagram:

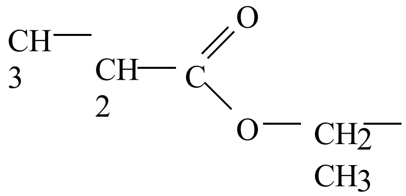


Many of these different types of isomerism were discussed in Unit 3 at AS level. Their relevance to the new types of molecule being introduced at A2 level will be briefly discussed.

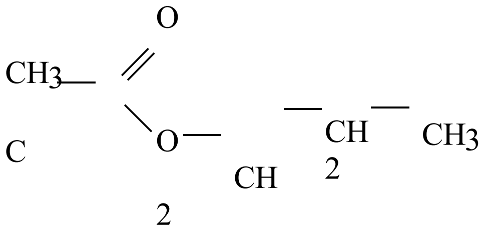
a) positional isomerism

In amides, acyl chlorides and carboxylate salts, the functional group is always at the end of the molecule and so these molecules cannot show positional isomerism. The other molecules, however, can show positional isomerism:

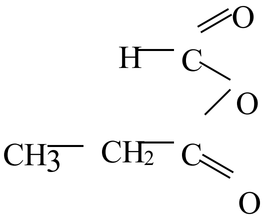
Eg



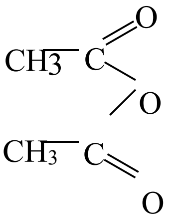
ethyl propanoate



propyl ethanoate



methanoic propanoic anhydride

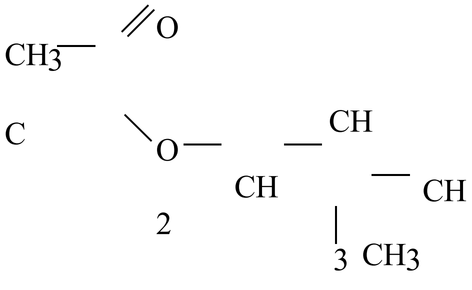


ethanoic anhydride

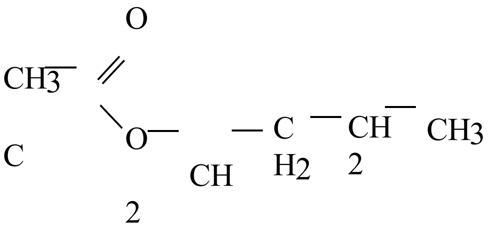
b) chain isomerism

All of the molecules in A2 chemistry can show chain isomerism:

Eg



2-methylpropyl ethanoate



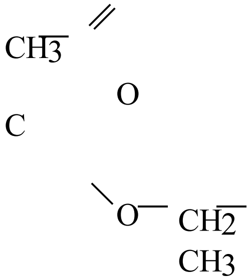
butyl ethanoate

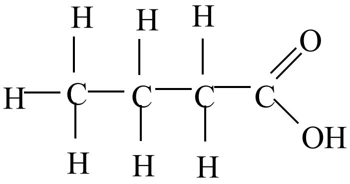
c) functional isomerism

In many cases, members of different homologous series can have the same general formula:

Carboxylic acids and esters have the same general formula $C_nH_{2n}O_2$.

Eg

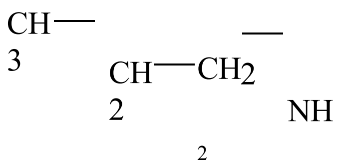


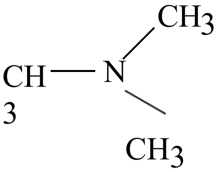


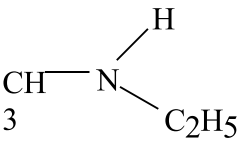
ethyl ethanoate butanoic acid

Primary, secondary and tertiary amines all have the same general formula $C_nH_{2n+2}N$.

Eg







1-aminopropane N,N-dimethylaminomethane N-methylaminoethane

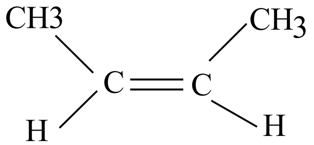
Other important groups which can show functional isomerism are:

- alcohols and ethers ($C_nH_{2n+2}O$)
- alkenes and cycloalkanes (C_nH_{2n})
- carbonyls, alkenols and cycloalcohols ($C_nH_{2n}O$)

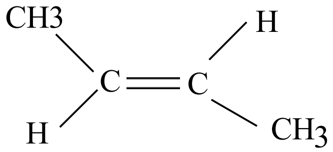
d) E-Z isomerism

Geometrical isomerism was introduced at AS-level. It occurs in alkenes when **both carbon atoms forming the double bond are attached to two different groups**.

Eg

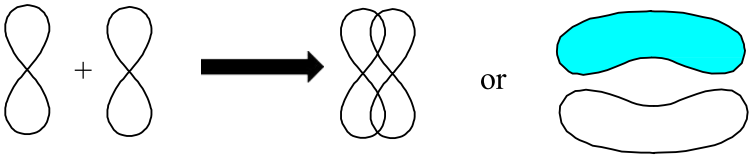


Z but-2-ene



E but-2-ene

In a double bond, the second bond is a **π**-bond. This is caused by the side-on overlap of two p-orbitals:



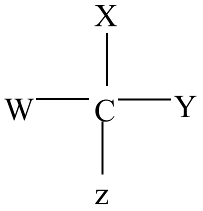
The result is an overlap in two places. This means that the bond cannot be twisted and as a result there is **restricted rotation about the π-bond**. This is why the cis and trans isomers cannot be interconverted and are therefore different.

e) optical isomerism

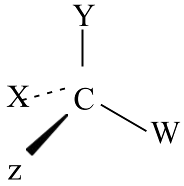
Optical isomerism is not required for AS-level. It will thus be explained in detail here.

i) Introduction

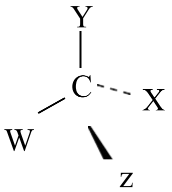
Consider the following molecule:



It is tetrahedral and is thus more accurately represented in the following way:



Since the carbon atom is attached to four different groups, it is asymmetric and so cannot be superimposed on its mirror image:



These two mirror images cannot be interconverted without breaking covalent bonds.

Molecules which contain a carbon atom which is attached to four different groups are said to be **chiral**. Chiral molecules cannot be superimposed on their mirror image.

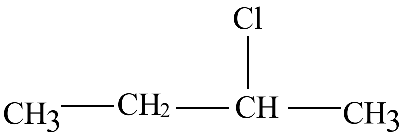
The two non-superimposable mirror images are **optical isomers** or **enantiomers**.

Any molecule which contains at least one carbon atom attached to four different groups will thus exhibit optical isomerism.

Consider the four structural isomers of C4H9Cl:

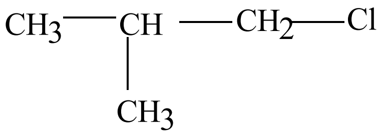
$CH_3-CH_2-CH_2-CH_2-Cl$

1-chlorobutane



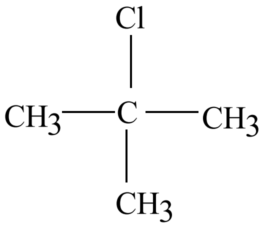
$CH_3-CH_2-\overset{Cl}{\overset{|}{CH}}-CH_3$

2-chlorobutane



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

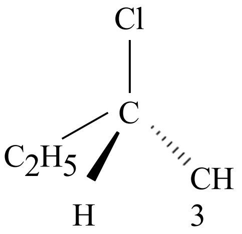
1-chloro, 2-methylpropane

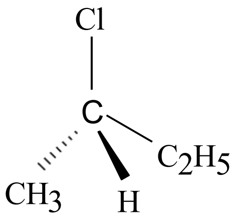


$CH_3-\underset{\underset{CH_3}{|}}{\overset{Cl}{\overset{|}{C}}}-CH_3$

2-chloro, 2-methylpropane

Of these molecules only 2-chlorobutane shows optical isomerism:

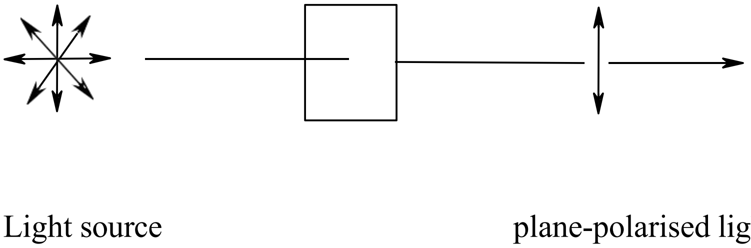




ii) Distinguishing between the different enantiomers

Optical isomers show identical physical and chemical properties in most respects.
In fact there is only one physical method by which they can be distinguished.

Plane-polarised light is light which has been filtered into a two-dimensional plane:



If plane-polarised light is passed through a liquid containing a chiral molecule, the plane of the light will be rotated. This can be detected using a polarimeter.

Molecules which are not chiral will not rotate the plane of plane-polarised light.

Chiral molecules will rotate plane-polarised light. Two optical isomers will rotate plane polarised light equally, but in opposite directions.
It is this difference in physical properties which enables them to be distinguished.

It is not possible to predict the direction in which a particular optical isomer will rotate plane polarised light, but two optical isomers will always rotate plane polarised light in opposite directions.

A substance which can rotate plane polarised light is said to be **optically active**.

The isomer which rotates plane polarised light clockwise is given the prefix (+) or D-.
The isomer which rotates plane polarised light anticlockwise is given the prefix (-) or L-.

iii) Importance of optical isomers in biochemistry

Optical isomers show identical chemical properties in most reactions. However, certain biochemical processes require the molecule to have a specific orientation of groups. Many drugs and enzymes are chiral and so only one of the optical isomers will be able to interact effectively with the target molecule in the body. Different optical isomers may therefore have very different biochemical effects.

iv) racemates

Optical isomers are often found together in a mixture in equal quantities. The opposite effect they have on the rotation of plane polarised light will thus result in no overall rotation. An equimolar mixture of two optical isomers will thus have no effect on plane polarised light and is thus not optically active.
Such mixtures are said to be **racemic mixtures** or **racemates**.

A racemic mixture is an equimolar mixture of two optical isomers. Racemic mixtures are not optically active.

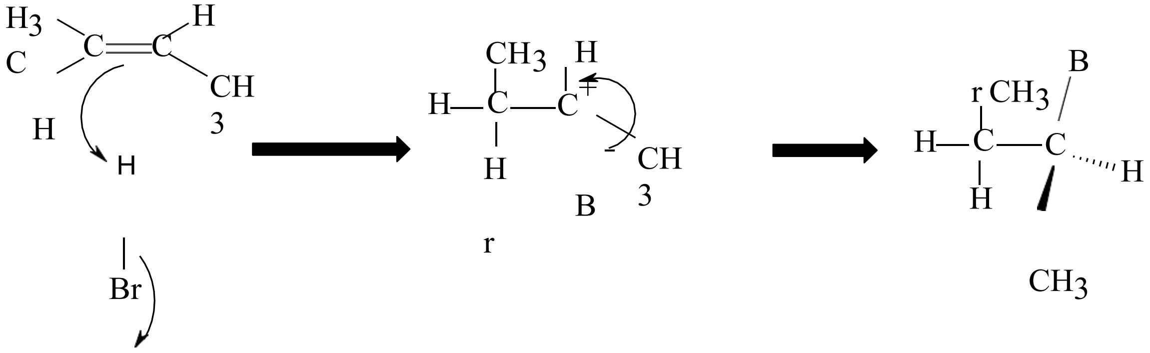
Thus chiral molecules will only show optical activity if one isomer is present in greater quantities than the other.

It is possible to predict whether a single enantiomer or a racemate will be produced, provided that the mechanism for the reaction is known.

If the chiral substance is produced by an addition reaction, then the product will always be a racemate as the attacking nucleophile or electrophile can attack the planar molecule from above or below with equal probability:

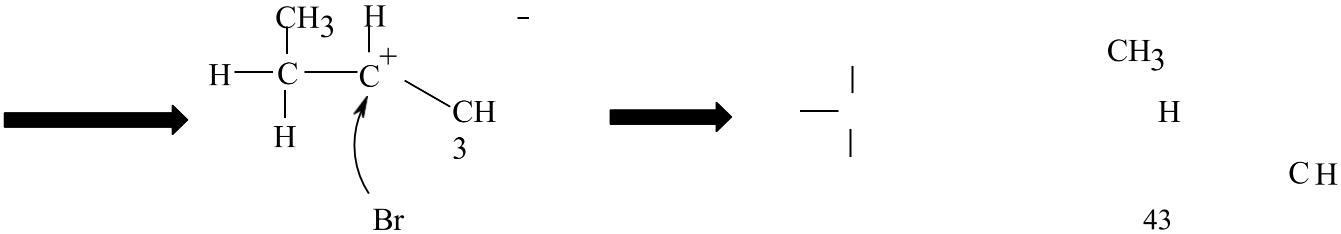
Eg formation of 2-bromobutane from but-2-ene (electrophilic addition)

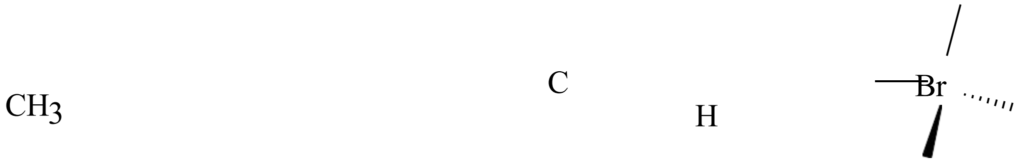
The bromide ion can attack the carbocation from above or below, producing an equimolar mixture of the two enantiomers – ie a racemate:



bromide attacks planar species from above

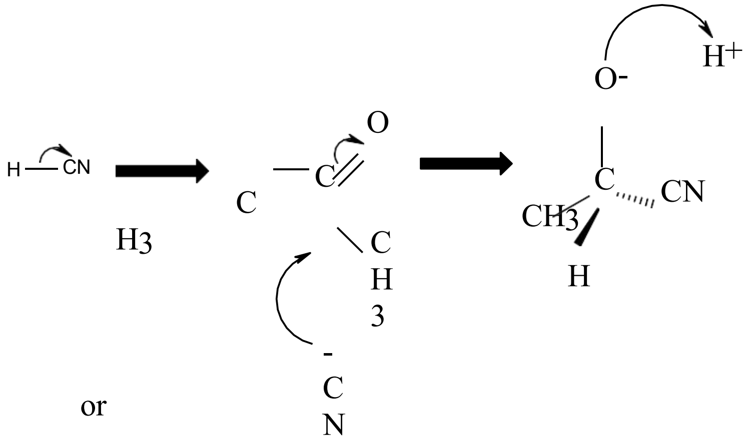
or



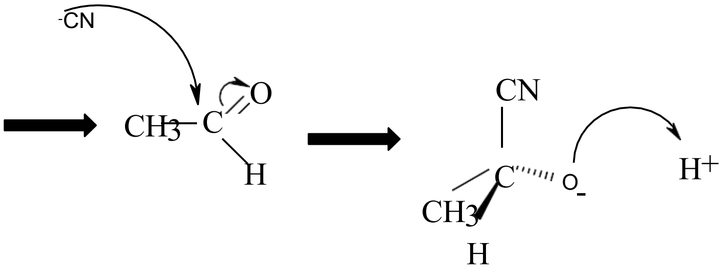


bromide attacks planar spcies from below

Nucleophilic addition reactions also produce racemates for the same reason. In the preparation of the chiral molecule 2-hydroxypropanenitrile from ethanal for example, the cyanide ion can attack the planar carbonyl group from above or below, producing a racemate.

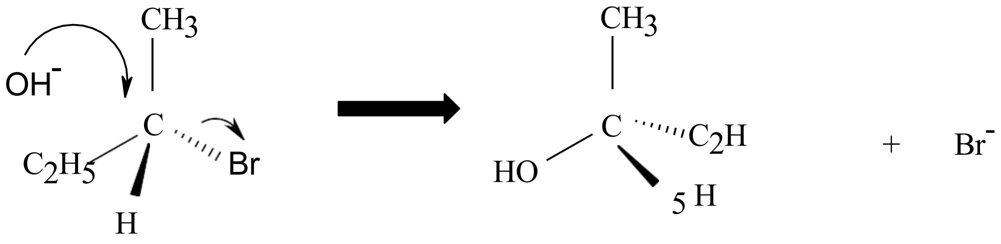


or



If the chiral molecule is produced by a substitution reaction and the starting molecule is a single enantiomer, then the attacking species can only attack from one side and a single enantiomer will be produced.

Eg preparation of butan-2-ol from 2-bromobutane



The hydroxide ion always attacks from behind, always producing the same enantiomer.

So nucleophilic substitution reactions produce single enantiomers provided that the substrate was also a single enantiomer. Nucleophilic and and electrophilic addition reactions always produce racemates.

INTRODUCTION:

The substance that contains mass and occupies space is known as Matter. Atoms and molecules constitute the matter. It has various physical and chemical properties. Matters are classified into solid, liquid and gas. The force of interaction present in them varies which gives rise to its physical properties. Gases have the least force of interaction, while solids have the highest force of interaction.

INTERMOLECULAR FORCES

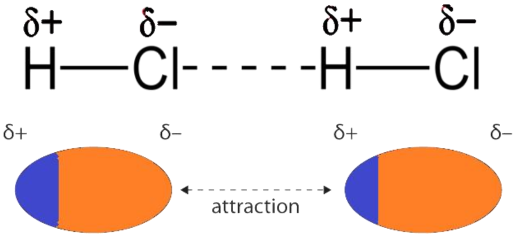
The molecules like solid, liquid or gas exhibit forces of attraction which are called intermolecular forces. Van der Waal forces are the collective of dipole-dipole, dipole-induced dipole and dispersion forces. Ion-dipole and ion-induced dipole are not Van der Waal forces. Hydrogen bonding is the strongest force of attraction.

The different types of intermolecular forces are:

Dipole-Dipole Interaction

Polar molecules exhibit dipole-dipole interactions. They have permanent dipole moments. The positive pole and negative pole are attracted in the molecule. For example, HCl.

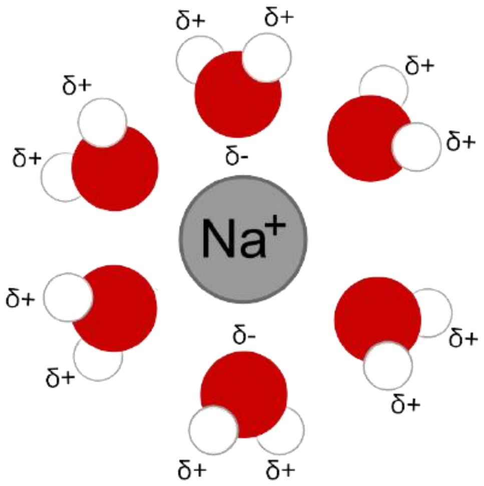
In HCl molecule, Cl is more electronegative than hydrogen. So, the chlorine atom acquires negative charge while, hydrogen atom acquires positive charge. Thus, dipole-dipole interaction takes place among them.



Ion-Dipole Interaction

The attraction between the cation, anion, and a polar molecule is known as ion-dipole interaction. For example, NaCl.

The polar water molecules are attracted towards Na and Cl on dissolving NaCl in water.

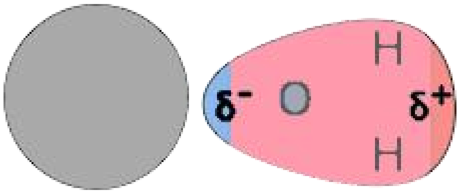


Ion-induced Dipole Interaction

The interaction between the non-polar molecules when a polarized ion is brought near to it is known as ion induced dipole interaction. For example, an iodine molecule which is not polar gets polarized in the presence of a nitrate ion.

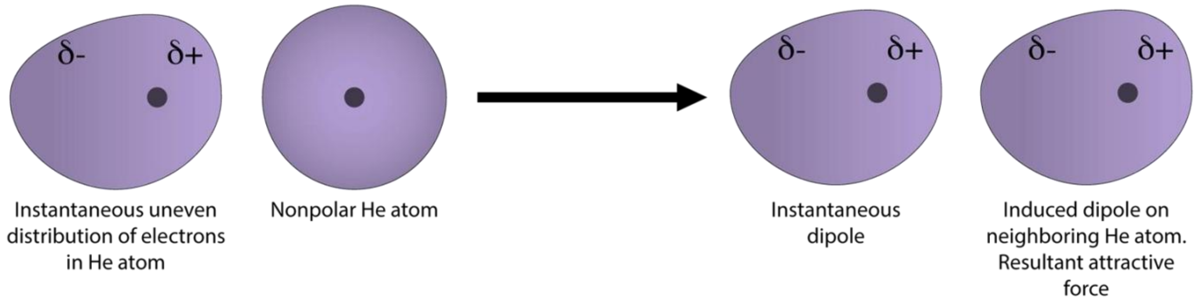
Dipole-induced dipole interaction

The interaction between the non-polar molecules when a polarized dipole is brought near to it is known as dipole-induced dipole interaction. For example, in the presence of polar molecules, noble gases get polarized.



London forces or Dispersion forces

For instance, the electron cloud of the molecule gets distorted for the generation of an instantaneous dipole. The momentary dipole is produced in the molecule in which one part of the molecule is more negative than the other part. The momentary dipole produced induces a dipole in the other molecule. Thus, the force of attraction between the induced momentarily dipole is known as London dispersion forces.



INTERMOLECULAR FORCES VERSUS THERMAL ENERGY

The force of interaction tries to bring the molecules closer. That is, the solid possesses the strongest intermolecular force of attraction, while the gases possess the least intermolecular force of attraction. The decreasing order is,

The thermal energy is possessed by the molecule. The kinetic energy helps in the movement of particles. The gas possesses the highest thermal energy, while the solidpossesses the least thermal energy. The decreasing order is,

Gas Liquid Solid

IDEAL GAS

An ideal gas is a hypothetical concept. There are various assumptions of an idealgas. Some of them are:

The force of interaction between the molecules is zero.

The volume of the molecules is very small. The molecules of the gas collide witheach other and with the walls of the container.

STATE OF A GAS AND STATE VARIABLE

The physical condition of the system is the state of a gas. The variables which areused to denote the physical condition of a gas are known as state variables. They are pressure, volume and temperature P, V and T .

Pressure

The force exerted on an object per unit area is known as pressure. The force applied is always perpendicular to the object. The unit of pressure is the pascal. Pressure canbe measured by various instruments. Barometer and manometer are used to measurepressure.

Volume

The volume of the gas is the same as the volume of the container in the case of rigid containers.

For non-rigid containers, the volume of the gas is determined by the number of moles and other state functions.

Temperature

The amount of heat contained in the gas can be measured by the physical term temperature. No heat flows in and out of the gas when the temperature of the gas is equal to the surrounding temperature. The thermometer is used to measure the temperature of the gas. The units of temperature are Celsius, kelvin, and Fahrenheit.

IDEAL GAS LAW

The laws relate the state variable of the gas in two states.

Boyle’s Law

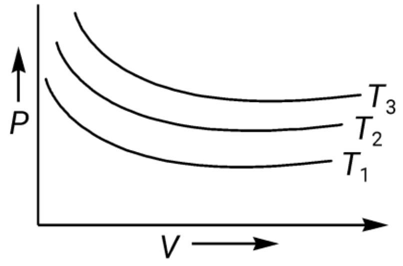
It gives the relation between pressure-volume. At a constant temperature, the pressure of a fixed amount of gas is inversely proportional to its volume. The value of the proportionality constant for each curve corresponds to a different constant temperature and is known as isotherm. Mathematically, it can be written as,

$$P \qquad \frac{1}{V}$$

$$P \qquad \frac{k}{V}$$

$$PV \qquad k$$

As, PV increases, the corresponding temperature will also increase.



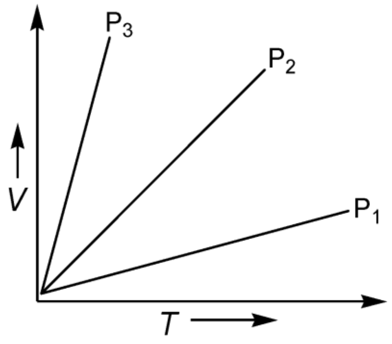
Charles's Law

It gives the relation between temperature-volume. At constant pressure, the volume of a fixed mass of gas is directly proportional to the absolute temperature. Mathematically, it can be written as,

$$V \qquad T$$

$$V \qquad kT$$

$$k \quad \frac{V}{T}$$



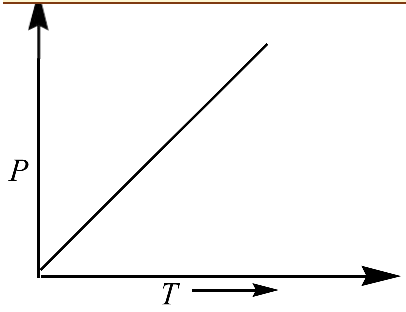
Gay-Lussac’s Law

It gives the pressure-temperature relationship. At fixed volume, the pressure of a fixed mass of gas is directly proportional to the absolute temperature. Mathematically, it can be written as,

$$P \quad T$$

$$P \quad kT$$

$$k \quad \frac{P}{T}$$



Avogadro’s Law

It gives the relation between amount of gas and volume. It states that all the gases ofequal volume under the same condition of temperature and pressure contain an equalnumber of molecules.

IDEAL GAS EQUATION

Combining all the three laws,

Boyle’s law: $P \quad \frac{1}{V}$

Charle’s law: $V \quad T$

Avogardo’s law: $V \quad n$

All the above laws when combined together give an equation, known as an ideal gasequation. Combining all the equations,

$$V \frac{nT}{P}$$

$$V \frac{nRT}{P}$$

$$PV \quad nRT$$

The above equation is known as ideal gas equation. Here, P is the pressure, V isthe volume, n is the amount of gas, T is temperature and R is universal gas constant.

The values of R varies with different units. The values of R are:

$$R \quad 8.314\ \text{J K}^{1}\ \text{mol}^{1}$$

$$R \quad 0.0821\ \text{L atm K}^{1}\text{mol}^{1}$$

$$R \quad 2\ \text{cal K}^{1}\ \text{mol}^{1}$$

If temperature, volume, and pressure varies from their initial state to final state, thenthe ideal gases exert increased the pressure difference gas equation can be rewrittenas,

$$nR \frac{P_1V_1}{T_1} \text{ and,}$$

$$nR \frac{P_2V_2}{T_2}$$

On combining the equation,

$$\frac{P_1V_1}{T_1} \frac{P_2V_2}{T_2}$$

The above equation is known as Combined Gas Law.

VARIATION OF THE IDEAL GAS EQUATION

The ideal gas equation is written as,

$$PV \quad nRT$$

On rearranging the above equation,

$$\frac{n}{V} \quad \frac{P}{RT}$$

Here, n is the number of moles which is equal to the given mass divided by molarmass.

The above equation can be written as,

$$\frac{m}{MV} \quad \frac{P}{RT}$$

$$\frac{d}{M} \quad \frac{P}{RT} \qquad d \quad \frac{m}{V}$$

On rearranging the above equation,

$$PM \quad dRT$$

DALTON’S LAW OF PARTIAL PRESSURE

At constant temperature and volume, the total pressure exerted by a mixture of non-reactive gases equals the sum of their partial pressures. The pressure exerted by individual gases is known as partial pressure. Mathematically, it can be shown as,

$$p_{total} \quad p_1 \quad p_2 \cdots p_3$$

KINETIC THEORY OF GASES

The postulates of the kinetic-molecular theory of gases are given below.

(i) Gases are made up of many similar particles (atoms or molecules). They are sosmall in size that the actual volume of the molecules is negligible.

(ii) At normal temperature and pressure, there is no force of attraction between the particles.

(iii) Particles of a gas are always in constant and random motion. They collide with one other and the container walls during their erratic mobility. The collision of the particles with the walls of the container is the total pressure exerted by the gas.

(iv) The collisions of gas molecules are perfectly elastic. This means that the total energy of molecules remains the same before and after a short-range collision.

(v) At any particular time, different particles in the gas have different speeds andhence different kinetic energies.

The distribution of speed remains constant even on changing the individual speeds of gases. If the gases will have variable speed, they must also have variable kinetic energy. The average kinetic energy of the gas molecule is directly proportional to the absolute temperature of the gas. Mathematically, the relation is shown as,

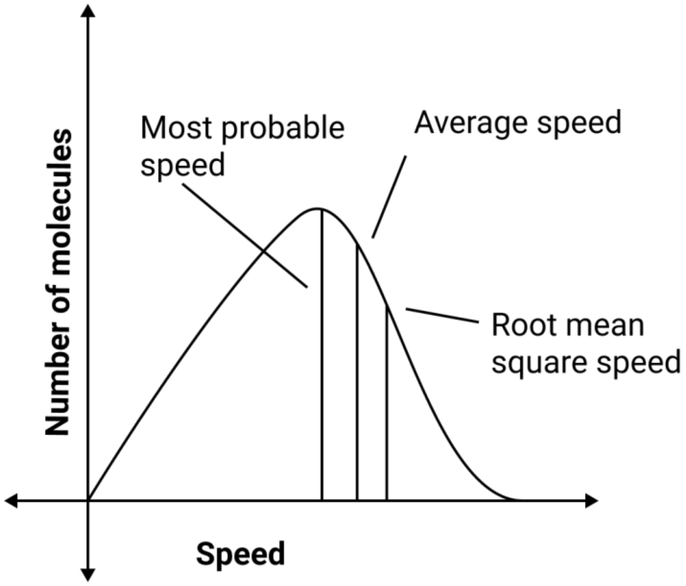
K.E per mole_ $\frac{3}{2} nRT$

K.E per molecule_ $\frac{3}{2} KT$

Here, K is known as Boltzmann's constant.

Molecular Distribution of Speed (Maxwell Boltzmann Distribution)

A plot of the fraction of molecules in the gas vs the speed of the gas molecule is the Maxwell Boltzmann distribution curve. The graph is shown below.



Salient features of graphs are:

(a) The percentage of molecules with a very high or very low speed is extremelysmall.

(b) Mostly, the molecules possess speed in the middle, which is known as the most probable speed.

(c) The total area covered by the graph gives the total number of molecules in thesample.

(d) There are two more speeds, root means square speeds and average speeds. Mathematically, they are shown as,

$$\text{rms}\sqrt{\frac{3RT}{M}}$$

$$\text{mp}\sqrt{\frac{2RT}{M}}$$

$$\text{avg}\sqrt{\frac{8RT}{\pi M}}$$

Note: Take molecular mass always in kilograms.

The ratio for the speeds of the gas at fixed temperature is,

$$\text{mp} : \text{avg} : \text{rms} \quad 1:1.128:1.224.$$

REAL GASES

The assumption taken for ideal gases becomes invalid in case of real gases. (i)We

thought that in an ideal gas, there are no interactions between molecules.

(ii) The volume of a gas's molecules is negligible compared to the entire volumeof gases.

LIQUID STATE

Properties of liquid:

There are very few empty spaces present in liquids. The interactive forces present inliquid are more than gases and less than solids. Liquids have a definite volume. Themolecules in the liquid move so fast with one another. They, therefore, acquire the shapes of the container.

Vapor pressure: The pressure exerted by the vapor present above the liquid in equilibrium with the liquid at a given temperature is known as vapor pressure. The vapor pressure depends on two factors-nature of the liquid and temperature.

Nature of liquid: The molecules leave the liquid phase and shift to the gaseous phase if the intermolecular attraction is weak. Thus, the vapor pressure becomes higher.

Effect of temperature: Vapor pressure increases with an increase in temperature.

Boiling point: The temperature at which the vapor pressure of the liquid becomes equal to the atmospheric pressure is known as the boiling point. When the external pressure is 760 mm Hg , boiling point is said to be a normal boiling point. When the external pressure is 1 bar, boiling point is said to be the standard boiling point.

The influence of external pressure on the boiling point is applied as follows:

Higher will be the external pressure, higher will be the boiling point. Because more heat will be required to make the vapor pressure equal to the external pressure and hence higher will be the boiling point. In hospitals, surgical instruments are sterilized in autoclaves, which raise the boiling point of water by covering the vent with a weight.

Similarly, the lower will be the external pressure, lower will be the boiling point. Therefore, on the top of a mountain, a liquid boils at a lower temperature (where pressure is low) than on the seashore.

Surface tension: The surface tension arises because the molecules of the liquid at the surface and in the interior portion are in a different situation.

The force acting at right angles to the surface along the one-centimeter length of the surface is surface tension. The units of surface tension are dynes per cm or Newtons per meter.

Important results of surface tension are:

The minimal surface area is why the spherical shape drops the lowest energy state of a liquid. The surface area of the liquid is decreased to the minimum due to the surface tension. The drops of a liquid are spherical because a sphere has a minimumsurface area.

Rise of a liquid in a capillary tube. The liquid is pushed into the capillary tube by the inward pull of surface tension acting on the surface, and so the liquid rises.

Effect of nature of the liquid on surface tension: Surface tension arises due to the intermolecular forces of attraction among the molecules. Greater will be the intermolecular forces of attraction, higher is the surface tension of that liquid.

Effect of temperature on surface tension: As the temperature increases, surface tension decreases. At the critical temperature, surface tension becomes zero. This is because as temperature increases, the kinetic energy of the molecules increases and, therefore, the intermolecular attraction decreases.

Viscosity: Viscosity is a measure of resistance to flow which arises due to the internal friction between layers of fluid as they slip past one another while liquid flows.

UNIT V - INTRODUCTION TO SPECTROSCOPY

It’s amazing how much we can learn about molecules and materials by shining light on them! In spectroscopy, we use light to determine a tremendous range of molecular properties, including electronic, vibrational, rotational, and electron and nuclear spin states and energies. From this information, we can often deduce a great deal of additional insight, including:

Molecular identities – what is the sample composed of? Molecular conformations, geometries, and sizes Chemical equilibria

Effects of liquid or solid-state surroundings on molecules

Dynamics, including the rates of chemical reactions, interchange among different molecular conformations, relaxation of molecular excited states, photosynthetic energy transfer, protein folding, etc.We also can use light to control, as well as study, some molecular properties and events. In photochemistry, light may be used for generation of new chemical products, sometimes with selectivity or yields that cannot otherwise be achieved. We depend on a wide range of photophysical processes like those in photosynthesis and vision. Modern laser sources allow the use of intense light pulses to manipulate materials and molecules in unique ways, inducing phase transitions, ablating material, initiating nuclear fusion, and so on. Laser micromachining and CD recording are examples of applications of these processes.

There are a great many ways in which spectroscopy may be conducted. In some cases, light of different wavelengths is shined on a sample and the wavelengths that get absorbed most strongly are measured. In others, you let the sample first absorb light and then measure the wavelength of light emitted. In yet others, you shine a pulse (or a sequence of pulses) of light on the sample and measure various time-evolving responses. There are countless variations on these themes, some routine and commercialized, others highly specialized and carried out only in scattered research labs around the world. Through an understanding of the general principles of spectroscopy, you can understand the way most spectroscopic measurements work and begin to think creatively about the broad range of spectroscopic possibilities.

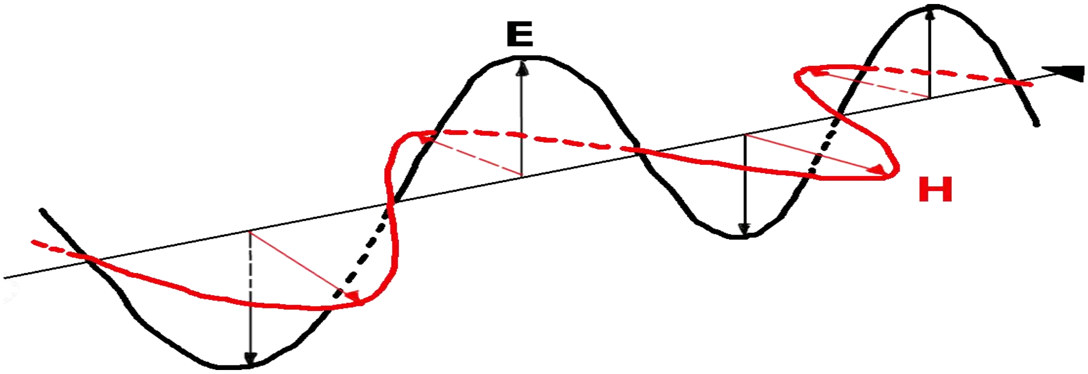
What is spectroscopy?

Seeing is spectroscopy: we perceive the world via the interaction of visible light with the light receptors in our eyes. The light is emitted from the sun or from other light sources. It is then reflected from (or transmitted through) the objects in our surroundings. In these processes, the color changes because some of the light is absorbed by the objects. How much and what spectral regions are absorbed depends on the atoms and molecules in these objects. The light not absorbed reaches our eyes. It carries the information of the molecular structure of our surroundings with it. In our eyes its color is analysed by 3 different types of photoreceptors which absorb different light in spectral regions. In this way we perform a spectroscopic experiment every time we look at things. There is a light source, and object that reflects, transmits, scatters and absorbs light and a wavelength dependent detector in our eyes. An apparatus for spectroscopic studies is called spectrometer and a plot of a particular property of matter against wavelength, frequency or energy of radition is called spectrum.

Not only light but also other types of electromagnetic radiation provide powerful information on biological systems. The study of the interaction of electromagnetic radiation with matter is called spectroscopy [CD, Wikipedia, Encyclopaedia Britannica, IUPAC Compendium of Chemical Terminology, 2nd ed.]. Because of the wave-particle dualism of matter, spectroscopy includes the related study of the interaction between matter and particles - like electrons and neutrons. With this definition X-ray diffraction, neutron scattering, electron microscopy, and NMR are spectroscopic methods. However, we will not discuss these techniques here, because they are covered in the structural biochemistry course. This course deals instead with the following techniques: UV/vis (ultraviolet/visible) spectroscopy, fluorescence, circular dichroism, Raman spectroscopy, Infrared spectroscopy, and electron spin resonance. Most of these use light in the UV/vis spectral range, infrared spectroscopy uses infrared light and electron spin resonance microwave radiation. In addition to explaining the fundamentals of these techniques, we will also discuss some of their applications to biological systems and biological processes.

The methods that we will discuss are very versatile. In the life sciences they are used to study the structure and dynamics of biomolecules. Apart from the spectroscopy of biological molecules, another impressive example of the power of spectroscopy is at the other extreme of dimensions: the study of space with astronomy. Nearly the only information that we have from outer space reaches us in form of electromagnetic radiation. One example is the recent discovery of water on Mars by the European Mars mission using the infrared spectral region. Other more exotic applications are named in the video. This should not give the impression that spectroscopy is a series of niche techniques. Instead the examples illustrate how widespread the use of spectroscopy is.

Electromagnetic radiation



Electric and magnetic components of an electromagnetic wave.

Molecules and their energy levels are one main ingredient of spectroscopy. The other main ingredient is the electromagnetic radiation that induces transitions between different energy levels. Let us therefore briefly recall what electromagnetic radiation is. There are two general ways of describing electromagnetic radiation: as a wave and as a particle. Some aspects of a experiment are best explained by the Wave concept, but others by the particle concept. We will use both views to explain the interaction of matter with radiation.

In some experiments and often in the interaction with molecules, electromagnetic radiation behaves particle- like. The particles are called photons. Each photon has a defined energy, which only depends on the frequency (color) of radiation.

$$E = h\upsilon$$

where h is Planck´s constant ($h = 6.63 \times 10^{-34}$ J s). The intensity (brightness) of radiation depends on the number of photons.

If radiation shows its wave face, electromagnetic radiation has two components: and electric field E and a magnetic field B. Both oscillate with the same frequency and are oriented perpendicular to each other and to the direction of propagation at all times. For the phenomena we will describe, it is often sufficient to consider only one of the two components. Light can be polarized, that is the electric and magnetic field oscillate each in one particular direction. In unpolarized light, the electric and magnetic field oscillate in all directions perpendicular to the direction of propagation.

Frequency of a wave and wavelength are related by

$$= c/$$

where c is the velocity of propagation of the wave. For electromagnetic radiation in a vacuum, $c = 3 \times 108$ m s^{-1}. Frequency and wavelength are often used to characterize electromagnetic radiation. Another quantity is the wavenumber $\tilde{\nu}$ measured in reciprocal centimeters. The wavenumber is the inverse of the wavelength.

$\tilde{\nu} = 1/$

Wavenumber is mainly used in vibrational spectroscopy. Its advantage is that is conveys the information about the wavelength (just calculate the inverse) and is also proportional to the energy or frequency.

Energy levels

We will now turn to molecules and start discussing their energy levels. A system (molecule) can adopt only certain energy values which are the eigenvalues of its Hamilton operator. Therefore the possible energy values, also called energy levels, are discrete and there are gaps between them. The state of lowest energy is named ground state. All states with higher energy are called excited states. Sometimes, two states have the same energy, then they called degenerate. This degeneracy can be lifted by a perturbation, i.e. by interaction with an external influence [CD]. An example are the energy levels of the nuclear and electronic spins. In the absence of an external magnetic field, they are degenerate, i.e. the energy does not depend on the spin orientation. However, when an external magnetic field is applied, the degeneracy is lifted and different spin orientations have different energies. One says that the magnetic field splits the spin energy levels.

ENERGY CONTRIBUTIONS

Often one can consider a molecule as being composed of several sub-systems (electron orbitals, electron spin, nuclear vibrations, nuclear spin, etc.) that are quite independent from each other. For example, one can consider the electron orbitals separately from the nuclear spin orientation. This is an approximation of the real case and assumes that it does not matter so much to the electrons what the nuclei do and vice versa. Or one can consider the nuclear spin without taking into account the nuclear vibrations and vice versa. Each of the sub-systems contributes to the total energy and the following equation lists the most important contributions [CD]:

$$\mathbf{E}_{\mathbf{total}} = \mathbf{E}_{\mathbf{electronic}} + \mathbf{E}_{\mathbf{vibration}} + \mathbf{E}_{\mathbf{rotation}} + \mathbf{E}_{\mathbf{electron\ spin\ orientation}} + \mathbf{E}_{\mathbf{nuclear\ spin\ orientation}} + \mathbf{E}_{\mathbf{translation}}$$

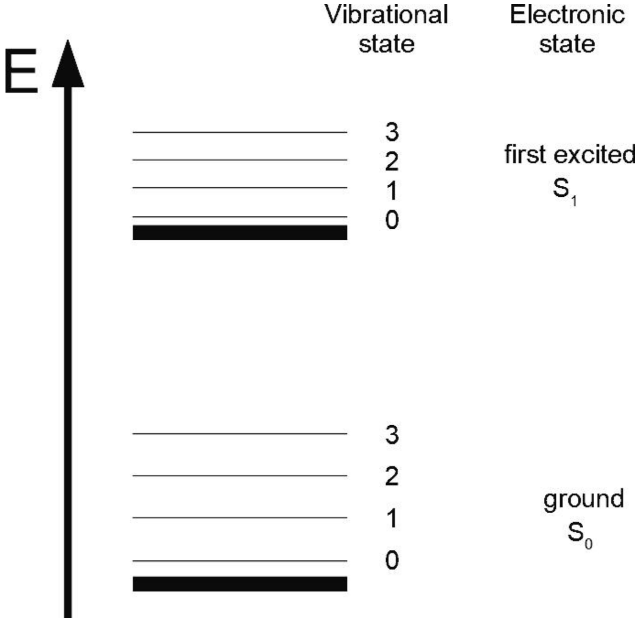
We have: the energy of the electrons in their orbitals (Eelectronic), the energy due to the vibrations of the atoms (Evibration), the energy of molecular rotations (Erotation), the energy due to the orientation of the spins of the electrons (Eelectron spin orientation), the energy due to the orientation of the spins of the nuclei (Enuclear spin orientation), and the energy due to the translational movement of the molecule in space (Etranslation), in other words, the thermal energy.

In the above equation, the energy contributions are listed according to the separation between energy levels. Electronic levels have the largest gaps between them and translational levels the smallest.

In order for a transition to occur for example from a lower to a higher energy level, energy must be provided. This energy might come from thermal energy but also from the absorption of a photon. The former means that higher energy levels are populated at higher temperatures (see below). The latter means that the photon energy has to match the energy gap between two energy levels. This is one of the fundamental rules (Bohr frequency rule, see below) of spectroscopy. Because the gaps are different for different sub-systems, different photon energies are needed to study different subsystems. For example high energy photons (UV / visible light) are used to study electronic transitions whereas low energy photons are needed for nuclear spin transitions (radio waves). In turn, the spectral range determines the technical implementation of the experiment, as different materials and different approaches are needed for different spectral ranges, for example to guide and detect radiation.

We will now discuss energy levels at the example of electronic energy levels and vibrational energy levels, which we will encounter in the next few lectures. The electronic energy is the sum of the energies of the electronic orbitals and the vibrational energy is the sum of the energies of all nuclear vibrations. The figure on the left shows a simple representation of the energy levels of the electronic ground state and the first electronically excited state and of the vibrational levels in these states. The vertical axis is the total energy of the molecule.

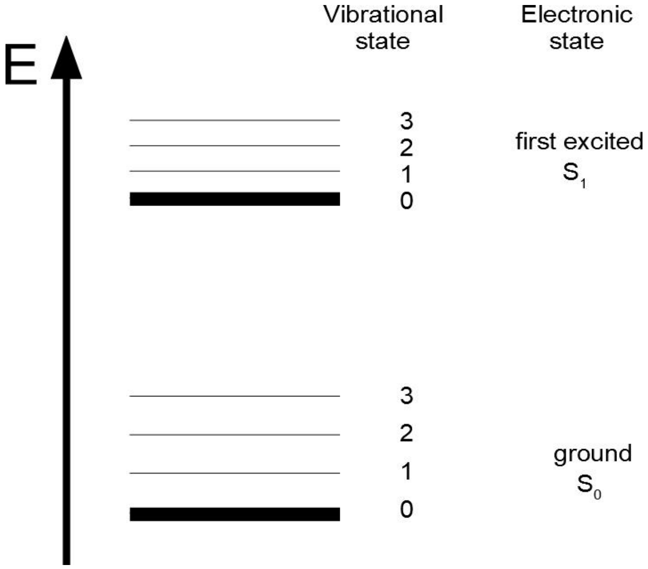
The bold lines consider only the energy of the electrons, whereas the thin lines consider the total energy of electrons and nuclei together. The bold line on the bottom is drawn for the electronic ground state and the. thin lines indicate a few of the vibrational levels which belong the electronic ground state.

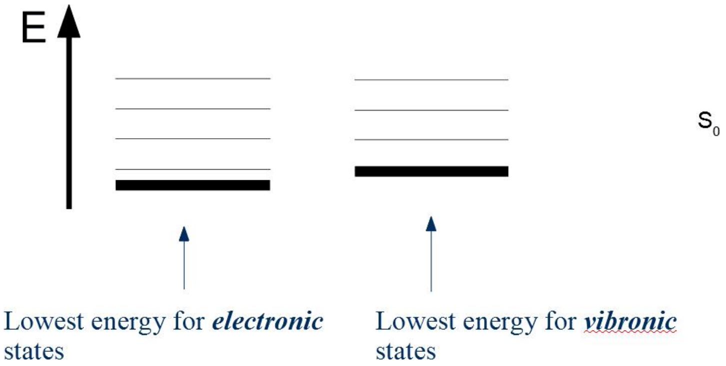


Simple representation of the electronic ground state and the first electronically excited state and of the vibrational levels

The thin lines show the total energy of the molecule in its particular electronic and vibrational state. Only the vibrational levels 0 to 3 are shown, but there are many more. I did not show them in order not to make the plot too confusing. The upper bold line illustrates the energy level of the electrons in the first excited state and the vibrational levels belonging to the electronically excited state are depictured above. As we will see in the vibrational spectroscopy lecture, there are many nuclear vibrations and each of them has its own ladder of energy levels.

In the above illustration, the electronic ground state energy is shown separately from the ground state energy of electrons and nuclear vibrations together. However, in many illustrations these two are combined as shown on the left. Here, the bold line illustrates the energy of the electrons in the electronic ground state plus the energy of the nuclear vibrations in their ground state. In other words, it illustrates the total energy of the molecule in the ground state. The upper bold line illustrates the energy in the electronically excited state and in the vibrational ground state of the electronically excited state. When one considers both the electronic states and the vibrational The difference between these two ways of illustrating energy levels is shown on the left. On the left hand side, we have the case where we consider the electronic and vibrational energy levels separately. The bold line illustrates the energy of the electronic ground state and ignores the energy of the nuclei. The lowest possible total energy is given by the energy of the electrons in their ground state plus the energy of the vibrations in their ground state. This energy corresponds to the lowest thin states together one uses the technical term vibronic state.





On the right hand side, the energy levels of vibronic states are plotted. Here the bold line corresponds to the lowest energy of electrons and nuclear vibrations together. Thus, it illustrates the ground state energy of the molecule and its energy equals that of the lowest thin line on the left hand side.

You can recognize which type of illustration is used by looking at the spacing between the bold line and the first vibrational level shown. On the left side, this spacing is much smaller than the spacing between the subsequent vibrational levels, whereas on the right hand side the spacing to the first vibrational level shown is the same as that to subsequent levels.

When the first spacing is smaller than the other spacings, then the first thin line corresponds to the vibrational ground state because the energy of the vibrational ground state is just half of the energy difference to the next vibrational states. In contrast, when the first spacing is the same as the other spacings, as on the right hand side, the energy of the vibronic states is shown. Then the bold line illustrates the lowest possible energy of the system.

INTERACTION PHENOMENA

When light interacts with matter, several phenomena can take place. Their analysis yields information on the biological system under investigation. The phenomena are:

Scattering

Matter scatters electromagnetic waves, i.e changes their direction of propagation. Scattering might occur elastically (Rayleigh scattering) or inelastically (one example is Raman scattering, after Sir Raman, an Indian scientist who discovered the effect), which mean with or without energy difference of scattered and incident light.